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DEVELOPMENTS IN GEOTECHNICAL ENGINEERING 41

CLAY IN ENGINEERING GEOLOGY

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**To Kitty
Rosemary, Fiona and Roger**

FOREWORD

Clays occur so widely in nature, and are now so extensively used - both directly and indirectly - as man extends his control over the surface of the earth, that their study has become an important part of several scientific disciplines. The pedologist is naturally concerned with clays as they occur close to the surface of the ground; agricultural soil studies have contributed greatly to an understanding of clays and clay minerals. The ceramicist must study the properties of the clays that are to be used for manufacturing processes; notable methods of investigation have thus been developed. The civil engineer cannot usually choose the clays with which he has to deal but has to accept, and work with, all the clays that are encountered in his excavation work. His only opportunity for choice is when clays have to be used as fill or as roadbed material; even then economic considerations will severely limit selection. Soil mechanics has, therefore, always included laboratory and theoretical studies of clays as a major part of its field throughout its forty year history as a recognized scientific discipline.

There is already, therefore, a vast literature on clays but this is still compartmentalized to a large extent, in line with the several applied scientific studies of clays and the more basic studies that are to be found in mineralogy. There is, naturally and happily, some cross referencing between the different approaches but this is still largely on an individual basis, dependent on the breadth of interest of the individual investigator. It is, therefore, a pleasure to see how Dr. J. E. Gillott has brought together within the covers of this volume a synthesis of selected studies in all fields of clay investigation, on the basis of his own wide reading probably influenced by the way in which he personally encounters such a wide variety of problems involving clay.

Some readers, depending on their own specialised interests, may question the relative attention that the author has given to one or other of the major topics into which he has broken down his overall subject. This is inevitable but the interdisciplinary approach that features this book is in itself so refreshing that many readers will gain a new appreciation of the great amount of work that has already been devoted to this most common of earth materials and should find the volume a most useful reference in their own work.

The cross fertilisation that can result from the linking of specialised approaches in this branch of scientific study is well shown by the adoption by engineers of the simple indicator tests originally devised by Atterberg for use with agricultural soils. One of the impediments to this development is illustrated by differences in terminology such as the different meanings, in

geology and engineering, for the words "compaction" and "consolidation". Publications such as this will help to show how desirable it is to have agreement upon the joint use of common terms. It is the consolidation test in soil mechanics that shows that many clays have built-in "memories", their consolidation characteristics giving a good indication of one phase of their geological history. It would be regrettable if differences of terminology prevented this significant aspect of the engineering study of clays from being widely shared.

The need for review volumes is a good indication of the rapidity of advance in any branch of scientific investigation; they constitute useful mileposts along the road of progress. And progress in the study of clay is as encouraging as it is necessary.

Ottawa

Robert F. Legget

PREFACE

This text is interdisciplinary and is restricted in scope to a discussion of the importance of clay in engineering geology. It is primarily addressed to geologists and mineralogists and to those civil engineers who are concerned with the geotechnical sciences. Its object is to introduce geologists and mineralogists to the often unfamiliar terminology and literature of some aspects of soil mechanics and correspondingly to introduce engineers to pertinent information in geology and mineralogy which relates to clay. Geologists and engineers sometimes use the same term with a different meaning and conversely they attach the same meaning to different words. For example, in engineering terminology compaction implies a mechanical process but to geologists it indicates decrease in void ratio due to natural causes. Likewise rock, generally regarded as a hard material, in the strict sense includes non-coherent mineral matter. This has been termed regolith by geologists and soil by engineers to the vexation of agricultural scientists. Confusion could be avoided by general agreement but in many instances it is likely that the question will be decided by usage.

It is hoped that the text will be of use to students, research workers in geology and engineering who require a summary of present knowledge in this field and to others not primarily concerned with clays who wish to keep abreast of developments in the application of clay science to practical problems of an engineering nature. Whilst the references given at the end of each chapter are not complete or exhaustive it is thought that sufficient material has been included to provide the reader with a starting point should he wish to obtain more detailed information on specific topics.

To the ancients clay was a variety of "earth" which was one of the four elements, the other three being air, water and fire. In modern usage the term clay is generally applied to earthy materials of very fine particle size which form as a sedimentary deposit, as a residue due to weathering or by hydrothermal action. Clay is cohesive, plastic and workable by hand when moist. It shrinks when dried and expands when wetted. In definitions used by ceramists its increase in strength when fired has been emphasized. The term is also generally interpreted to imply a composition of hydrous aluminium silicates or sometimes hydrous magnesium silicates. The classification and origin of clay is discussed in the first three chapters of the book.

The mineralogical composition, fabric and physical chemistry of clays is reviewed in Chapters 4 and 5. Moisture interaction is discussed in Chapter 6 and modern views concerning the deformation and strength properties of clays are outlined in Chapter 7. In Chapter 8 methods for improving the engineering

properties of clay soil are described. This is of great importance in the modern world particularly because of the great increase in the volume of construction of roads, airfields and similar works.

The importance of clays as raw materials is discussed in Chapter 9. There is some overlap here with industrial mineralogy and ceramic engineering particularly in the section dealing with the strength of fired clay products. It was included with some misgiving since the subject is a large one; nonetheless many of the industrial products made from clay are of vital concern in engineering as materials of construction. Some understanding of the technical processes of manufacture, nature of product and mechanism of strength development where applicable is therefore desirable. In industry other raw materials used with clay sometimes have major importance in the manufacturing process. As clay is the major subject of this text, however, their significance is touched upon only lightly.

The final three chapters deal with mineralogical, physical and engineering analysis. It is thought that many readers will have some previous experience of X-ray diffraction methods and for this reason the discussion is at a more advanced level than for some other topics. The account is necessarily limited to the most commonly used methods of clay analysis and in a book of this length cannot hope to be comprehensive. Thus there are some omissions, for instance, there is no discussion of nuclear magnetic resonance or the spin echo technique in particular which has important structural applications to do with understanding the nature of surface sorbed water. Nonetheless it is hoped that sufficient information is given, particularly when supplemented by the fuller accounts to be found in some of the references, to serve as an introduction to modern methods of analysis upon which our understanding of the nature of all materials is ultimately so dependent.

Clay has played an important role in satisfying human needs from the very earliest times. It is of major importance in agriculture and industry as well as in geology and engineering. Owing to differences in objectives and interest the study of clays has tended to become increasingly the domain of "specialists". This general trend towards increased specialization has been criticized and the fear expressed that knowledge is becoming divided into unduly small compartments between which communication tends to diminish and may ultimately break down altogether. While these warnings are timely and to some extent justified one may derive reassurance from the fact that despite ever increasing specialization and apparent diversity of interest a unifying bond exists. This is found in the fundamental nature of the material. As basic principles become better understood it should become increasingly possible to predict properties rather than to rely on empirical observation.

Such information transgresses the bounds imposed by specialty and is of

truly interdisciplinary significance. An attempt has been made in this book to summarize the principles as they are presently understood which underlie clay behaviour and to illustrate their importance in describing the properties of clay soils and clay rocks in engineering applications. There are still many areas, such as that dealing with the strength of clay soils, in which knowledge of the basic principles has not yet advanced to the point at which a clear understanding has been obtained of all the observations. This should cause no surprise and is to be expected in an active and developing subject and indeed where controversy exists it provides the stimulus for further research.

PREFACE TO THE SECOND EDITION

The plan of the book has remained unchanged since the first edition was published in 1968 but the text and reference lists have been extensively updated. The purpose of the book, to summarize present knowledge in this field, also remains the same and likewise it is addressed primarily to the same readership. The inclusion of new material and illustrations has lengthened the book but it is felt that it remains reasonable for a review volume.

I wish to express my sincere thanks to the many individuals, agencies and publishers who have generously supplied information, photographs and diagrams. These are too numerous to mention here individually by name. I have taken care to request permission from the proper authorities to reproduce original material and I hope that due acknowledgement has been made in all cases as footnotes. Should any feel that this is not so I hope that this will be regarded as due to accidental omission rather than design.

I also wish to acknowledge the help of several colleagues, students and research associates, (particularly Eliza Grabowski, Lucie Jermy and Cheryl Turner), and I am especially grateful to Mrs. Norma Wilson for her patience in preparing several redrafts of the typescript and to all those who helped in other ways including those named in the first edition.

Jack E. Gillott

Engineering Geology

"The application of the geological sciences to engineering practice for the purpose of assuring that the geologic factors affecting the location, design, construction, operation and maintenance of engineering works are recognized and adequately provided for". (HOWELL, J.V., Editor, 1960. Glossary of Geology and Related Sciences. American Geological Institute, Washington, D.C., 72 pp.)

Clay-geological

"The term clay as used today carries with it three implications: (1) a natural material with plastic properties, (2) an essential composition of particles of very fine size grades, and (3) an essential composition of crystalline fragments of minerals that are essentially hydrous aluminium silicates or occasionally hydrous magnesium silicates." (HOWELL, J.V., Editor, 1960. Glossary of Geology and Related Sciences. Americal Geological Institute, Washington, D.C., 72 pp.)

Clay-engineering

"A fine-textured soil, with grains colloidal in size, composed mainly of hydrated silicate of aluminium mixed with various impurities. It is plastic and cohesive, shrinks when dry, expands when wet, and gives up its water when compressed." (HAMMOND, R., 1965. Dictionary of Civil Engineering. Philosophical Library Inc., New York, N.Y., 253 pp.)

CHAPTER 1

THE NATURE AND CLASSIFICATION OF CLAYS AND SOILS

The word "clay" is derived from old English and has a Teutonic root. The word "soil" is probably from the Latin solum taken in the sense of meaning ground. The two terms are often used loosely and convey different things to different people. In scientific terminology clay is a natural earthy material with plastic properties when moist, of very fine grain-size and composed largely of hydrous aluminium and magnesium silicates. In some definitions emphasis is placed upon the preservation of a moulded shape upon drying and the increase in strength with shape retention upon firing. The upper limit of grain-size for mineral particles in the clay-size range is commonly taken as $2\mu\text{m}$ ($1\mu\text{m} = 0.000001\text{ m}$). The adoption of the word "soil" by all groups of scientists and engineers as a general term for unconsolidated earth material (regolith) has been suggested and is commonly used in that sense by engineers and geologists (LEGGET, 1953, p.575; 1962, P.68; FAIRBRIDGE and FINKL, 1979, p.434). When used in this way the word "soil" carries no implication as to ability to support plant life. Clay soils are of considerable geotechnical importance because of their properties as foundation materials and widespread occurrence. Clays have many industrial uses and are important raw materials for the manufacture of building materials such as bricks, tiles, pipes and cement.

GEOLOGICAL CLASSIFICATION

Clay containing earth materials are referred to by a variety of terms many of which have had long usage but are not always clearly defined. Field conditions often make sophisticated methods of analysis impossible and general terms have practical utility. When clays which were deposited in water are indurated they are sometimes termed claystones. When silt and sand-sized particles are also present in undetermined amounts the term mudstone may be used. A clay deposit is referred to as shale when it has a fissile or laminated structure parallel to the bedding. When the rock is better indurated it is termed an argillite. It does not possess the well developed cleavage of a slate which is formed during metamorphism due to strong directed pressure. When it is desired to avoid the compositional implication of the word clay for rocks in the clay or silt-size range which when mixed with water form mud the term lutite (from the Latin, lutum, mud) is often used. The latin-derived term argillaceous may be used for clayey rocks of sedimentary origin and the term of greek roots, pelitic, for their metamorphic equivalents (TYRRELL, 1921, p.501). The better methods of analysis

now available have made it possible to place more precise limits on the various classes of material. Sediments of intermediate and fine grain-size may be subdivided on the basis of the proportions of sand, silt and clay. One such scheme recommended by SHEPARD (1954) on the basis of a questionnaire is shown in Fig. 1. Similar systems though with subdivisions placed at different proportions of sand, silt and clay are used by engineers and engineering geologists in organizations such as the U.S. Bureau of Public Roads (American Association of State Highway and Transportation Officials); other terms such as loam are included in some systems.

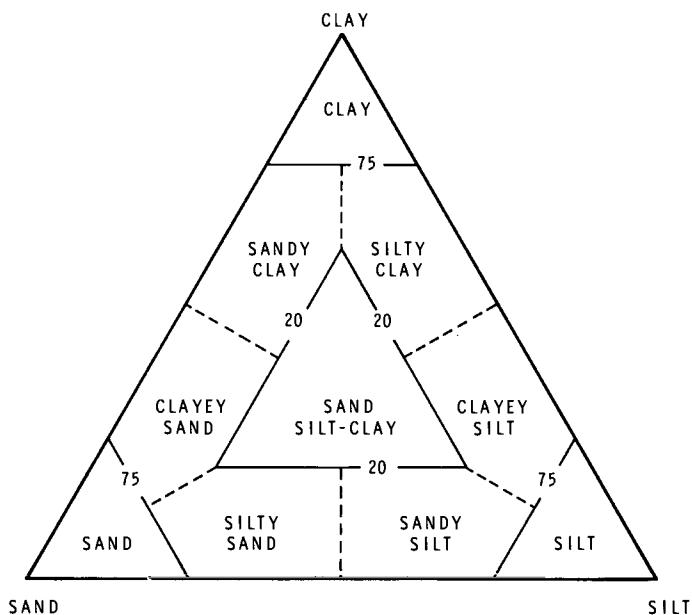


Fig. 1. Classification of intermediate and fine-grained sediments. (After SHEPARD, 1954; by permission of the Editor, Journal of Sedimentary Petrology.)

In geological classification composition and texture are related to origin. Understanding of the principles underlying geological classification is helpful to engineers since important variables such as probable extent of a deposit as well as engineering behaviour depend on conditions at the time of formation as well as on subsequent events. Clay-soils may be subdivided into two groups, the transported and the residual.

Transportation may be effected by gravity, water, ice or wind. In much of the northern hemisphere transported superficial deposits formed during and after the retreat of the Pleistocene ice sheets. A widespread ice-transported soil is boulder clay or till. It is a silty or sandy clay which contains boulders

sometimes showing ice striations. When clay-sized material is dominant the deposit is known as clay till. Its high density is believed to result from compaction by the heavy load of ice. While sediments of this sort are generally illsorted, stratified drift is often present due to deposition in lake or sea. The nature and properties of glacial till have been reviewed recently (LEGGET, 1976).

The glacial deposits such as moraines and hard basal till which overlie bedrock are often themselves covered by soft soils. These deposits are associated with serious geotechnical problems such as landslides, creep, strain softening, low bearing capacity, high settlement with structural breakdown, irreversible drying shrinkage and difficulties in predicting engineering behaviour (GILLOTT, 1982). Many soft soils formed under post-glacial conditions which differed from those of the present. In Canada, for example, crustal depression by the weight of ice together with the eustatic rise of sea-level when the ice melted led to extensive marine transgression. Release of large volumes of fresh-water and blockage of drainage channels by retreating ice resulted in formation of lakes which migrated with time in the general direction of the withdrawing ice sheets.

Soft clayey soils may be subdivided into waterlaid tills, lacustrotills, mudflow deposits, turbidity current deposits, varved clays and marine clays (QUIGLEY, 1980). Waterlaid tills and lacustrotills are thought to be deposited in lakes below floating ice through only a shallow depth of water so that only very imperfect sorting and stratification is evident. If subject to flow sliding such deposits may show effects indicative of slumping and may grade laterally into turbidity current deposits. During melting of the continental ice sheet sediment loads were heavy and turbidity currents of high density were probably common carrying sediments across lake bottoms during summer. Such currents deposited laterally extensive, poorly sorted beds of silt, sand and clay which are often banded probably because the currents were intermittent. As the ice front of the continental glacier receded sediment load diminished and low density overflows and interflows became more common.

Varved clays are believed to form in glacial lakes. Each varve is composed of a pair of beds one of which is coarse and one fine (Fig. 2, 4.14, 4.17). It is believed that each varve represents an annual deposit. In summer, melt water from a thawing glacier carries large volumes of sand, silt and clay into a lake. The sand and coarse silt is deposited but the clay remains in suspension owing to disturbance of the water. In winter streams which continue to flow beneath a frozen surface carry a smaller sediment load leading to lower density overflows across frozen lakes. This material together with fines which remained in suspension from the previous summer settles out in the relatively quiet water. Much of the fine suspended glacial material is rock flour consisting of primary minerals ground to the clay size range ($<2\mu\text{m}$); sediments composed of significant

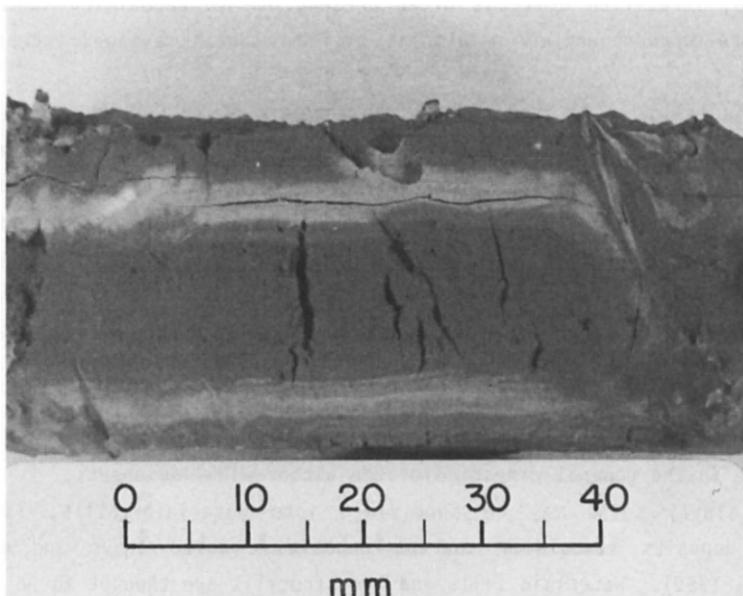


Fig. 2. Varved clay, Olga, N. Quebec.

amounts of this material have distinctive engineering properties. Many of the principles of sedimentology to do with deposits formed by glacial and post-glacial sedimentation are reviewed in a report of the Society of Economic Paleontologists and Mineralogists edited by Jopling and McDonald (1975).

Loess, a wind-transported silt, is a massive, buff-coloured, unstratified silt containing 10 to 20% clay and some fine sand (Fig. 4.17c). It is derived from glacial floodplains or deserts. It is an important soil in the mid-west of North America, parts of Europe, the Soviet Union and China. Flows of loess composed of a silt-in-air suspension and sometimes triggered by earthquakes have caused heavy damage and loss of life in Asia.

Residual clay soils are most commonly formed by weathering involving little lateral movement. The composition and fabric reflect that of the parent material, weathering regime, topography, age and other factors. Soils of this sort are common in many areas of the world such as large parts of Africa and India. Soils formed by hydrothermal action are also residual and have been found to have distinctive microstructures (SERGEYEV, et al, 1980) and compositions. Minerals, including clay minerals, are also formed in place by diagenesis and are now recognized to be relatively common; they are sometimes of considerable engineering importance (Chapter 4).

ENGINEERING CLASSIFICATION

A principal objective of engineering classification is to place similar soils into groups so that the complexity of the testing procedure to characterize soil behaviour may be reduced or better directed. Several systems are in use in the United States including that developed by the American Association of State

NOTES TO FIG. 3A Unified soil classification system (see pp6-11)

Field identification procedures for fine-grained soils or fractions.

These procedures are to be performed on the minus No. 40 sieve size particles, approximately 1/64 inch. For field classification purposes, screening is not intended, simply remove by hand the coarse particles that interfere with the tests.

Dilatancy (reaction to shaking). After removing particles larger than No. 40 sieve size, prepare a pat of moist soil with a volume of about one-half cubic inch. Add enough water if necessary to make the soil soft but not sticky. Place the pat in the open palm of one hand and shake horizontally, striking vigorously against the other hand several times. A positive reaction consists of the appearance of water on the surface of the pat which changes to a livery consistency and becomes glossy. When the sample is squeezed between the fingers, the water and gloss disappear from the surface, the pat stiffens, and finally it cracks or crumbles. The rapidity of appearance of water during shaking and of its disappearance during squeezing assist in identifying the character of the fines in a soil. Very fine clean sands give the quickest and most distinct reaction whereas a plastic clay has no reaction. Inorganic silts, such as a typical rock-flour, show a moderately quick reaction.

Dry strength (crushing characteristics). After removing particles larger than No. 40 sieve size, mold a pat of soil to the consistency of putty, adding water if necessary. Allow the pat to dry completely by oven, sun, or air-drying and then test its strength by breaking and crumbling between the fingers. This strength is a measure of the character and quantity of the colloidal fraction contained in the soil. The dry strength increases with increasing plasticity. High dry strength is characteristic for clays of the CH-group. A typical inorganic silt possesses only very slight dry strength. Silty fine sands and silts have about the same slight dry strength, but can be distinguished by the feel when powdering the dried specimen. Fine sand feels gritty whereas a typical silt has the smooth feel of flour.

Toughness (consistency near plastic limit). After particles larger than the No. 40 sieve size are removed, a specimen of soil about one-half inch cube in size, is molded to the consistency of putty. If too dry, water must be added and if sticky, the specimen should be spread out in a thin layer and allowed to lose some moisture by evaporation. Then the specimen is rolled out by hand on a smooth surface or between the palms into a thread about one-eighth-inch in diameter. The thread is then folded and rerolled repeatedly. During this manipulation the moisture content is gradually reduced and the specimen stiffens, finally loses its plasticity, and crumbles when the plastic limit is reached. After the thread crumbles, the pieces should be lumped together and a slight kneading action continued until the lump crumbles. The tougher the thread near the plastic limit and the stiffer the lump when it finally crumbles, the more potent is the colloidal clay fraction in the soil. Weakness of the thread at the plastic limit and quick loss of coherence of the lump below the plastic limit indicate either inorganic clay of low plasticity, or materials such as kaolin-type clays and organic clays which occur below the A-line. Highly organic clays have a very weak and spongy feel at the plastic limit.

(By permission of United States Army Engineer, Waterways Experiment Station, Corps of Engineers).

| Major Divisions | | Group Symbols | Typical Names | Field Identification Procedures (Excluding particles larger than 3 in. and basing fractions on estimated weights) | |
|---|---|--|--|---|---------------------------------|
| 1 | 2 | 3 | 4 | 5 | |
| Fine-grained Soils More than half of material is smaller than No. 200 sieve size. The No. 200 sieve size is about the smallest particle visible to the naked eye. | Sands and Clays Liquid limit is less than 50 | Gravels More than half of coarse fraction is smaller than No. 4 sieve size. (For visual classification, the $\frac{1}{4}$ -in. size may be used as equivalent to the No. 4 sieve size) | GW | Well-graded gravels, gravel-sand mixtures, little or no fines. Wide range in grain sizes and substantial amounts of all intermediate particle sizes. | |
| | | | GP | Poorly graded gravels or gravel-sand mixtures, little or no fines. Predominantly one size or a range of sizes with some intermediate sizes missing. | |
| | | | GM | Silty gravels, gravel-sand-silt mixture. Nonplastic fines or fines with low plasticity (for identification procedures see ML below). | |
| | | | GC | Clayey gravels, gravel-sand-clay mixtures. Plastic fines (for identification procedures see CL below). | |
| | | | SW | Well-graded sands, gravelly sands, little or no fines. Wide range in grain size and substantial amounts of all intermediate particle sizes. | |
| | | | SP | Poorly graded sands or gravelly sands, little or no fines. Predominantly one size or a range of sizes with some intermediate sizes missing. | |
| | | | SM | Silty sands, sand-silt mixtures. Nonplastic fines or fines with low plasticity (for identification procedures see ML below). | |
| | | | SC | Clayey sands, sand-clay mixtures. Plastic fines (for identification procedure see CL below). | |
| | | | | | |
| | | | Identification Procedures on Fraction Smaller than No. 40 Sieve Size | | |
| Sands and Clays Liquid limit is greater than 50 | | ML CL OL MH CH OH | Dry Strength (Crushing characteristics) | Dilatancy (Reaction to shaking) | Toughness (Consistency near PL) |
| | | | None to slight | Quick to slow | None |
| | | | Medium to high | None to very slow | Medium |
| | | | Slight to medium | Slow | Slight |
| | | | Slight to medium | Slow to none | Slight to medium |
| | | | High to very high | None | High |
| Highly Organic Soils | | Pt | Peat and other highly organic soils. | Readily identified by color, odor, spongy feel and frequently by fibrous texture. | |

(1) Boundary classifications: Soils possessing characteristics of two groups are designated by combinations of group symbols. For example GW-GC, well-graded gravel-sand mixture with clay binder.

Fig. 3A. Unified soil-classification system for roads, airfields, embankments and foundations (By permission of United States Army Engineer, Waterways Experiment Station, Corps of Engineers). Identification and description. (Explanation and notes see p.5.)

| Information Required for Describing Soils 6 | Laboratory Classification Criteria 7 | | | | | | | | |
|--|--|--|---|--|---|---------------|-----------|--|--|
| <p>For undisturbed soils add information on stratification, degree of compactness, cementation, moisture conditions, and drainage characteristics.</p> | <p>Determine percentages of gravel and sand from grain-size curve. Depending on percentage of fines (fraction smaller than No. 200 sieve size) coarse-grained soils are classified as follows:</p> <table border="1" style="margin-left: auto; margin-right: auto;"> <tr> <td style="text-align: center;">Less than 5%</td> <td style="text-align: center;">GW, GP, SW, SP, GM, GC, SM, SC.</td> <td style="text-align: center;">Atterberg limits below "A" line or PI less than 4</td> <td style="text-align: center;">Above "A" line with PI between 4 and 7 are <u>borderline</u> cases requiring use of dual symbols.</td> </tr> <tr> <td style="text-align: center;">More than 12%</td> <td style="text-align: center;">5% to 12%</td> <td style="text-align: center;">Atterberg limits above "A" line with PI greater than 7</td> <td></td> </tr> </table> | Less than 5% | GW, GP, SW, SP, GM, GC, SM, SC. | Atterberg limits below "A" line or PI less than 4 | Above "A" line with PI between 4 and 7 are <u>borderline</u> cases requiring use of dual symbols. | More than 12% | 5% to 12% | Atterberg limits above "A" line with PI greater than 7 | |
| Less than 5% | GW, GP, SW, SP, GM, GC, SM, SC. | Atterberg limits below "A" line or PI less than 4 | Above "A" line with PI between 4 and 7 are <u>borderline</u> cases requiring use of dual symbols. | | | | | | |
| More than 12% | 5% to 12% | Atterberg limits above "A" line with PI greater than 7 | | | | | | | |
| <p>Give typical name; indicate approximate percentages of sand and gravel, maximum size; angularity, surface condition, and hardness of the coarse grains; local or geologic name and other pertinent descriptive information; and symbol in parentheses.</p> | <p>Not meeting all gradation requirements for GW</p> <table border="1" style="margin-left: auto; margin-right: auto;"> <tr> <td style="text-align: center;">$C_u = \frac{D_{60}}{D_{10}}$ Greater than 4</td> <td style="text-align: center;">$C_c = \frac{(D_{30})^2}{D_{10} \times D_{60}}$ Between 1 and 3</td> </tr> </table> | $C_u = \frac{D_{60}}{D_{10}}$ Greater than 4 | $C_c = \frac{(D_{30})^2}{D_{10} \times D_{60}}$ Between 1 and 3 | | | | | | |
| $C_u = \frac{D_{60}}{D_{10}}$ Greater than 4 | $C_c = \frac{(D_{30})^2}{D_{10} \times D_{60}}$ Between 1 and 3 | | | | | | | | |
| <p>Example: <u>Silty sand</u>, gravelly; about 20% hard, angular gravel particles $\frac{1}{2}$-in. maximum size; rounded and subangular sand grains, coarse to fine; about 15% nonplastic fines with low dry strength; well compacted and moist in place; alluvial sand; (SM).</p> | <p>Not meeting all gradation requirements for SW</p> <table border="1" style="margin-left: auto; margin-right: auto;"> <tr> <td style="text-align: center;">Atterberg limits below "A" line or PI less than 4</td> <td style="text-align: center;">Limits plotting above "A" line with PI between 4 and 7 are <u>borderline</u> cases requiring use of dual symbols.</td> </tr> <tr> <td style="text-align: center;">Atterberg limits above "A" line with PI greater than 7</td> <td></td> </tr> </table> | Atterberg limits below "A" line or PI less than 4 | Limits plotting above "A" line with PI between 4 and 7 are <u>borderline</u> cases requiring use of dual symbols. | Atterberg limits above "A" line with PI greater than 7 | | | | | |
| Atterberg limits below "A" line or PI less than 4 | Limits plotting above "A" line with PI between 4 and 7 are <u>borderline</u> cases requiring use of dual symbols. | | | | | | | | |
| Atterberg limits above "A" line with PI greater than 7 | | | | | | | | | |
| <p>For undisturbed soils add information on structure, stratification, consistency in undisturbed and remolded states, moisture and drainage conditions.</p> | <p>Comparing Soils at Equal Liquid Limit Toughness and Dry Strength Increase with Increasing Plasticity Index</p> <p>PLASTICITY INDEX</p> <p>LIQUID LIMIT</p> <p>PLASTICITY CHART</p> <p>For laboratory classification of fine-grained soils</p> | | | | | | | | |
| <p>Give typical name; indicate degree and character of plasticity; amount and maximum size of coarse grains; color in wet condition; odor, if any; local or geologic name and other pertinent descriptive information; and symbol in parentheses.</p> <p>Example: <u>Clayey silt</u>, brown; slightly plastic; small percentage of fine sand; numerous vertical root holes; firm and dry in place; loess; (ML).</p> | <p>(2) All sieve sizes on this chart are U. S. standard.</p> | | | | | | | | |

| Major Divisions (1) | Major Divisions (2) | Symbol | | | Name (6) | Value as Sub-grade When Not Subject to Frost Action (7) | Value as Sub-base When Not Subject to Frost Action (8) | Value as Pase When Not Subject to Frost Action (9) |
|------------------------|---------------------------------------|---------------|-----------------|--------------|--|--|---|---|
| | | Letter (3) | Hatching (4) | Color (5) | | | | |
| COARSE-GRAINED SOILS | GRAVEL AND GRAVELLY SOILS | GW | | Red | Well-graded gravels or gravel-sand mixtures, little or no fines | Excellent | Excellent | Good |
| | | GP | | | Poorly graded gravels or gravel-sand mixtures, little or no fines | Good to excellent | Good | Fair to good |
| | | GMd | | Yellow | Silty gravels, gravel-sand-silt mixtures | Good to excellent | Good | Fair to good |
| | | Gu | | | | Good | Fair | Poor to not suitable |
| | | GC | | Yellow | Clayey gravels, gravel-sand-clay mixtures | Good | Fair | Poor to not suitable |
| | SAND AND SANDY SOILS | SW | | Red | Well-graded sands or gravelly sands, little or no fines | Good | Fair to good | Poor |
| | | SP | | | Poorly graded sands or gravelly sands, little or no fines | Fair to good | Fair | Poor to not suitable |
| | | SMd | | Yellow | Silty sands, sand-silt mixtures | Fair to good | Fair to good | Poor |
| | | Sc | | | Clayey sands, sand-clay mixtures | Fair | Poor to fair | Not suitable |
| FINE-GRAINED SOILS | SILTS AND CLAYS LL IS LESS THAN 50 | ML | | Green | Inorganic silts and very fine sands, rock flour, silty or clayey fine sands or clayey silts with slight plasticity | Poor to fair | Not suitable | Not suitable |
| | | CL | | | Inorganic clays of low to medium plasticity, gravelly, sandy, silty, and lean clays | Poor to fair | Not suitable | Not suitable |
| | | OL | | | Organic silts and organic silt-clays of low plasticity | Poor | Not suitable | Not suitable |
| | SILTS AND CLAYS LL IS GREATER THAN 50 | MH | | Blue | Inorganic silts, micaceous or diatomaceous fine sandy or silty soils, elastic silts | Poor | Not suitable | Not suitable |
| | | CH | | | Inorganic clays of high plasticity, fat clays | Poor to fair | Not suitable | Not suitable |
| | | OH | | | Organic clays of medium to high plasticity, organic silts | Poor to very poor | Not suitable | Not suitable |
| | HIGHLY ORGANIC SOILS | Pt | | Orange | Peat and other highly organic soils | Not suitable | Not suitable | Not suitable |

Notes:

- Column 3, division of GM and SM groups into subdivisions of d and u are for roads and airfields only. Subdivision is on basis of Atterberg limits; suffix d (e.g., GMd) will be used when the liquid limit is 25 or less and the plasticity index is 5 or less; the suffix u will be used otherwise.
- In column 13, the equipment listed will usually produce the required densities with a reasonable number of passes when moisture conditions and thickness of lift are properly controlled. In some instances, several types of equipment are listed because variable soil characteristics within a given soil group may require different equipment. In some instances, a combination of two types may be necessary.
 - Processed base materials and other angular materials. Steel-wheeled and rubber-tired rollers are recommended for hard, angular materials with limited fines or screenings. Rubber-tired equipment is recommended for softer materials subject to degradation.
 - Finishing. Rubber-tired equipment is recommended for rolling during final shaping operations for most soils and processed materials.
 - Equipment size. The following sizes of equipment are necessary to assure the high densities required for airfield construction:
Crawler-type tractor -- total weight in excess of 30,000 lb.

Fig. 3B. Unified soil-classification system for roads, airfields, embankments, and foundations. (By permission of United States Army Engineer, Waterways Experiment Station, Corps of Engineers). Characteristics pertinent to roads and airfields. (Explanation and notes see p.5.)

| Potential Frost Action (10) | Compressibility And Expansion (11) | Drainage Characteristics (12) | Compaction Equipment (13) | Unit Dry Weight lb per cu ft (14) | Typical Design Values | |
|-----------------------------|------------------------------------|--------------------------------|--|-----------------------------------|-----------------------|---|
| | | | | | CBR ^a (15) | [Subgrade Modulus k lb per cu in.] (16) |
| None to very slight | Almost none | Excellent | Crawler-type tractor, rubber-tired roller, steel-wheeled roller | 125-140 | 40-80 | 300-500 |
| None to very slight | Almost none | Excellent | Crawler-type tractor, rubber-tired roller, steel-wheeled roller | 110-140 | 30-60 | 300-500 |
| Slight to medium | Very slight | Fair to poor | Rubber-tired roller, sheepfoot roller; close control of moisture | 125-145 | 40-60 | 300-500 |
| Slight to medium | Slight | Poor to practically impervious | Rubber-tired roller, sheepfoot roller | 115-135 | 20-30 | 200-500 |
| Slight to medium | Slight | Poor to practically impervious | Rubber-tired roller, sheepfoot roller | 130-145 | 20-40 | 200-500 |
| None to very slight | Almost none | Excellent | Crawler-type tractor, rubber-tired roller | 110-130 | 20-40 | 200-400 |
| None to very slight | Almost none | Excellent | Crawler-type tractor, rubber-tired roller | 105-135 | 10-40 | 150-400 |
| Slight to high | Very slight | Fair to poor | Rubber-tired roller, sheepfoot roller; close control of moisture | 120-135 | 15-40 | 150-400 |
| Slight to high | Slight to medium | Poor to practically impervious | Rubber-tired roller, sheepfoot roller | 100-130 | 10-20 | 100-300 |
| Slight to high | Slight to medium | Poor to practically impervious | Rubber-tired roller, sheepfoot roller | 100-135 | 5-20 | 100-300 |
| Medium to very high | Slight to medium | Fair to poor | Rubber-tired roller, sheepfoot roller; close control of moisture | 90-130 | 15 or less | 100-200 |
| Medium to high | Medium | Practically impervious | Rubber-tired roller, sheepfoot roller | 90-130 | 15 or less | 50-150 |
| Medium to high | Medium to high | Poor | Rubber-tired roller, sheepfoot roller | 90-105 | 5 or less | 50-100 |
| Medium to very high | High | Fair to Poor | Sheepfoot roller, rubber-tired roller | 80-105 | 10 or less | 50-100 |
| Medium | High | Practically impervious | Sheepfoot roller, rubber-tired roller | 90-115 | 15 or less | 50-150 |
| Medium | High | Practically impervious | Sheepfoot roller, rubber-tired roller | 80-110 | 5 or less | 25-100 |
| Slight | Very high | Fair to poor | Compaction not practical | - | - | - |

Notes Cont'd:

2. c. cont'd Rubber-tired equipment -- wheel load in excess of 15,000 lb, wheel loads as high as 40,000 lb may be necessary to obtain the required densities for some materials (based on contact pressure of approximately 65 to 150 psi). Sheepfoot roller -- unit pressure (on 6- to 12-sq-in. foot) to be in excess of 250 psi and unit pressures as high as 650 psi may be necessary to obtain the required densities for some materials. The area of the feet should be at least 5 per cent of the total peripheral area of the drum, using the diameter measured to the faces of the feet.

3. Column 14, unit dry weights are for compacted soil at optimum moisture content for modified AASHO^{**} compaction effort.
 4. In column 15, the maximum value that can be used in design of airfields is, in some cases, limited by gradation and plasticity requirements.

^a California Bearing Ratio.

^{**} American Association of State Highway Officials.

| Major Divisions (1) | Major Divisions (2) | Letter (3) | Symbol | | Name (6) | Value for Embankments (7) |
|-----------------------------|------------------------------------|---------------|-----------------|--------------|--|--|
| | | | Hatching (4) | Color (5) | | |
| COARSE- GRAINED SOILS | GRAVEL AND GRAVELLY SOILS | GW | | Red | Well-graded gravels or gravel-sand mixtures, little or no fines | Very stable, pervious shells of dikes and dams |
| | | GP | | | Poorly-graded gravels or gravel-sand mixtures, little or no fines | Reasonably stable, pervious shells of dikes and dams |
| | | GM | | | Silty gravels, gravel-sand-silt mixtures | Reasonably stable, not particularly suited to shells, but may be used for impervious cores or blankets |
| | | GC | | | Clayey gravels, gravel-sand-clay mixtures | Fairly stable, may be used for impervious core |
| | SAND AND SANDY SOILS | SW | | Yellow | Well-graded sands or gravelly sands, little or no fines | Very stable, pervious sections, slope protection required |
| | | SP | | | Poorly-graded sands or gravelly sands, little or no fines | Reasonably stable, may be used in dike section with flat slopes |
| | | SM | | | Silty sands, sand-silt mixtures | Fairly stable, not particularly suited to shells, but may be used for impervious cores or dikes |
| | | SC | | | Clayey sands, sand-silt mixtures | Fairly stable, use for impervious core for flood control structures |
| FINE - GRAINED SOILS | SILTS AND CLAYS | ML | | Green | Inorganic silts and very fine sands, rock flour, silty or clayey fine sands or clayey silts with slight plasticity | Poor stability, may be used for embankments with proper control |
| | | CL | | | Inorganic clays of low to medium plasticity, gravelly, sandy, silty, and lean clays | Stable, impervious cores and blankets |
| | | LL < 50 | | | Organic silts and organic silt-clays of low plasticity | Not suitable for embankments |
| | | OL | | | Inorganic silts, micaceous or diatomaceous fine sandy or silty soils, elastic silts | Poor stability, core of hydraulic fill dam, not desirable in rolled fill construction |
| | SILTS AND CLAYS LL > 50 | MH | | Blue | Inorganic clays of high plasticity, fat clays | Fair stability with flat slopes, thin cores, blankets and dike sections |
| | | CH | | | Organic clays of medium to high plasticity, organic silts | Not suitable for embankments |
| | | OH | | | Peat and other highly organic soils | Not used for construction |
| | | Pt | | | | |

Notes: 1. Values in columns 7 and 11 are for guidance only. Design should be based on test results.

2. In column 9, the equipment listed will usually produce the desired densities with a reasonable number of passes when moisture conditions and thickness of lift are properly controlled.

Fig. 3C. Unified soil-classification system for roads, embankments and foundations. (By permission of United States Army Engineer, Waterways Experiment Station, Corps of Engineers). Characteristics pertinent to embankments and foundations.
(Explanation and notes see p.5.)

| Permeability Cm Per Sec (8) | Compaction Characteristics (9) | Std AASHO Max Unit Dry Weight Lb Per Cu Ft (10) | Value for Foundations (11) | Requirements for Seepage Control (12) |
|-----------------------------------|--|---|--|---|
| $k > 10^{-2}$ | Good, tractor, rubber-tired, steel-wheeled roller | 125 - 135 | Good bearing value | Positive cutoff |
| $k > 10^{-2}$ | Good, tractor, rubber-tired, steel-wheeled roller | 115 - 125 | Good bearing value | Positive cutoff |
| $k = 10^{-3}$ to 10^{-6} | Good, with close control, rubber-tired, sheepfoot roller | 120 - 135 | Good bearing value | Toe trench to none |
| $k = 10^{-6}$ to 10^{-8} | Fair, rubber-tired, sheepfoot roller | 115 - 130 | Good bearing value | None |
| $k > 10^{-3}$ | Good, tractor | 110 - 130 | Good bearing value | Upstream blanket and toe drainage or wells |
| $k > 10^{-3}$ | Good, tractor | 100 - 120 | Good to poor bearing value depending on density | Upstream blanket and toe drainage or wells |
| $k = 10^{-3}$ to 10^{-6} | Good, with close control, rubber-tired, sheepfoot roller | 110 - 125 | Good to poor bearing value depending on density | Upstream blanket and toe drainage or wells |
| $k = 10^{-6}$ to 10^{-8} | Fair, sheepfoot roller, rubber tired | 105 - 125 | Good to poor bearing value | None |
| $k = 10^{-3}$ to 10^{-6} | Good to poor, close control essential, rubber-tired roller, sheepfoot roller | 95 - 120 | Very poor, susceptible to liquefaction | Toe trench to none |
| $k = 10^{-6}$ to 10^{-8} | Fair to good, sheepfoot roller, rubber tired | 95 - 120 | Good to poor bearing | None |
| $k = 10^{-4}$ to 10^{-6} | Fair to poor, sheepfoot roller | 80 - 100 | Fair to poor bearing, may have excessive settlements | None |
| $k = 10^{-4}$ to 10^{-6} | Poor to very poor, sheepfoot roller | 70 - 95 | Poor bearing | None |
| $k = 10^{-6}$ to 10^{-8} | Fair to poor, sheepfoot roller | 75 - 105 | Fair to poor bearing | None |
| $k = 10^{-6}$ to 10^{-8} | Poor to very poor, sheepfoot roller | 65 - 100 | Very poor bearing | None |
| Not used for Construction | Compaction not practical | | Remove from Foundations | |

Notes Cont'd:

3. Column 10, unit dry weights are for compacted soil at optimum moisture content for Standard AASHO (Standard Proctor) compactive effort.

Highway and Transportation Officials for highway construction (1982,1978), the Federal Aviation Administration for design of airport pavements (1974) and the Unified Soil Classification System (Fig. 3) developed by the Bureau of Reclamation and the Corps of Engineers (U.S. ARMY ENGINEER WATERWAYS EXPERIMENT STATION, 1967). These systems have been compared and described by several authors (WAGNER, 1957; BOWLES, 1979). Soil characteristics most used in engineering classification are particle size and consistency. In the Unified Soil Classification System soils are classified as coarse-grained, fine-grained or organic. These three divisions are subdivided into fifteen groups which have distinct engineering properties. In this system a soil is classified on the basis of its behaviour in simple tests the results of which reflect physical properties, composition, moisture content, etc. The information obtained enables the quality of a soil to be assessed as a material for construction or as a foundation.

The system is a development and expansion of a scheme set up by CASAGRANDE (1948). The consistency is of basic importance in the classification of fine-grained soils. This may be estimated by manual examination or measured more accurately by the limit tests. Limits were originally established by ATTERBERG (1911). Those now in common use are the liquid limit, the plastic limit and the shrinkage limit. The liquid limit is defined as the water content of a soil (expressed in %, dry weight) having a consistency such that two sections of a soil cake, placed in a cup and separated by a groove, barely touch but do not flow together under the impact of several sharp blows. In other words it is the water content below which the soil no longer behaves as a liquid. The plastic limit is defined as the water content (expressed in %, dry weight) at which a soil will crumble when rolled into a thread 3 mm (1/8 inch) in diameter; that is the soil loses its plastic properties at lower water contents. The shrinkage limit of a soil is defined as the amount of moisture which is sufficient to fill the voids in the soil mass at the maximum amount of shrinkage or, in other words, "the shrinkage limit is reached when volume change with decrease in water content ceases" (CUMMINGS and HART, 1959, pp. 8-12 to 8-13; MERRITT, 1976, pp. 7-8). Soil shrinkage results in settlement of compressible soils.

The range in moisture content over which the soil is plastic is defined by the difference between the liquid limit and the plastic limit; this difference is known as the plasticity index, I_p . The liquidity index is obtained by calculation from the natural moisture content, the plastic limit and the liquid limit. It is evaluated by substitution of the appropriate values in the following expression:

$$I_L = \frac{w - w_p}{w_L - w_p}$$

in which I_L = liquidity index; w = natural moisture content; w_p = plastic limit; w_L = liquid limit. When the moisture content of the sample is equal to the liquid

limit the liquidity index is equal to unity. When the natural moisture content is equal to the plastic limit the liquidity index is zero. As the moisture content of a soil is reduced there is a proportional reduction in volume until the shrinkage limit. When the moisture content is reduced below the shrinkage limit there is a little further decrease in volume and the soil becomes hard and almost brittle.

The highest values for index properties are commonly shown by soils with a high clay content. In general smectites have the highest liquid and plastic limits, illites have intermediate values and kaolinites have the lowest values. Nature of exchange ion, particle size, fabric, presence of non-clay minerals and other factors influence the values obtained. Certain organic soils also give high values of index properties. Casagrande graphically illustrated the range in values which can be obtained by means of the plasticity chart. On this,

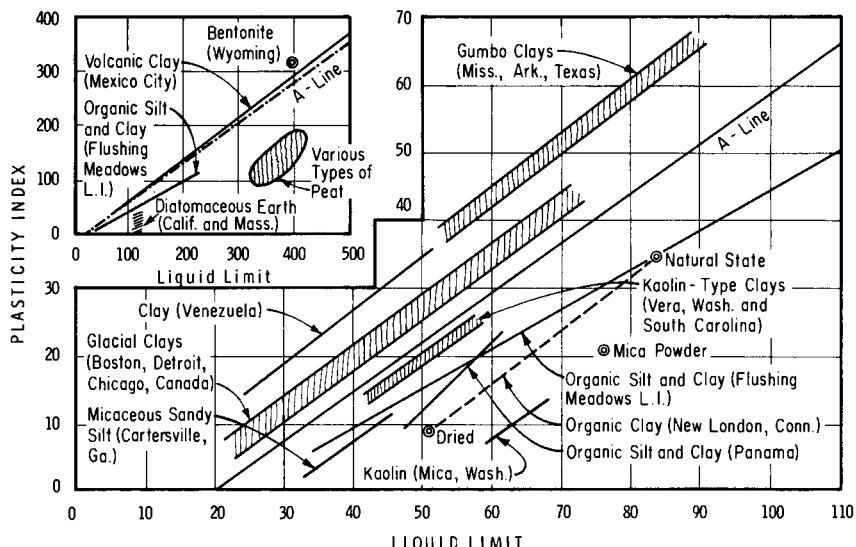


Fig. 4. Relationship between liquid limit and plasticity index for typical soils. (After CASAGRANDE, 1948, fig. 5.)

plasticity index is plotted as ordinate versus liquid limit as abscissa. CASAGRANDE (1948, p.921) classified soils with reference to an empirical boundary termed the "A-line" (Fig. 4). This runs from a liquid limit of 20 and plasticity index zero through the point which has a liquid limit of 50 and a plasticity index of 22. He found that typical inorganic clays have plastic properties which plot above the A-line whereas plastic soils which contain organic colloids plot below it. Inorganic silts, silty clays and clays composed of rock flour generally fall below the A-line but some plot slightly above it. According to TERZAGHI (1955,

p. 565) different grain-size fractions of a ground-up mineral have plastic properties which plot on a line which is approximately parallel to the A-line. If different samples of a composite sedimentary deposit have plastic properties which, when plotted on the plasticity chart, lie on very different lines "it is almost certain that the sediments were derived from two different sources".

CERAMIC CLASSIFICATION

In ceramics engineering and materials science clays are often described as china clays, ball clays, and various kinds of refractory clays such as fire clays and flint clays. China clays are white and composed largely of kaolinite. They are used for the manufacture of whitewares, special refractories, and insulators. When impurities are present such as iron-bearing minerals the clays may become discoloured on burning. They are less valuable commercially. Ball clays contain illite and sometimes montmorillonite as well as kaolinite. They have a fine particle size and a high plasticity. They are commonly darker in colour than china clays. Flint clay, a kaolinitic mudstone, is a refractory raw material. It was produced by diagenesis during accumulation within the environment and climate typical of Coal Measures. Reactions involved desilication and partial removal of iron, alkalies and alkaline earths from parent aluminosilicates (KELLER, 1981). It has been suggested that flint clays, toasted clays, tonsteins and bauxitic clays have sufficient in common to justify grouping them in a single sedimentary facies (LOUGHNAN, 1978).

Refractory clays are those in which fusion does not occur until a temperature of not less than 1,500°C. They generally have a high content of alumina. They may be classified in terms of the temperature of softening or on the basis of the pyrometric cone equivalent. Standard pyrometric cones are made of mixtures of known composition shaped into pyramidal form with triangular bases. The height is about three to four times the side of the base. The cones are shaped so that the centre of gravity is displaced and the tip of the apex bends over when the material softens due to being heated. Cones are made of different compositions and assigned numbers from the most easily fusible to the most refractory. A standard heating rate is employed and the standard temperature for the cone is taken as the point at which the tip bends over and touches the base. This is actually a function of both heat treatment as well as temperature. A refractory clay sample is heated in the same way as the cone and assigned the number of the cone which performs in the same manner. Methods for measurement of refractoriness have been laid down in standardized form (AMERICAN SOCIETY FOR TESTING AND MATERIALS, C24-79, 1981, pp. 9-13; BRITISH STANDARDS INSTITUTION, 1966). Workability is also considered in the classification of refractory clays. Flint clays are hard and do not become plastic when mixed with water; those which soften and become workable when water is added are termed plastic fire clays. The flint clays generally have the highest pyrometric cone equivalent.

PEDOLOGICAL CLASSIFICATION

Soil scientists or pedologists term the total thickness of the weathered surface zone of the crust the soil profile. Properties such as colour, texture, structure, and composition change with depth and pedologists subdivide the profile into layers termed horizons (Fig. 4.20). The surface layer has been termed the A horizon, the layer below, or subsoil, the B horizon and the underlying soil parent material the C horizon. Subdivisions are often recognized within each of these horizons. They are indicated by a numerical subscript following the letter as A₁, A₂, B₁, B₂. Many systems of classification have been developed for use in agriculture and for the preparation of soil-survey maps. These maps often contain information of use to engineers and geologists.

In the United States the "Comprehensive Soil Classification System" was developed by successive approximations (U.S. Dept. Agriculture, 1951; 1960; 1975) and is based on quantitatively defined properties of the soil including moisture and temperature regimes. It is the result of international consultation in the hope that the system will be of use in countries outside the U.S.A. Tables are included relating terms used in soil taxonomies developed earlier in the U.S.A. and those used in France, the Soviet Union and Canada (Canada Dept. Agriculture, 1978). A principal objective is to classify soils so that more reliable predictions of soil behaviour can be made from knowledge of related soils. In the classification it is recognized that more knowledge is available for some soils than others such as those of the tropics, permafrost regions and of organic composition.

The system includes six categories which are the order, suborder, great group, subgroup, family and series. There are ten orders differentiated by the presence or absence of diagnostic horizons within the complete soil profile. Firstly mineral soils are distinguished from organic soils. The diagnostic horizons of mineral soils include six surface horizons and seventeen subsurface horizons. The term epipedon is used for surface horizons but it is not a synonym for the A horizon since it may include part of the B horizon if this is darkened by organic materials from the surface. The diagnostic surface horizons are:

1. Mollic: dark surface horizon, often containing 2:1 clay minerals; bivalent cations generally dominant in the exchange complex; at least 18 cm thick with 1 per cent or more organic matter; common to the soils of the steppes of the Americas, Europe and Asia.
2. Anthropic: similar to the mollic but the level of phosphorus is higher and if not irrigated is dry during more than 9 months of the year in more than 7 years out of 10.
3. Umbric: similar to the mollic in colour, organic carbon, phosphorus content, consistence, structure and thickness; base saturation is < 50 percent.
4. Histic: thin horizon of peat or muck if not ploughed which contains at least

12 percent organic matter; if not drained artificially is saturated for 30 consecutive days in most years.

5. Plaggen: man-made surface layer which commonly contains artifacts such as bits of pottery and brick; more than 50 cm thick; produced by long continued manuring.

6. Ochric: Light coloured surface horizon which may be both hard and massive when dry.

The diagnostic subsurface horizons are:

1. Agric: thin layer formed by cultivation composed of silt, clay and humus;

2. Albic: horizon from which clay and free iron oxides have been removed; colour determined by primary sand and silt.

3. Argillic: horizon of clay accumulation by illuviation or formation.

4. Calcic: horizon of calcium carbonate or calcium and magnesium carbonate accumulation; 15 cm or more thick.

5. Cambic: a leached horizon which has lost sesquioxides or bases including carbonates, or both; most of original rock structure destroyed.

6. Duripan: a horizon cemented by silica and accessory cements such as iron oxide and calcium carbonate; air dry fragments will not slake in water or acid.

7. Fragipan: a horizon which is seemingly cemented when dry but fragments slake or fracture in water; from 15 to 200 cm thick; attributed to the weight of glaciers or permafrost; impedes movement of water which stands above the pan in level soil and moves laterally along the pan in sloping soil.

8. Gypsic: horizon of sulphate accumulation which is 15 cm or more thick.

9. Natric: special argillic horizon with exchangeable sodium; prismatic or columnar structure.

10. Oxic: very weathered horizon at least 30 cm thick; consists of hydrated oxides of Fe or Al or both with 1:1 layer structure clay minerals and highly insoluble minerals such as quartz; no primary minerals that weather with release of bases, iron or aluminium.

11. Petrocalcic: cemented or indurated calcic horizon; dry fragments do not slake in water; hard or extremely hard when dry and very firm or extremely firm when moist; hydraulic conductivity slow to very slow; generally much thicker than 10 cm.

12. Petrogypsic: a gypsic horizon that is so strongly cemented that dry fragments do not slake in water; gypsum content usually exceeds 60 per cent; found in arid climates with parent materials rich in gypsum; common in parts of Africa and Asia.

13. Placic: a thin black to dark reddish pan cemented by Fe, by Fe and Mn or by Fe-organic complex; generally 2 to 10 mm thick; found in humid or perhumid climates.

14. Salic: a horizon which contains a secondary enrichment of salts more soluble in cold water than gypsum; 15 cm or more thick; contains at least 2 per cent salt and the product of its thickness in cm and salt percentage by weight is 60 or

more.

15. Sombric: a horizon formed under free drainage thought to be restricted to cool moist soils of the high plateaux and mountains in tropical or subtropical regions; base saturation low because of leaching.
16. Spodic: horizon of precipitation of amorphous materials composed of organic matter and aluminium with or without iron; the material has high exchange capacity, large surface area and high water retention; found in humid environments.
17. Sulfuric: horizon composed of mineral or organic material that has both pH<3.5 and is mottled yellow due to the mineral jarosite; forms due to artificial drainage and oxidation of sulfide-rich mineral or organic materials.

The ten orders based on these horizons are:

1. Alfisols: have an argillic or matric horizon or fragipan; no spodic or oxic horizon over argillic.
2. Aridisols: have an ochric or anthropic surface horizon; found principally in arid environments.
3. Entisols: have few or no diagnostic horizons; no calcic, petrocalcic, gypsic or petrogypsic horizon or duripan in upper 1 m and no fragipan.
4. Histosols: organic soils, found generally in swamp or marsh, but may be drained.
5. Inceptisols: have any surface horizon; commonly have cambic horizon; no gypsic or petrogypsic horizon in upper 1 m.
6. Mollisols: have a mollic surface horizon; no spodic horizon in upper 2 m; no oxic horizon; generally found in subhumid to semiarid regions.
7. Oxisols: have an oxic horizon; are saturated at some time in most years; found in tropics or subtropics.
8. Spodosols: have a spodic horizon in upper 2 m or placic horizon over fragipan; coarse textured; found in humid environments.
9. Ultisols: have an argillic horizon or fragipan below; found principally in warm, humid environments.
10. Vertisols: have a minimum of 30 per cent clay (principally expansive) to at least 50 cm depth; generally found in subhumid to arid environments.

The name indicates the position of a soil taxon in all categories above the series, in general, similarities in important properties being reflected by similarities in names. Orders can be recognized as such by the ending "sol". This ending is preceded by the connecting vowel "i" or "o" which links the ending to the first part of the order name. The first part of the name, "contains a formative element that begins with the vowel next preceding the connecting vowel and ends with the last consonant preceding the connecting vowel" (U.S. Dept. Agriculture, 1975, p. 83). For example the formative element in Entisol is "ent" and in Aridisol it is "id". Suborders, great groups and subgroups have names

which end in the formative element of the appropriate order. For example the ending "ent" indicates that a taxa belongs to the Entisol order. The names of suborders have two syllables the first of which refers to diagnostic properties of the soils and the second syllable is the formative element of the order thereby facilitating appropriate recognition within the system. Formative elements and their meaning are described in "Soil Taxonomy" (U.S. Dept. Agriculture, 1975) and those of most significance to engineers have been summarized by Philipson et al. (1973).

An objective of the U.S. system is the prediction of soil behaviour from the properties of other similar soils rather than being primarily concerned with more theoretical topics such as genesis. Much valuable information to do with soil behaviour may be derived from the system and it is to be hoped that engineers and geologists will not be daunted by the unfamiliarity and apparent complexity of the terminology. Purposes of soil classification, its basis and application to engineering have been discussed previously RUTKA (1961), De BAKKER (1970), STEILA (1976), HINER et al. (1979), BUOL et al. (1980) and DENT and YOUNG, (1981).

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Chapter 2

PHYSICAL GEOLOGY

The earth is one of the nine major planets in the solar system. Its orbit lies between that of Venus and Mars at a distance of about 93 million miles from the sun. The earth has a radius at the equator of approximately 6,378 km. The planet has a structure in which three major layers can be recognized. These are the core, the mantle, and the crust. The mantle is about 2,900 km thick and this is overlain by the crust which varies in thickness from 6-8 km beneath the oceans to more than 30 km beneath the continents. There is a sudden increase in the velocity of earthquake waves between the crust and mantle and the sharp boundary is known as the Mohorovicic discontinuity in recognition of the discoverer of this fact. The crust has an estimated age of 4,500 million years and the planet itself is somewhat older. Geological time is divided into eras, systems, and periods (Table 2.1) and finer subdivisions are employed in the detailed study of regions. The geology of clay mainly concerns events in the outermost skin of the crust though some economically important clay deposits originated at elevated temperatures below the surface.

TABLE 2.1

The Division of Geological Time
(Age data from HOLMES, 1964)

| Eras | Systems | Periods | Duration (years) |
|----------------------------|---|---|--|
| Kainozoic | Quaternary Tertiary | Holocene or Recent Pleistocene or Glacial Pliocene Miocene Oligocene Eocene Paleocene | $2-3 \cdot 10^6$ $9-10 \cdot 10^6$ $13 \cdot 10^6$ $15 \cdot 10^6$ $20 \cdot 10^6$ $10 \cdot 10^6$ $65 \cdot 10^6$ |
| Mesozoic | Cretaceous Jurassic Triassic Permian | | $45 \cdot 10^6$ $45 \cdot 10^6$ $45 \cdot 10^6$ $45 \cdot 10^6$ |
| Palaeozoic | Carboniferous Devonian Silurian Ordovician Cambrian | Pennsylvanian Mississippian | $80 \cdot 10^6$ $50 \cdot 10^6$ $40 \cdot 10^6$ $60 \cdot 10^6$ $100 \cdot 10^6$ |
| Precambrian | | | $3,000 \cdot 10^6$ |
| Formation of earth's crust | | | About $4,500 \cdot 10^6$ |

GEOMORPHOLOGY

Topography is the expression at the earth's surface of internal and external dynamic processes. In geomorphology changes in the surface form of the earth are related to changes in the dynamic processes in time and space. The origin of clay and the behaviour of clay soils takes place within the geomorphic framework. Geomorphology has potential applications in engineering geology in such fields as urban development and planning and may be usefully linked with such modern methods as remote sensing (VERSTAPPEN, 1977).

Towards the end of the last century and in the early years of this a general theory of geomorphic development was proposed by W.M. Davis(1954). He concluded that landscape develops by an evolutionary process now generally termed the cycle of erosion or geomorphic cycle. This was regarded as commencing with a newly uplifted land into the surface of which streams rapidly cut V-shaped channels with steeply sloping sides. As the cycle progressed the steep hills were reduced in height and the angle of the slopes declined (Fig. 2.1A). A region as well as a single valley were both considered to undergo a cyclical development. The process was regarded as controlled by the base level which is "the level below which a land surface cannot be reduced by running water" (WEBSTER, 1961). The ultimate base level is the sea but the local base level may be the bed of the principal stream. Three main stages were recognized in the geomorphic cycle termed youth, maturity and old age. A river valley with a steep gradient and V-shaped cross-section with little or no flood-plain was considered to be "graded". A stream is graded when the amount of detritus being supplied is just equal to the stream's load carrying capacity so that a state of equilibrium is attained. When a river valley has been reduced to base level erosion takes place laterally rather than vertically. A mature river shows development of a flood-plain and falls and rapids have mainly disappeared. A river in the old age stage of development meanders

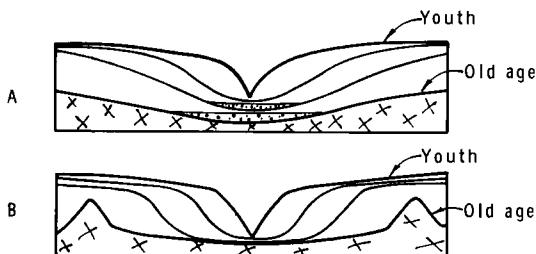


Fig. 2.1. Cross-sections of valley during stages in development of geomorphic cycle. A. According to concept of declining slope angle. B. According to concept of constant slope angle.

across a broad flood-plain showing ox-bow lakes formed from isolated segments of the former river channel. The general aspect of the topography is considered to become a nearly featureless detritus-covered plain, termed a peneplain, crossed by sluggish meandering streams. Other geomorphic cycles such as the glacial cycle, the arid cycle, the cycle of coastal development and a cycle for limestone regions have been proposed.

The Davis concept of erosion has great value as it provides a general framework into which many commonly observed landscape features may be fitted and conditions of transportation, erosion and other aspects of the physical geography of a region can be to some extent anticipated. The cyclic model is not, however, universally accepted since the initial assumptions are regarded by some as specialized and restrictive in nature. An underlying assumption of the Davis model is that the study of a topographic form enables the processes responsible for its development as well as its past history to be deduced. The more modern view is that different combinations of processes or different histories can lead to development of similar topographic forms (CHORLEY, 1965). Also in the cycle proposed by Davis the development of the morphology of such temperate regions as New England was treated as "normal". Critics have pointed out that the topography of such regions is still much affected by the climatic extremes of the Pleistocene so that their development has been far from "normal". Flat valley floors may result from filling by sediment rather than from lateral erosion of valley walls. The generally broad, explanatory and descriptive nature of the Davis approach has also prompted criticism that insufficient emphasis is placed on specific topics such as mechanics and the behaviour of different varieties of solid and fragmental rocks (YATSU, 1966). The suggestion that the geomorphic cycle starts with an initial uplift which takes place during a relatively short interval of geological time has been criticized. Instead it has been proposed that the elevation of a land-mass takes place slowly and perhaps intermittently so that the theory expounded by Davis may be unrealistic. The idea that hillside slopes flatten as denudation progresses has also not gone unchallenged. An alternative proposition is that once slopes have assumed an angle which is stable for the local conditions this angle is maintained as the hillsides are worn back (Fig. 2.1B) (PENCK, 1953). The gently inclined surface remaining after the parallel recession of the hillslope has been termed a pediment. Continued erosion should lead to the extension and eventual coalescence of many such surfaces into a more extensive plain, termed a pediplain, surrounding steep residuals (KING, 1953, p.723). The scheme is most readily fitted to the geomorphology observed in arid and semi-arid domains though parallel back-wearing (rather than down-wearing) of soil covered slopes is now thought possible (OBERLANDER, 1974). Attempts have been made to reconcile the alternative suggestions of slope recession at a

constant angle and recession with decrease in angle of slope. C.D. HOLMES (1955, p.379) for example suggests that two fundamental types of slope exist, termed wash slopes and gravity or derivation slopes. Wash slopes are "graded surfaces of sediment transport" and gravity slopes are "surfaces which supply the sediment". The two types are present in both humid and arid environments of erosion but the arrangement and relative proportion of the two types differ because of differences in erosion caused by differences in climate and the amount of vegetation. Gravity slopes are considered to recede at a constant angle which is determined by the local conditions and so in this respect they possess Penckian characteristics. TWIDALE (1978) has similarly concluded that pediments are surfaces of transportation for detritus derived from adjoining uplands. Studies of pediments from regions of folded sediments, flat-lying strata and crystalline rocks mostly cut in weak or weathered rocks led him to conclude that none of the landscapes evolved exclusively by decline or recession of the slopes and that the pediments had not evolved cyclically. He also stressed that the term pediplain should only be used when upland residuals survive because otherwise the landform produced by coalescence of pediments is indistinguishable from a peneplain.

There are also workers who reject the idea that equilibrium or quasi-equilibrium in landscape development is arrived at by an evolutionary process operating on a time scale measured on the geological scale. HACK (1960, p.84) for example believes that most streams are in a state of quasi-equilibrium which is arrived at very rapidly as so many alternative adjustments are possible due to the large number of variables. Erosion under steady state conditions was suggested by STRAHLER (1950) and similar conclusions are also reached by LEOPOLD and LANGBEIN (1962, p.A19). In these concepts the idea of landscape evolution is not denied but the seemingly reasonable proposition is made that with every change in environment caused by natural processes or human activity the quasi-equilibrium state is re-established relatively quickly. Mathematical considerations led GRAF (1977) to conclude that the return towards a steady state does take place very rapidly at first but at later ages progressively more time is required for readjustment. He considers that the whole process may be described by a rate law which has the form of a negative exponential similar to that used to define relaxation times of other physical systems. The ready availability of equipment for data extraction such as the digitizer and advent of computer technology generally have encouraged greater use of mathematical techniques in this field as elsewhere. For example, the hydraulic geometry of drainage basins has been investigated quantitatively in terms of parameters defined with respect to the drainage network. Data have been analyzed using a probabilistic-topological approach involving a random model base (JARVIS, 1977; THURNES, 1978; FLINT, 1980). A Geomorphology

Symposium is held annually and trends in research in this field may be followed from these publications (THORN, 1982).

HYDROLOGICAL CYCLE

Water is classified as meteoric water when it is derived from the atmosphere by precipitation, as juvenile water when it originates from within the earth due to igneous activity, and as connate water when it is trapped in sediments at the time of deposition. The hydrological cycle constitutes the general pattern of water movement at and near the earth's surface and chiefly involves meteoric water. The cycle is powered in part by solar energy and in part by gravity. Water is evaporated to form clouds, precipitated as rain or snow and eventually finds its way to the oceans. A large proportion of the water precipitated on the land-surface is returned to the atmosphere by evaporation and by transpiration from plants.

Some of the water which falls on the land infiltrates into the soil under the influence of gravitational and capillary forces and finds its way to the underlying bedrock via cracks, joints and cleavages and by percolation through pore-spaces. Subsurface water is commonly classified by its relation to the ground-water table or phreatic surface (KUENEN, 1955, p.184; FLINT and SKINNER, 1977). Below this plane void spaces are filled with water and the water is termed ground-water (MEINZER, 1923, p.38). The pressure below the ground-water table increases linearly with depth as does the pressure below a free water surface. At the water table the ground-water is at atmospheric pressure; it is the level to which water rises in a bore-hole. Its depth varies seasonally, with the amount of water abstracted and with the barometric pressure. For example fluctuations have been recorded due to variations in microbarometric pressure caused by atmospheric pressure waves resulting from nuclear explosions (INESON, 1963, p.22). A perched water-table occurs if a permeable water-bearing layer overlies an impermeable bed which is separated from the main water-table by unsaturated strata. In the unsaturated zone moisture moves due to gravitational and capillary forces and by diffusion in the vapour phase. Some of this does not reach the ground-water table but is trapped in voids and crevices. It is called pendulate water (KUENEN, 1955, p. 186). Movement of water by vapour-phase diffusion can be enhanced by such disconnected drops which shorten the diffusion path length (RUSE, 1963, p.260) so the hydraulic conductivity (or capillary conductivity) depends upon moisture content as well as on soil fabric. Closer to the water-table capillary spaces are occupied by water which is continuously connected to the ground-water table. The thickness of this zone is determined by the height of capillary rise. It is thicker for clays than coarse-grained deposits as capillary forces are more significant due to the fine pore structure though hydraulic conductivity is lower. The height

of capillary rise in sands is about 0.3m and in clays it is about 1.0m (RODDA et al., 1976, p.138). Ground-water is of great importance as a source of potable water for drinking and other purposes. It plays an active part in the break-up of the land by aiding and participating in chemical attack on the rocks and by removing soluble products. A decline in redox potential, E_h has been measured as ground-water migrates from upland recharge areas to lowland discharge areas. This has been attributed to a sequence of reactions and three oxidation-reduction zones in groundwater flow have been identified. These are: (1) oxygen-nitrate, (2) iron-manganese, and (3) sulphide (CHAMP et al., 1979). Ground-water ultimately reaches the sea by slow percolation, by re-emergence as surface water at springs and by discharge into streams and rivers as baseflow.

If the rocks exposed near the surface have low permeability, as do most argillaceous rocks, a higher proportion of the precipitation runs off as surface water. The volume of run-off is the balance of the total precipitation after subtraction of losses due to evaporation, transpiration and infiltration into the ground. Surface water is one of the chief agents of weathering, erosion and transportation. Its effectiveness in denudation depends on its chemical composition and on the nature and amount of solids being moved. Rain-water generally contains some free oxygen, ammonia, carbon dioxide and other gases and particularly in coastal regions it often contains sodium chloride believed derived from sea-spray. Rain-water generally has an acid reaction (pH less than 7) due to the small amount of CO_2 in solution. Carbon dioxide is relatively soluble in water so its concentration in rainwater is higher than in the atmosphere. Strong acids such as nitric and sulphuric and soot have been found in the rain-water of industrial countries (CLARKE, 1924, pp.54-55; GORHAM, 1955, p.233). The pH of surface and near surface waters ranges from acid to alkaline. In alkaline soils the pH may exceed 9 whereas peat and mine waters often have a pH of 3 or 4. In acid thermal springs the pH is as low as 1 or 2 (MASON, 1966, p.165). Hydrolytic reaction with the freshly exposed surfaces of abraded minerals gives run-off waters a pH which depends upon the nature of the country rock (KELLER, 1958, 1960; KELLER and REESMAN, 1963; KELLER et al., 1963). Granites and rocks of similar composition are associated with acid surface waters whereas the drainage tends to be alkaline when nepheline syenites and rocks rich in ferro-magnesian minerals are exposed. The composition and salinity of the water in different rivers is very variable due to differences in the solubilities of the various minerals in the rocks with which the water comes in contact, due to differences in the proportion of water derived from direct run-off and from ground-water seepage and due to variations in the composition and pH of the water itself. Calcium is abundant in the water of rivers in limestone districts and magnesium becomes increasingly

important when the limestone is dolomitic. The bicarbonate ion in river water owes its presence not only to the relatively high concentration of CO_2 in rain-water but also to the amount picked up from the soil atmosphere by infiltrating ground-water. Below ground level oxygen and carbon dioxide vary in a complimentary fashion and CO_2 content may be much higher than in the open atmosphere due in part to biological agents in the soil, (DeJONG and PAUL, 1979, p.10-19). Sulphate content rises when ground-water enters the rivers after infiltration into saline soils or rocks containing gypsum or sulphide minerals undergoing oxidation. Silica is derived from silicate minerals and the proportion increases when chert is locally available particularly when the water is above about pH 9. The solubility of alumina is high at both low and high values of pH and is considerably less soluble over intermediate pH ranges between about pH 4 to pH 9 or 10. Alkali ions in river-water may originate from exchange reactions involving clay minerals. Average values for the principal constituents are shown in Table 2.2. According to SODERBLOM (1963) waters which contain substances which favour clay-mineral dispersion exert a more vigorous erosive action on argillaceous strata than do waters which tend to flocculate the clay minerals. Some organic compounds may be important in this respect and also in regard to the concentration of elements such as iron, nickel and copper.

TABLE 2.2 Mean Composition of River Waters

| Component | Concen- tration ppm | % of Total(1) salt | % of Mean(2) total concen- tration |
|----------------|---------------------------|-----------------------|---|
| HCO_3 | 58.4 | 48.7 | 54.6 |
| Ca | 15.0 | 12.5 | 13.9 |
| SiO_2 | 13.1 | 10.9 | 12.3 |
| SO_4 | 11.2 | 9.3 | 9.6 |
| Cl | 7.8 | 6.5 | |
| Na | 6.3 | 5.2 | 2.5 |
| Mg | 4.1 | 3.4 | 3.4 |
| K | 2.3 | 1.9 | 2.1 |
| NO_3 | 1.0 | 0.8 | 0.9 |
| Fe | 0.67 | 0.6 | 0.7 |
| | 120 | 99.8 | |

(1) Data from: D.A. Livingstone, 1963. Chemical Composition of Rivers and Lakes. In, M. Fleischer, Data of Geochemistry, 6'th Edit. p. G41. Reproduced by courtesy of U.S. Geological Survey, Washington, D.C.

(2) Data from: Ian Statham, 1977. Earth Surface Sediment Transport. Clarendon Press Oxford, p.140. Reproduced by permission of the publisher.

TABLE 2.3 Major Salt Constituents of Seawater

| Component | Concentration (%) | % of Total Salt |
|--------------------------------|-------------------|-----------------|
| Cl | 18.980 | 55.04 |
| Na | 10.543 | 30.61 |
| SO ₄ | 2.465 | 7.68 |
| Mg | 1.272 | 3.69 |
| Ca | 0.400 | 1.16 |
| K | 0.380 | 1.10 |
| HCO ₃ (b) | 0.140 | 0.41 |
| Br(b) | 0.065 | 0.19 |
| H ₃ BO ₃ | 0.024 | 0.07 |
| Total | 34.455 | 99.5 |

(a) Values in grams per kilogram (%) based on chlorinity of 19%

(b) Varies to give equivalent CO₃²⁻ depending on pH. Value given is essentially true for Ph 7.50 at 20°C.

(c) Corresponds to a salinity of 34.325%.

Table from: D. W. Hood, 1972. Seawater, chemistry. In: R.W. Fairbridge (Editor). The Encyclopedia of Geochemistry and Environmental Sciences p. 1063. Reproduced by permission of Van Nostrand Reinhold Co. Copyright (c) 1972.

In the open sea the water has a salinity of about 35⁰/oo (parts per thousand). The composition is complex and about 50 elements have been detected by analysis. The major constituents of sea-water are shown in Table 2.3. In sea-water the relative proportions of the ions present are different from their relative proportions in river water (Table 2.2). In sea-water the relationships are Na > Mg > Ca and Cl > SO₄ > CO₃ whereas in average river water the proportions are Ca > Na > Mg and CO₃ > SO₄ > Cl. Sea-water contains a relatively lower proportion of calcium, due to the large amount removed by marine organisms in formation of shells and skeletons, and a relatively much higher ratio of sodium to potassium than river water. In rivers draining tropical regions the SO₄ contents are relatively low whereas iron, alumina and silica are relatively high (RANKAMA and SAHAMA, 1949, p.272). KRUMBEIN and GARRELS (1952, p.2) in discussing the formation of chemical sediments of marine origin have summarized the characteristics of the water in a variety of environments including normal marine with open circulation, restricted humid, and restricted arid (evaporite). Conditions in the open sea are normally mildly alkaline (pH 7.5-8.5) and mildly oxidizing; in the restricted humid environment the pH may be alkaline or acid (as in some fjords) and either oxidizing or reducing conditions may prevail; under arid evaporite conditions of restricted circulation the pH is thought to increase with increasing salinity and high temperatures also reduce oxygen content. MASON (1966, p.197) notes that sea-water contains 34-56 ml/l CO₂ as dissolved gas and while the atmosphere regulates the amount present in surface waters the

relationship is complex because CO_2 is present in sea-water in four distinct forms - free CO_2 , carbonate ions, bicarbonate ions, and undissociated H_2CO_3 . CARROLL and STARKEY (1960, p.82) point out that the Ca^{2+} in sea-water is probably involved in the buffering mechanism whereby the pH range is controlled. The ocean is probably in an approximately steady state condition and its composition has probably not varied much for as long as 10^8 years. The maintenance of this balance undoubtedly involves complex reactions between dissolved constituents and degraded clay minerals. Such reactions may be also in part responsible for the composition of the atmosphere (HOLLAND, 1965; KRAMER, 1965; MACKENZIE and GARRELS, 1966; LERMAN, 1972).

Water plays a major role in geology as an agent of erosion and transportation, as the medium in which a great many chemical reactions occur and as an important reactive compound. The composition of water is also of importance to engineers and engineering geologists in regard to control of both corrosion and deposition of excessive amounts of carbonate precipitates in water pipes. The chemical principles and use of the "Saturation Index" have been described by LANGELIER (1936).

EROSION AND TRANSPORTATION

Erosion has been defined as "The general process or the group of processes whereby the materials of the Earth's crust are loosened, dissolved, or worn away, and simultaneously moved from one place to another, by natural agencies, which include weathering, solution, corrosion, and transportation" (BATES and JACKSON, 1980, p.210). Erosion is brought about by chemical, mechanical and biological agencies including man. In natural processes gravity provides the ultimate source of energy which results in movement from higher to lower elevations of the earth's land surface. The proportions of solid, liquid and gaseous phases vary widely in earth materials undergoing different kinds of movement. When an agent such as water, ice or wind is a major factor in transportation the movements are often referred to as mass-transport processes. Such transportation may occur in a confined channel involving rivers or valley glaciers or may take place on a wider scale as in a continental ice sheet or dust-storm. Unlike water, ice and wind have the ability to transport solid particles uphill as well as down. When an agent of transportation is not primarily involved the process is often distinguished as mass wasting or mass movement. Mass movements involve soil creep and solifluction, landslides, rockfalls and mudflows.

Waves and currents are responsible for erosion and transportation beneath the surface of bodies of water such as lakes and the sea. In wave action there is an oscillatory movement in the water and currents have a translational motion subject to variation in strength and direction. Sediment carrying

fresh-water streams are generally less dense than sea-water because of the high salt-content of the latter. Therefore sediment is transported into the sea as overflows. Clay minerals should be rapidly flocculated as the fresh-water mixes with the salt. Organisms such as plankton digest and excrete the floccs producing organic-rich agglomerations and pellets. The particles in the agglomerations and pellets are sometimes sufficiently strongly bonded to resist disaggregation by turbulence so agglomerations and pellets together with floccs form the settling units and have been observed by electron microscopy in sediments (see Fig.4.13a). Further biological activity as well as early diagenesis may continue to modify the sediment before it is affected by more drastic consolidation, diagenesis and eventually desiccation in the subaerial environment of the present. Density currents and turbidity currents are thought by some to have considerable erosive power and to be at least partly responsible for subaqueous bottom features such as submarine canyons. A density current is "a gravity-induced flow of one current through, over, or under another, owing to density differences. Factors affecting density differences include temperature, salinity, and concentration of suspended particles" (BATES and JACKSON, 1980). A turbidity current is a variety of density current in which the density difference results from suspended sediment due to turbulence in the suspension medium and the term turbidity current is therefore more restricted than density current (FRIEDMAN and SANDERS, 1978). Characteristic features have been long associated with turbidite deposits (KUENEN and MIGLIORINI, 1950). Submarine erosion and transportation is of importance in connection with harbours and coastal protection and its engineering significance is increasing as structures erected on the sea-bed become more common. The mechanisms of erosion have been analysed from observational evidence of regional topography, from detailed study of localized areas and on the basis of models.

Mass Movements

The engineer and engineering geologist often regard slope failure as the most serious problem with which they have to deal since the movements can occur with catastrophic suddenness. Slow movements, commonly termed creep, can nonetheless be destructive and may involve costly maintenance. Soil and rock behaviour concerns type and rate of movement and is affected by drainage conditions, degree of saturation and position of ground-water table, geological structure such as nature of bedding and jointing, presence of fissures and slickensides, soil profile, and genesis, composition and microstructure of soil material (SCHUSTER and KRIZEK, 1978; Can. GEOTECH. J., 1980). It was recognized in the early years of this century that cohesion, resulting from the plasticity of clay, strongly influences soil behaviour.

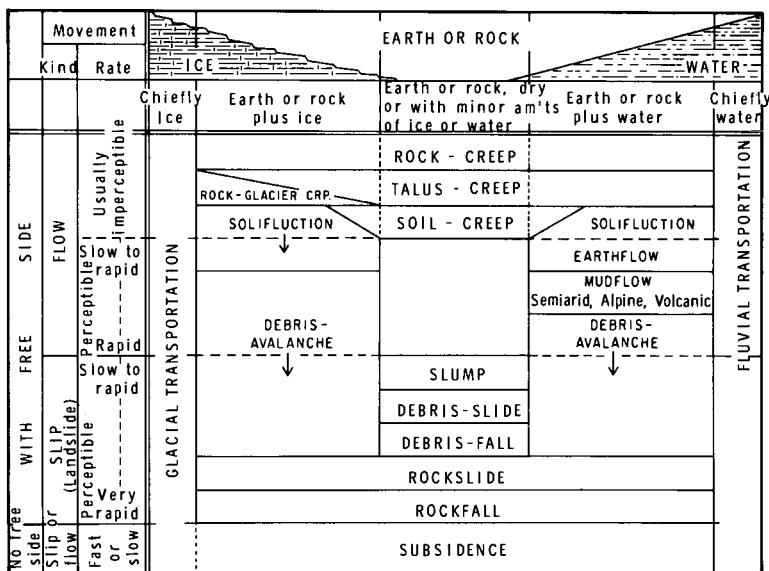


Fig. 2.2 Classification of landslides and related phenomena. (After SHARPE, 1960, by permission of Cooper Square Publishers, Inc.)

SHARPE (1960, p.17) classified mass movements on the basis of kind and rate. He distinguished movements on a slip plane as slides from movements involving flowage in which no slip plane is present and deformation affects all parts of the moving mass. Subdivisions of his classification involve consideration of the kind of material and the amount of ice or water relative to earth material within the mass (Fig. 2.2).

| TYPE OF MOVEMENT | | | TYPE OF MATERIAL | | |
|------------------------|---------------|------------|--|-----------------------------|----------------------------|
| | | | BEDROCK | ENGINEERING SOILS | |
| | | | | Predominantly coarse | Predominantly fine |
| FALLS | | | Rock fall | Debris fall | Earth fall |
| TOPPLES | | | Rock topple | Debris topple | Earth topple |
| SLIDES | ROTATIONAL | FEW UNITS | Rock slump | Debris slump | Earth slump |
| | TRANSLATIONAL | MANY UNITS | Rock block slide | Debris block slide | Earth block slide |
| LATERAL SPREADS | | | Rock slide | Debris slide | Earth slide |
| FLOWS | | | Rock spread | Debris spread | Earth spread |
| | | | Rock flow (deep creep) | Debris flow (soil creep) | Earth flow (soil creep) |
| COMPLEX | | | Combination of two or more principal types of movement | | |

Table 2.4. Abbreviated classification of slope movements (After D.J. Varnes, 1978. Landslides Analysis and Control. p.11. Reproduced with permission of Transp. Res. Board, Washington, D.C.).

A more up-to-date classification was developed from this and the work of many others, by VARNES (1978) (Table 2.4). Six types of movement and two classes of material (bedrock and engineering soils) are recognized. Slides are subdivided into rotational, where failure occurs on a concave surface (Fig. 2.3) and translational where the failure surface is more or less planar; movements of the latter kind are controlled by surfaces of weakness and movement may occur on one or several surfaces. Spreads and flows overlap to some extent since liquified mud flows belong to both. The "complex" category recognizes that slope movements are often of more than one type. Slow downhill movements are included as flows. When movements result mainly from frost-

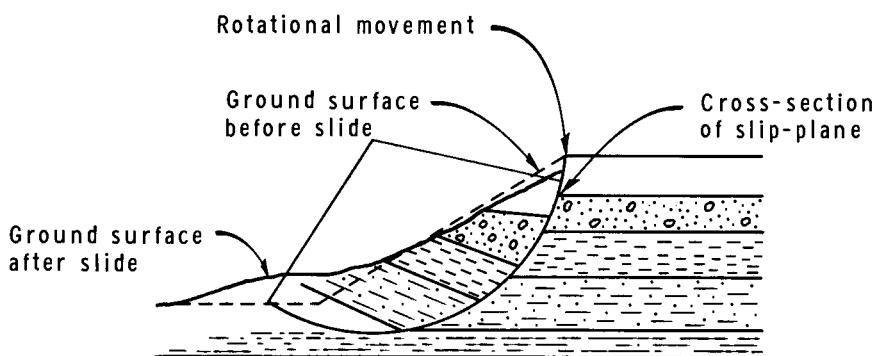


Fig 2.3. Shear-failure by rotational slide in cohesive strata.

action the term solifluction is used. The term creep is used when the movements result mainly from seasonal and diurnal heating and cooling, burrowing and wedging by animals and plants and plastic deformation of clay. Slow movements of this sort commonly precede more catastrophic failure. Studies have shown that primary, secondary and tertiary stages of creep, recognized in other materials, may be observed in soil and rock. Rates of soil creep have been measured in the field and the phenomenon has been studied experimentally in the laboratory (SINGH and MITCHELL, 1969; FLEMING and JOHNSON, 1975).

Slides may be either shallow or deep. In surface slides the ratio of thickness to length is of the order of 5%; this ratio is of the order of 20% in rotational slips (SKEMPTON, 1953, p.48). Deep-seated slides are to be expected when, as depth increases, there is a more rapid increase in shear stress than in shear strength; these conditions are not uncommon in certain relatively thick and homogeneous clay soils. Field examination by borings of actual slope failures by sliding has shown that in cohesive strata the slip surface is approximately cylindrical. This was first established by the Swedish State

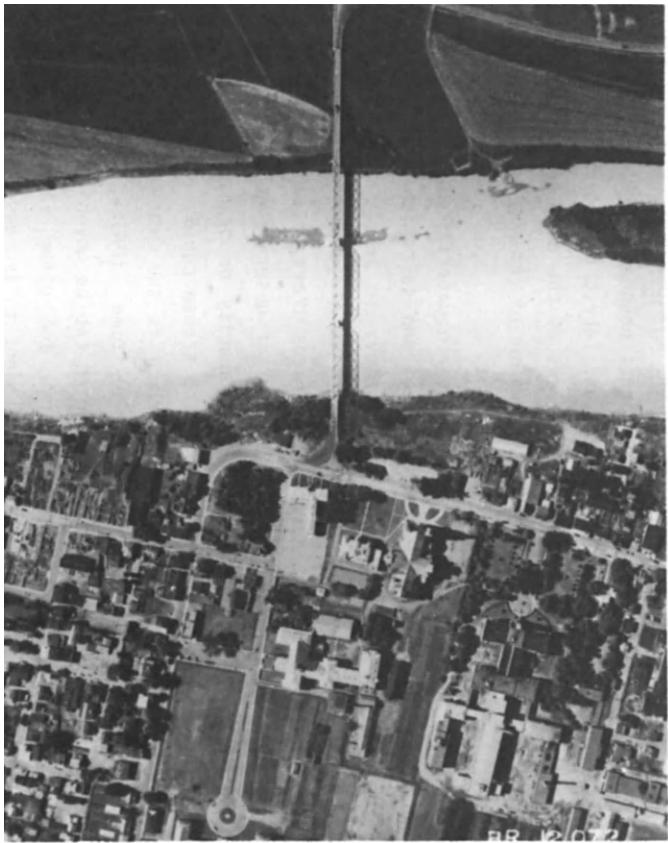
Railways Geotechnical Commission (STATENS JARNVAGARS GEOTEKNISKA KOMMISSION, 1922, p.57). A rotational movement of material occurs on a curved shear-plane with minor distortion within the rotating mass. The form of the surface of failure may be modified by the presence of weak layers of clay which become softened by the action of percolating waters. In cross-section the cylindrical slip-surface is a circular arc (Fig.2.3). Analytical procedures for engineering use have been developed by which the position of the critical surface, the surface most likely to fail by shear-slip, may be deduced. Slides are the only type of movement to which quantitative slope stability analyses may be applied by the conventional sliding wedge or circular arc techniques. Several alternative methods of analysis are available and the calculations may be made in terms of total or effective stresses. In the case of translational slides analyses may be made of failure on a planar surface neglecting end effects. The methods assume an average shearing resistance on the failure surface which is found from a finite number of analyses and by evaluation of mechanical properties of the material such as shear strength and by consideration of drainage conditions, depth of piezometric and ground-water surfaces (TAYLOR, 1948; U.S. ARMY CORPS OF ENGINEERS, 1952; ECKEL, 1958; SKEMPTON and HUTCHINSON, 1969).

Changes in slope result from a variety of natural causes such as mountain-building movements, isostatic uplift following removal of such loads as the Pleistocene ice-cap, deposition and undercutting by rivers, glaciers and the sea. The development of slopes and the cross-sectional profile of valleys has been discussed by WOOD (1942), in terms of a slope cycle. Proposed mathematical models for the derivation of slopes have been reviewed by SCHEIDECKER (1961). Differential equations have been developed and a series of solutions obtained within the framework of various special restrictions. Statistical techniques were employed in slope analysis by STRAHLER (1950). Man-made embankments, cuttings and excavations also alter the slope and stability of earth materials. Engineers estimate stability in terms of the factor of safety which is the ratio of the shear resistance to the shear stress and conditions become unstable when the value of this ratio falls to unity. In practice a value of about 1.5 or even less may be used to minimize costs but use of such low values requires that soil properties are well understood and that analyses are performed with sufficient precision. The factor of safety may be defined with respect to parameters such as height of slope or engineering properties of the earth material such as cohesion or shear strength. In uncemented material slope stability is dependent upon the composition, size of the particles, degree of consolidation, porosity, previous history, percentage saturation and drainage conditions. Slope stability is also affected by the height and steepness of the slope, the climate, and

frequency and intensity of earthquakes and other forms of natural and artificial vibrations.

Decreased stability results either from an increase in the shearing stress or from a decrease in the shearing resistance of the material (TERZAGHI, 1950, p.88). Such a loss of strength may result from an increase in pore water pressure due to a rise in the ground-water table or a decrease in cohesion due to a cause such as removal in solution of intergranular cement. Saturation due to a rise in level of the water-table fills voids and causes surface tension forces to vanish between particles within the mass. Uplift or downcutting by rivers tends to lower the ground-water table; human activities can also lower the water-table for example by drainage of lakes or by rapid drawdown of a reservoir. In relatively impermeable clay soils the slow rate of adjustment of ground-water level and piezometric surface will result in an increase in pore pressure causing a decrease in shear strength so that slope failure may result. Clays which have been heavily compacted by former deep burial may undergo slow softening when a deep excavation or cutting is made which decreases the load on the flanks. The clay expands and there is an initial fall in pore pressure. The expansion allows joints and fissures to open up so water gains access but a clay soil is relatively impermeable so pore pressure rises only slowly. As the overburden pressure is diminished, because of the removal of load, softening and a slow loss of strength results which eventually may lead to failure (SKEMPTON and HUTCHINSON, 1969). In this regard joints or faults with a filling of montmorillonite are particularly likely to contribute to slide failure due to the high swelling capacity on moisture uptake of this clay mineral (BREKKE and SELMER-OLSEN, 1965). Highly fluid mass movements occur in "quick clays" of a high sensitivity⁽¹⁾. Landslides of "flow" type are common in certain extra-sensitive post-glacial sediments in Canada, Scandinavia, Alaska and elsewhere. These sometimes have a characteristic shape in plan (Fig. 2.4) and may have a narrow neck through which the outflow of material took place. A typical example has been described by CRAWFORD and EDEN (1963). Movements of sensitive silt and clay often occur as lateral spreads; the principal type of movement is translation rather than rotation. Difficulties of classification occur because there is a wide range of gradation between movements in which the sediment becomes almost completely liquified to ones in which greater coherence is retained within the moving mass. Discussions of the nature and behaviour of sensitive soils have been given by many authors (COULTER and MIGLIACCIO, 1964; FRANSHAM and GADD, 1977; PENNER and BURN, 1978; SMALLEY, 1979).

(1) Sensitivity is defined as the ratio of the strength of the undisturbed material to its strength after being remoulded.



A



B

Fig. 2.4. Aerial photographs before (A), and after (B) slide to show shape in plan
(After Crawford and Eden, 1963, p.46).

The sites where ancient slides occurred can often be identified, particularly on aerial photographs, by recognition of the characteristic scar in the topography. Excellent summaries of how geological and engineering factors may combine to give a very large landslide have been given in connection with the Vajont reservoir and other disasters (KIERSCH, 1965; ANDERSON and TRIGG, 1976). When the relative amount of water increases transportation passes via rainwash and sheetfloods on slopes to transportation by streams and rivers which involves flow in a channel.

Mass Transport Processes

(a) Erosion and transportation in channels

Sediment transport in an alluvial channel is of interest to engineers in connection with such problems as river control in estimating water and sediment discharge (SCHUMM and BEATHARD, 1976), and in channel design in irrigation projects where earth canals are often employed as distributaries of the water. In the latter case a stable channel is required which is neither subject to excessive erosion by the moving water nor to silting due to sediment deposition (LANE, 1955, p.1235). Engineers have formulated rules for the understanding of open channel hydraulics derived from practical experiments and field experience. Mathematical models have been developed to describe flow, the influence of particles and behaviour at channel boundaries (BAGNOLD, 1966; 1973). Geologists try to relate the structure and fabric of sediments to flow conditions, depositional environment, etc. Reviews of the application of some of the principles of fluid mechanics to the formation of sedimentary structures are given by MIDDLETON (1965).

When water flows in a channel it transports earth material in solution, in suspension and along the bottom by surface creep and saltation. The latter process involves particles which are just too heavy to remain in continuous suspension but which travel along the bed in a series of jumps. The term load is employed for "the total weight of solid detritus transported in unit time past the cross-section of the river at the place of observation" (A. HOLMES, 1964, p.510). This is usually less than the capacity or transporting power which is the maximum amount of material which the stream could transport. The flow of water is described as the discharge which is the "rate of flow at a given moment expressed as volume per unit of time" (BATES and JACKSON, 1980,p178). The size of the solid particles which can be moved by a stream or its competence is a function of the discharge and other variables. The velocity of flow of rivers has generally been thought to decrease downstream as the longitudinal profile flattens in that direction. Flow data obtained at stream-gaging stations in the United States, however, led LEOPOLD (1953, p.610) to conclude that this is incorrect and in fact the velocity corresponding to

mean discharge tends to increase with increasing discharge downstream. Increase in discharge also leads to downstream changes in width and depth and to changes in velocity and depth at a given location. It is also probable that there is a downstream decrease in competence due to a decrease in the vertical velocity gradient between rate of flow near the stream bed and rate of flow nearer the surface of the stream.

The ability of flowing water to move particles depends largely on its velocity and turbulence and on the weight or depth of the water. Importance has long been attached to impact, frictional drag and hydraulic uplift. The impact hypothesis is the basis of the so-called "sixth power law". According to this law "the weight or volume of the largest particles moved varies as the sixth power of the velocity of the stream" (RUBEY, 1937, p.123). The velocity has to be measured as close to the stream bed as possible and is difficult to measure in practice. The sixth power variation underlines the great increase in the transporting power of a stream with increase in velocity. Rubey concluded that this law described the movement of sand and gravel more closely than the movement of silt and clay. In addition to the velocity of flow of the water it was realized by DU BOYS (1879) that the depth is also a factor in determining the onset of movement of particles on a stream-bed. He introduced the idea of a "critical tractive force" and developed a formula in which velocity is left out and force is related to the slope of the stream bed and depth of the water.

In the presence of a steep velocity gradient there is, according to Bernoulli's principle, a resultant upward component of force. A vertical gradient in the velocity of the stream flow is to be expected near the bottom and the resulting "hydraulic lift" has been invoked as a mechanism in the lifting of particles from a stream-bed. More modern attempts to deal with the problem of stream transport in mathematical terms have been reviewed by BRUUN and LACKEY (1962). They conclude that the bed load involves a basically different mode of transportation from the suspended load both of which have to be considered in attempting to estimate the total load transported.

Sediment transport by moving water is not a simple problem (BROOKS, 1958, p.527) and it has been investigated by laboratory studies in which some of the variables may be controlled as in flume experiments. Flow phenomena have been described by use of the term "flow regime". This terminology has been used differently by different workers depending on the approach. SIMONS et al (1965) apply the term to a range of flows which have similar bed forms, resistance to flow, mode of sediment transport and phase relations between form of bed and water surface. Resistance to flow and sediment transport were found to be related to bed roughness. This in turn is affected by the slope, the depth of flow, fall velocity or effective fall diameter of the bed material and

the shape of the channel. Two regimes of flow, termed an upper and a lower flow regime with a transition between, were recognized each with distinctive forms of bed (Fig.2.5). In the lower flow regime the bed forms are ripples and dunes and resistance to flow is large. The undulations of the surface of the water are out of phase with the surface of the bed. In the upper flow regime plane bed, standing waves and antidunes are characteristic, resistance to flow is small and sediment transport is large; the water surface is in phase with the bed surface except when an antidune breaks. Thus as velocity of flow increases an initially flat bed develops ripples which increase in length, and are termed dunes, as velocity further increases. Ripples on dunes develop which are washed out and replaced by a flat bed in the transition between lower and upper flow regime. At still higher flow velocity antidunes, in phase with the water surface, develop; antidunes are finally replaced by chutes and pools at the highest velocity. Ripples and dunes move slowly downstream whereas antidunes and the corresponding waves at the surface of the water move upstream. In the upper regime the size distribution of the transported material was found to be the same as that of the bed material and there was no appreciable segregation. In the lower regime there was always some sorting or segregation. The concept of flow regime is of practical use because it combines several variables together under one heading. It is now thought that

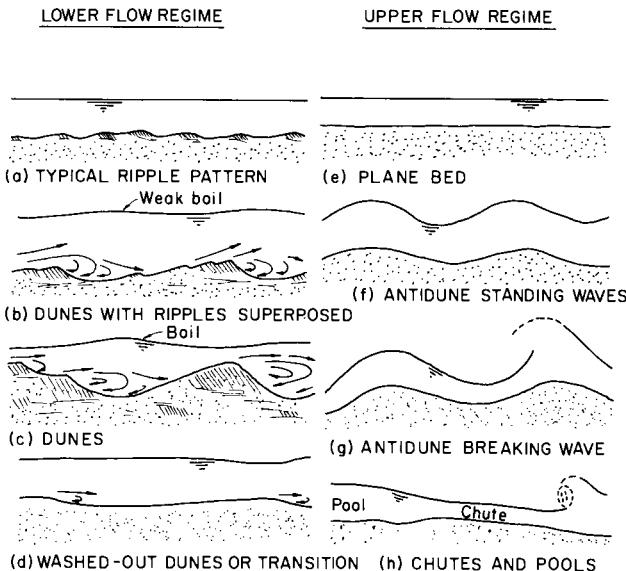


Fig.2.5. Forms of bed roughness in alluvial channels. (After SIMONS et al., 1965, p.36)

it may be possible to interpret flow environment in terms of flow regime from observation of sedimentary structures such as stratification even though it may not be possible to deduce more specific information such as depth or velocity of flow (HARMS and FAHNESTOCK, 1965). In flume studies of the transport of pebbles and cobbles on a bed of 0.33 mm sand it was found that the pebbles on the sand bed were transported consistently downstream only when the flow was in the upper regime and provided the forces were sufficient to set the rock in motion. When the flow was in the lower regime the pebbles moved upstream and down into the sand (FAHNESTOCK and HAUSHILD, 1962, pp.1435-1436). Experimental studies concerning the influence of the depth of water on the erosion of cohesive soils have been reported by MIRTSKHULAVA and DANELIYA (1962). They found that as the water depth was increased from 35 to 235 cm cohesive soils showed increased resistance to erosion. Non-cohesive soils showed no corresponding increase in resistance to erosion.

Dissolved substances and fine sediment such as clay both in suspension and in bed material have been shown by theoretical and experimental studies to affect sedimentary structures and transport phenomena (SIMONS et al., 1963). Such studies are important in connection with waste and sewage disposal and the possibility of stream contamination for example by radioactive materials. GLOVER (1964) concluded that dispersion is achieved by a diffusion mechanism but dispersion rates for natural streams were many times higher than those indicated by the analytical work. Lateral diffusion coefficients were found to be much smaller than the coefficients for longitudinal dispersion as turbulence is largely responsible for lateral diffusion.

Most of the clay minerals have a well-developed cleavage and in the case of those with layer structures platelet thickness is likely to decrease during transportation. Sodium montmorillonite for example will disperse in water to particles with a thickness normal to the basal plane of the order of one unit cell.

(b) Erosion and transportation by wind

It is in arid and semi-arid regions that wind is of most importance as an agent of erosion and transportation though it is significant elsewhere when plant cover is absent. Such situations include beaches, fields stripped bare of vegetation by human activities and very active flood-plains such as probably existed at the margins of the withdrawing continental glaciers at the close of the Pleistocene. Erosion caused by sand carried by the wind is termed wind abrasion. It is most effective within a few feet of the surface and tends to cause undercutting. Lowering of the land surface by wind removal of dry surface layers of incoherent material is termed deflation. Depressions can be excavated below sea-level by wind action, the Quattara depression in western

Egypt, for example, having a depth of about 125 m below sea-level; the ground-water table sets the lower limit of depth to this kind of erosion. Movement of light winds over smooth surfaces involves laminar flow but strong winds are the effective agents of erosion and transportation where air movement mainly involves turbulent flow.

Wind, like flowing water, transports particles both as bed-load and in suspension. Bed-load consists of coarser particles such as sand grains which roll or move in a series of jumps. Impact by these moving grains scatters fine particles into the air where they are kept in suspension by turbulence, vortices and eddies. Lift may involve Bernoulli's principle and result from pressure differences as flowing air moves over particles with velocity differences developing between upper and lower surfaces; shear may also be a factor, particularly in movement. These processes are evidently sufficient to overcome the resistance offered by the strong cohesive forces between fine particles of silt and clay. Dry clay cracks and sometimes rolls-up so it presents rougher, more vulnerable, surfaces to wind action. Fine-grained soil constituents such as clay may be transported great distances by wind. Erosion by wind action has caused serious loss of agricultural land in the U.S.S.R., the U.S.A., and elsewhere due to incorrect farming methods in semi-arid regions (U.S. DEPT. AGRICULTURE, 1938). As discussed elsewhere in this volume loess is a characteristic and widespread wind transported soil the behaviour of which has considerable engineering importance. Its origin and lithology have been described in detail by SMALLEY (1977). Loess often contains clay minerals (Fig. 4.17C) which may have acted as nucleation sites for raindrop condensation and so have been washed out of atmospheric suspension together with the grains of quartz; precipitation may also have involved electrical effects. Calcium carbonate is common in some deposits of loess. Cementation of intergranular contacts by this compound and increased cohesion due to the clay probably contribute to the unusual engineering and physical properties of loess such as its ability to support steep cliffs.

(c) Erosion and transportation by ice

Detritus transported by a glacier is derived from above, by weathering of the valley sides, and from below by abrasion of the bedrock. Some of this material is transported on the surface (supraglacial), some is transported at the base (subglacial) and some becomes incorporated within the ice (englacial). Deep chemical weathering may have occurred during the long period preceding the Pleistocene (FEININGER, 1971). The later cooling trend was no doubt accompanied by significant frost-action before the onset of glacial conditions. Abundant loose material was therefore probably available to be picked-up and used as an abrasive agent when the ice advanced.

The classical view of erosion by ice was that it removes blocks of bedrock by frictional drag; it was thought that the ice works its way into cracks, joints and other partings tearing away projecting pieces of rock. This plucking process provides moving ice with "tools" for abrasion so the surface of the bedrock becomes scraped and scratched. The rate of abrasion has been reported to be approximately proportional to the cube of the velocity of the ice (HOLMES, 1964, p.643). A valley glacier is therefore a more effective erosive agent than is the slower-moving ice of a continental ice-sheet. Generally glaciers move slowly at a rate of about 30m per year. Some glaciers however have been observed to advance much more rapidly for a period at a rate which may be more than 100x normal. During such "surges" velocities of up to 120m per day have been recorded.

In modern work it is proposed to distinguish cold (or polar) from temperate glaciers. In a cold glacier it is thought that the basal ice is frozen to the bedrock and that principal mechanisms of movement are slip on shear-planes and plastic flow within the ice mass. It appears that this kind of movement results in much less abrasion than is caused by temperate glaciers. In a temperate glacier the ice is at a temperature close to its pressure melting-point and a zone of melting is believed to exist between the base of the ice and the bedrock. The water is thought to have a lubricating action and to facilitate sliding. A process of melting and regelation as the ice moves over obstacles has been described (NYE, 1973). Pressure on the upslope side of obstacles is relatively high and causes melting; refreezing occurs on the downstream side. When solutes are considered it seems that the rate of movement should be less than that calculated for a pure water-ice system. In limestone districts subglacially precipitated deposits of carbonates have been attributed to chemical dissolution and re-precipitation processes implied by this mechanism (HALLET, 1976). It has also been suggested that the basal ice melts because of a reversed temperature gradient there being a slight increase of temperature from the base of the ice upwards towards the surface which prevents the escape of geothermal heat. If the water at the base builds up due to being unable to escape as fast as it is produced unstable conditions and surging may follow (COLLINS, 1971). Cyclical surging has been explained by relating increase in pressure gradient in the water at the base of a glacier to the derivative of the basal shear stress (ROBIN and WEERTMAN, 1973). The meltwater beneath a temperate glacier may exert a scouring action particularly when flow occurs in tunnels and in any case it seems that a rigid distinction should not be made between glacial and fluvioglacial erosion. It is probable that Pleistocene glaciers in lower latitudes were mainly of the temperate variety.

The crushing, fracturing and abrasion which takes place during glacial

erosion produces rock-flour - a material which includes significant amounts of primary minerals such as quartz reduced to angular particles in the micrometre size range. The ground-up rock and weathered material is carried away from the snout of a glacier by streams of meltwater. The suspended material often gives glacial streams and lakes a milky and sometimes bluish-green appearance. At the close of the Pleistocene the glacial outwash was often deposited in lakes or seas and as till or boulder clay in such characteristic features as moraines. Processes of glacial erosion and deposition have been discussed by EMBLETON and KING (1975) and SUGDEN and JOHN (1976).

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Chapter 3

THE ORIGIN AND EVOLUTION OF CLAY MINERALS AND CLAYS

Clay minerals commonly form at the expense of primary rock-forming minerals. A clay is composed of an accumulation of clay-sized mineral particles of which clay minerals generally make up a significant proportion. The clay minerals in sedimentary rocks are largely detrital and were deposited following transportation to their present locations after erosion of the parent material. It is however now abundantly clear that authigenic clay minerals are also present, often in void spaces, in rocks of all kinds (see Fig. 4.19A to F). Such minerals may have formed by chemical reactions involving crystallization of gels or may owe their delicate euhedral form to precipitation of new material and epitactic growth upon detrital clay particles. Reactions leading to growth of authigenic minerals probably occur under conditions of weathering, diagenesis and hydrothermal action.

PARENT MATERIALS OF CLAYS AND SOILS

The composition of a clay is affected by the mineralogical and chemical composition of the parent material. This may be the solid bedrock or a non-lithified superficial layer such as boulder clay resting on bedrock. If the parent material contains clay minerals, as do many sedimentary rocks and superficial deposits, some proportion of these may be incorporated in the clay which also inherits some of those non-clay minerals which are resistant to physical and chemical attack. Strictly, a rock is any natural aggregate of mineral matter whether coherent or not so that in this sense loose sands, gravels and clays are included. Rocks may be broadly divided into three classes which are igneous, metamorphic and sedimentary.

Igneous rocks are aggregates mainly of silicate minerals. They form by solidification of a hot siliceous melt termed magma. A magma generally incorporates some proportion of volatiles such as water, CO₂, CO, HCl, S vapour and oxides, H₂S, and other gases. There is a general order or sequence in which minerals are known to crystallize from a cooling magma. This sequence was deduced by BOWEN (1928) and subsequent workers. Those igneous rocks which formed by solidification of the magma at depth below the surface are termed intrusive. They are classed as plutonic when crystallization took place slowly at great depth and hypabyssal when cooling occurred nearer the surface as in many dikes, sills and veins. Igneous rocks formed at the surface by cooling of volcanic lavas are extrusive. Some volatiles commonly escape prior to solidification of such rocks.

Although there are about 1,000 recognized minerals less than a dozen groups compose over 99% by weight of igneous rocks. The common minerals and mineral groups are quartz, feldspar, pyroxenes, amphiboles, micas, olivines, nepheline, leucite, oxides of iron and titanium, and apatite (CLARKE and WASHINGTON, 1924, p.3). Minerals may be distinguished as "saturated" and "unsaturated". Saturated minerals are those which are compatible with an excess of silica in the magmatic melt and include the feldspars, pyroxenes, amphiboles, micas, magnetite, ilmenite, and accessory minerals such as apatite, zircon and sphene. Distinctive unsaturated minerals are olivine, feldspathoids, and melilites which crystallize on the cooling of a melt deficient in silica. Light minerals such as quartz, feldspars and feldspathoids are often referred to as "felsic", and dark, ferro-magnesian minerals such as olivine, pyroxenes, hornblende and biotite as "mafic". The composition of some of the more important igneous rocks is shown in Fig. 3.1 in a form which emphasizes that the compositional boundaries are gradational. Igneous rocks may be classified on the basis of the relative abundance of felsic and mafic minerals, the presence or absence of quartz or unsaturated minerals, and the nature of the feldspars.

The most abundant igneous rocks by volume are granites and granodiorites among plutonic rocks and basalt and andesite among volcanics. The average chemical composition of igneous rocks as given by CLARKE (1924, p.34) is shown in Table 3.1. A metamorphic rock is defined as, "any rock derived from pre-existing rocks by mineralogical, chemical, and/or structural changes, essentially in the solid state, in response to marked changes in temperature, pressure, shearing stress, and chemical environment, generally at depth in the Earth's crust "(BATES and JACKSON, 1980, p.393). Igneous and sedimentary rocks may be altered by metamorphic processes and metamorphic rocks themselves may be affected by more than one sequence of changes. Metamorphic rocks include among others quartzite, marble, hornfels, slate, phyllite, schist, gneiss, amphibolite, and migmatite. Important minerals in metamorphic rocks are chlorite, the micas, garnet, staurolite, kyanite, sillimanite, andalusite and cordierite. Feldspars, amphiboles and quartz are also common, the particular mineral assemblage being a reflection of the original composition of the rock and the degree and type of metamorphism. Average analyses of clays and their metamorphosed equivalents are shown in Tables 3.2 and 3.3.

Sedimentary rocks form by the accumulation and cementation of the disintegration products of other rocks and the remains of organisms. They form a discontinuous layer at the surface of the crust which varies from 0 to 3 km but locally attains a thickness of 20 km. They are composed of mineral grains, rock fragments, and the hard parts of organisms such as shells, tests and other skeletal remains. New minerals formed during the accumulation of the detritus

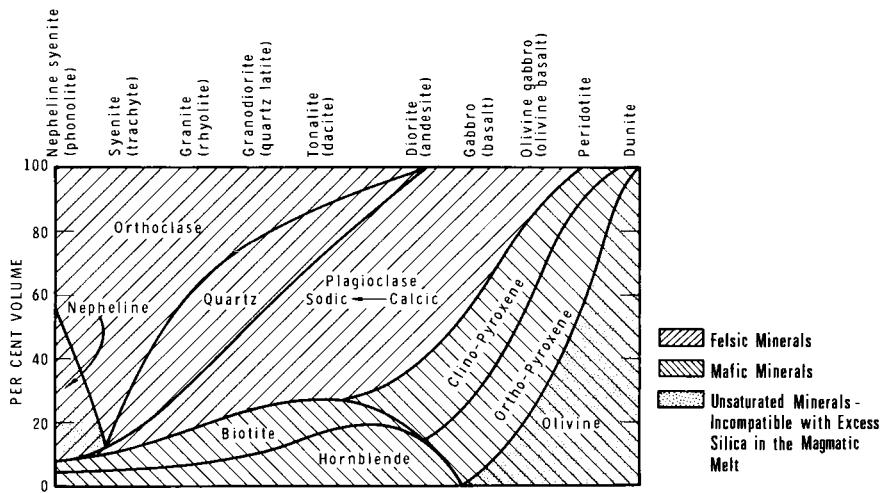


Fig. 3.1. Approximate mineralogical composition of the commoner types of igneous rocks (volcanic rocks in brackets). (After MASON, 1958).

may be incorporated in the rock. Sedimentary rocks characteristically show bedding or stratification but this is absent in certain glacial deposits such as boulder clay and tillite. They are classified on the basis of size of constituent particles and composition. Among coarse sediments are boulder beds, conglomerates, breccias and gravels, those of intermediate grain-size include sands, and fine sediments include muds and clays. In terms of composition sediments may be classified into limestones, sandstones and shales. Of the land area of the earth 75% of the surface is composed of sedimentary rocks (PETTIJOHN, 1957, p.8) so that they are very important as parent materials of soils and clays. Shales and sandstones make up more than three quarters of the sedimentary rocks and of this fraction argillaceous (clayey) rocks make up the largest proportion (PETTIJOHN, 1957, p.10). The average chemical composition of the chief varieties of sedimentary rocks as given by CLARKE (1924, p.34) is shown in Table 3.1. Comparison shows that the average shale contains more than twice as much K_2O as Na_2O whereas these elements are present in about equal proportions in the "average" igneous rock. There is therefore a retention of K_2O relative to Na_2O in shales. There is also a considerable increase in the proportion of H_2O . It has been suggested that the composition of the upper continental crust has gradually changed from mafic to felsic during geological time; corresponding changes in the composition of sedimentary rocks have been reported. MCLENNAN (1982) concluded however that this idea was not supported for sedimentary rocks of post-Archean age by either the average composition or trace element patterns. He felt

TABLE 3.1
AVERAGE CHEMICAL COMPOSITION OF PRINCIPAL ROCKS
(After CLARKE, 1924, p.34.)

| | Igneous | Shale | Sandstone | Limestone | Weighted Average |
|--------------------------------|---------|--------|-----------|-----------|------------------|
| SiO ₂ | 59.14 | 58.10 | 78.33 | 5.19 | 59.08 |
| Al ₂ O ₃ | 15.34 | 15.40 | 4.77 | 0.81 | 15.23 |
| Fe ₂ O ₃ | 3.08 | 4.02 | 1.07 | 0.54 | 3.10 |
| FeO | 3.80 | 2.45 | 0.30 | | 3.72 |
| MgO | 3.49 | 2.44 | 1.16 | 7.89 | 3.72 |
| CaO | 5.08 | 3.11 | 5.50 | 42.57 | 5.10 |
| Na ₂ O | 3.84 | 1.30 | 0.45 | 0.05 | 3.71 |
| K ₂ O | 3.13 | 3.24 | 1.31 | 0.33 | 3.11 |
| H ₂ O | 1.15 | 5.00 | 1.63 | 0.77 | 1.30 |
| TiO ₂ | 1.05 | 0.65 | 0.25 | 0.06 | 1.03 |
| ZrO ₂ | 0.039 | | | | 0.037 |
| Co ₂ | 0.101 | 2.63 | 5.03 | 41.54 | 0.35 |
| C _l | 0.048 | | | 0.02 | 0.045 |
| F | 0.030 | | | | 0.027 |
| S | 0.052 | | | 0.09 | 0.049 |
| SO ₃ | | 0.64 | 0.07 | 0.05 | 0.026 |
| P ₂ O ₅ | 0.299 | 0.17 | 0.08 | 0.04 | 0.285 |
| Cr ₂ O ₃ | 0.055 | | | | 0.052 |
| V ₂ O ₃ | 0.026 | | | | 0.023 |
| MnO ₃ | 0.124 | | | 0.05 | 0.118 |
| NiO | 0.025 | | | | 0.024 |
| BaO | 0.055 | 0.05 | 0.05 | | 0.051 |
| SrO | 0.022 | | | | 0.020 |
| Li ₂ O | 0.008 | | | | 0.007 |
| Cu,Zn,Pb | 0.016 | | | | 0.016 |
| C | | 0.80 | | | 0.040 |
| Total | 100.000 | 100.00 | 100.00 | 100.000 | 100.000 |

however that there was good evidence to show that Archean sedimentary rocks were richer in Na, Mg and Ca and poorer in Si and K than post-Archean sedimentary rocks reflecting a more mafic upper crust during Archean times. The composition of the earth's crust has been discussed by PARKER (1967) and the mineralogical and chemical composition of clays and soils has been described in numerous recent publications (WEAVER, et al., 1975; GREENLAND and HAYES, 1978).

FORMATION OF CLAY MINERALS

Replacement of the primary rock-forming minerals by clay minerals generally involves both physical and chemical processes; biological agencies are also important in the zone of weathering. In general physical processes are thought to be of most importance in low temperature regions and chemical processes become more important when temperatures are higher, provided adequate water is available. When physical processes predominate disintegration is more

important than decomposition which is the main result of chemical processes. Attempts have been made to compare the relative importance of these processes between different areas and formulae have been proposed in attempts to make these comparisons more quantitative. In South Africa, WEINERT (1965) used the ratio of evaporation to precipitation as an index and found that disintegration was predominant in areas where the ratio was greater than 5 and decomposition was more important where the ratio was less than 5. The type of clay minerals in soils in different areas was also linked to the index. A similar technique has been applied elsewhere (SAUNDERS and FOOKE, 1970). A measure of weathering in which frost-action is considered is used by the American Society for Testing and Materials. In this system the weathering index is defined as the product of the annual number of freezing cycle days and the average annual winter rainfall in inches or millimetres (ASTM, 1982a, p.142, Note 1). The clay minerals are stable under a wide range of conditions.

| | Shales ^{1A} (%) | Shales ^{2A} (%) | Pelagic clays ^A (%) | Glacial clays ^B (Norway) (%) | Ave. Igneous rock ^B Norway and Iceland (%) |
|--------------------------------|-----------------------------|-----------------------------|--------------------------------------|--|---|
| SiO ₂ | 58.9 | 50.7 | 54.9 | 59.19 | 59.83 |
| TiO ₂ | 0.78 | 0.78 | 0.78 | 0.79 | 1.64 |
| Al ₂ O ₃ | 16.7 | 15.1 | 16.6 | 15.82 | 16.08 |
| Fe ₂ O ₃ | 2.8 | 4.4 ^a | } 7.7 | 3.41 | 3.65 |
| FeO | 3.7 | 2.1 ^a | | 3.58 | 3.21 |
| MnO | 0.09 | 0.08 | 2.0 | 0.11 | 0.10 |
| MgO | 2.6 | 3.3 | 3.4 | 3.30 | 2.26 |
| CaO | 2.2 | 7.2 | 0.72 | 3.07 | 3.64 |
| Na ₂ O | 1.6 | 0.8 | 1.3 | 2.05 | 5.10 |
| K ₂ O | 3.6 | 3.5 | 2.7 | 3.93 | 3.52 |
| H ₂ O+ | 5.0 | 5.0 | 9.2 | 3.02 | 0.75 |
| P ₂ O ₅ | 0.16 | 0.10 | 0.72 | 0.22 | 0.12 |
| C ₇ CO ₂ | 0.6/1.3 | 0.67/6.1 | computed carbonate free | | |
| S/SO ₃ | 0.24/n.d. | n.d./0.6n.d. | | | |

1. Mainly from geosynclines
2. From Platforms
- A. Data from Wedepohl, 1969
- B. Data from Parker, 1967.

TABLE 3.2 Average Chemical Composition of Clays and Shales Compared with Igneous Rock

Physical processes

Physical processes cause the mechanical break-up of the parent material. This is of two-fold importance to clay-mineral formation. In the first

TABLE 3.3
AVERAGE CHEMICAL COMPOSITION OF CLAY, SHALE, SLATE AND SCHIST
(After CLARKE, 1924, p.631.)

| | Clays and soils ¹ | Shales ² | Slates ³ | Schists ⁴ |
|--------------------------------|------------------------------|---------------------|---------------------|----------------------|
| SiO ₂ | 54.28 | 58.38 | 61.90 | 65.74 |
| Al ₂ O ₃ | 14.51 | 15.47 | 16.54 | 17.35 |
| Fe ₂ O ₃ | 6.25 | 4.03 | 2.73 | 1.90 |
| FeO | 0.77 | 2.46 | 3.63 | 3.35 |
| MgO | 2.99 | 2.45 | 2.99 | 1.90 |
| CaO | 5.04 | 3.12 | 1.07 | 1.25 |
| Na ₂ O | 1.21 | 1.31 | 2.57 | 1.78 |
| K ₂ O | 2.12 | 3.25 | 3.15 | 3.28 |
| H ₂ O | 8.41 | 5.02 | 3.84 | 2.01 |
| TiO ₂ | 0.42 | 0.65 | 0.82 | 0.55 |
| CO ₂ | 3.53 | 2.64 | 0.59 | None |
| P ₂ O ₅ | 0.09 | 0.17 | 0.04 | 0.12 |
| SO ₃ | 0.08 | 0.65 | 0.03 | 0.03 |
| Cl | 0.02 | | Trace | Trace |
| F | | | Trace | 0.07 |
| MnO | 0.08 | Trace | Trace | 0.03 |
| SrO | | None | Trace | Trace |
| BaO | | 0.05 | 0.01 | 0.05 |
| Li ₂ O | | Trace | Trace | Trace |
| FeS ₂ | | | 0.11 | |
| C | 0.24 | 0.81 | 0.22 | 0.58 |

¹ Average of twelve analyses of clays and soils. ² Average or composite analysis of 78 shales. ³ Average of 22 analyses of slates. ⁴ Average of five analyses of schists.

place water and active solutions gain access to the rock and in the second place disintegration leads to an increase in specific surface (surface area per unit weight or volume). Surfaces are chemically active and an increase in specific surface leads to an increase in rate of chemical reaction.

Mechanical damage results from five major physical processes. These are unloading, thermal expansion and contraction, crystal growth including frost action, colloid plucking, and organic activity (REICHE, 1950, pp. 9-15). Under hydrothermal conditions steam and other gases and vapours exert pressure which may be relieved explosively with accompanying mechanical damage. Transportation of all kinds also causes mechanical damage.

Chemical processes

The tendency for a chemical reaction to take place is determined by the potential or gradient. This is estimated in terms of four characteristic thermodynamic functions termed the internal energy, the heat content or enthalpy, the Helmholtz free energy and the Gibbs free energy. From these four functions others may be derived and employed in a mathematical analysis when convenient (GUGGENHEIM, 1959, pp.25-26). A recent attempt to apply thermo-

dynamic concepts to the weathering stability of minerals has been made by CURTIS (1976; 1977). He calculated the net change in standard free energy for certain proposed weathering reactions and showed that the weathering stability of a number of primary minerals correlates well with the total energy released on breakdown into weathering products. Nonetheless, CURTIS and others have pointed out that, rate of chemical reactions often does not correlate quantitatively with magnitude of energy change since kinetic factors are involved. Reaction rate is linked to the activation energy of a reaction which itself depends upon the reaction mechanism or path. In the theory of absolute rate processes it is proposed that reactions take place in one or more steps in which an intermediate activated complex forms. If the energy of formation of the activated complex is larger than that of the initial or final phases an energy barrier has to be overcome before a reaction can proceed. Whether this barrier is, or is not present, and its size, depends upon the reaction path; this is influenced by many factors including nucleation mechanism, epitaxy, catalysts, nature of starting materials, etc. Solute activities and the composition of non-crystalline, reactive compounds associated with mineral surfaces are also thought to have an important effect on the stability of clay minerals. Hence these factors have to be considered as well as the thermodynamics (WEAVER et al., 1976; VAN OOSTERWYCK-GASTUCHE and LA IGLESIAS, 1978).

A major class of chemical reactions in which one solid is converted into another involves an intermediate stage in which the reactants are in true or colloidal solution. There are three major types of such reaction. These are: interaction between acids and bases as for example in carbonation and hydroxylation; electron transfer as in oxidation and reduction; and free radical interaction. Another important class of reactions involves no intermediate solution stage and reorganization of the atoms or ions takes place in the solid state. The crystal structure of the parent material often exerts some control over the orientation of the crystal structure of the product. If the control is in three dimensions the reaction is termed topotactic; if the control is in two dimensions the term epitactic is used.

The principal processes by which chemical change takes place on weathering are solution, carbonation, hydration, hydrolysis, chelation and redox reactions. Clay-mineral formation by a solution mechanism has been proposed by many authors. The strong probability that processes of this sort are of major significance follows in part from the rather low solubility of both alumina and silica in the pH range from 4 to 9 common in surface waters. These compounds, together with potassium, tend to combine forming the relatively stable clay minerals. Other ionic species particularly the alkali and alkaline earth cations are significantly more soluble in the normal pH range (LOUGHNAN,

1969). The solubility of silica increases considerably above about pH9 and alumina becomes much more soluble at both lower and higher pH. The presence of carbonic acid, formed by combination of CO_2 with water, is important in the dissolution of many minerals such as the carbonates and feldspars. Stronger mineral acids, such as H_2SO_4 , formed by biogeochemical oxidation of sulphides, also aid solution processes (see Ch. 4). Chemical effects of this sort sometimes lead also to physical weathering as, for example, when products of increased volume such as gypsum (or jarosite) are formed (ASTM, 1982b, p.19). The importance of hydration and hydrolysis in weathering and formation of clay minerals has been emphasized by many workers (MEUNIER and VELDE, 1976) and consideration has also been given to the subtle effects of exchangeable ions on the state and structure of sorbed water (PROST, 1976). Chelating agents are undoubtedly involved in weathering reactions; for example they have been reported to aid the weathering of biotite and the conversion of halloysite to kaolinite (LA IGLESIAS and GALLAN, 1975; ROBERT and RAZZAGHE-KARIMI, 1975). Other factors which have been considered include the influence of the mineral surfaces, the nature of the crystal structure itself and the redox potential.

There are two major natural environments in which clay-mineral formation takes place. These are in the zone of weathering and at a depth where hydrothermal action occurs. Under conditions of atmospheric weathering temperatures are normal and water is in the liquid state; under hydrothermal conditions temperature and pressure are above normal and water may be above the boiling point at the prevailing temperature and pressure.

Chemical processes at normal temperatures

Weathering leads to the formation of soil which is a loose surface mantle upon the underlying rock. Clay-mineral formation is an important aspect of the wider problem of pedogenesis or the origin of soil. The differences in soil properties reflected in the soil horizons result from changes with depth in the physical and chemical processes of weathering and from the migration of soil materials. These are transported vertically and laterally in solution and suspension. Removal of material is termed eluviation and its deposition in an underlying layer illuviation. Methods have been developed for the quantitative estimation of the gains and losses of the soil constituents between illuvial and eluvial horizons and the soil parent material (BARSHAD, 1964).

Pedologists have recognized since the end of the last century that the direction and rate of the chemical reactions involved are affected by the prevailing environmental conditions. They have considered climate, parent material, relief, biological agencies and time to be the major "factors of soil formation". Much data have been published on the use of these factors (JACKSON, 1959; JENNY, 1961) and attempted quantitative comparisons have been

made between soil properties and soil genesis. This has often been only partly successful. The five factors of the pedologists define the chemical environment in which mineralogical transformations take place.

Climate governs the distribution and amount of solar radiation and precipitation so the temperature and the availability of water are affected. Temperature is important since according to Van't Hoff's principle the velocity of a chemical reaction increases by a factor of 2 or 3 for every 10°C rise of temperature. Availability of water also depends upon the degree of saturation which in turn depends upon the depth of the water table. Weathering may take place at the surface under subaerial conditions, below the surface but above the water table, where the relative humidity and composition of the gaseous phase depart significantly from those at the surface, and under subaqueous conditions beneath the water table. Once clay mineral formation has occurred that in itself affects moisture availability since clay minerals have a high capacity for water retention due to their high specific surface area, colloid chemical properties and ability to decrease permeability by blocking pores. The amount of free water available influences the concentration and chemical activity of solutions in the system. Water also participates as a reactant in chemical changes which involve hydration and hydrolysis. These factors are indirectly affected by relief which is interrelated with climate and controls rate of run-off.

Biological agencies also have an important effect on the chemical composition of the pore solutions. They extract CO_2 , N_2 and other gases from the atmosphere and their metabolic processes and decomposition products affect the partial pressure of gases such as CO_2 , H_2S , and NH_3 in the soil atmosphere. They synthesize complex organic molecules which may affect pH, act as protective colloids, deflocculants, chelating (complexing) agents, or have other properties. They also extract and concentrate trace elements required in their life cycle. Some plants accumulate major amounts of elements such as silicon, aluminium, calcium, manganese and iron (LOVERING, 1959). Microorganisms are involved in the production of H_2SO_4 by oxidation of pyrite (see Ch. 4) and are undoubtedly involved in many other reactions; for example they have been found to induce more rapid breakdown of biotite than hornblende in estuarine sands (FRANKEL, 1977).

Although the same soil may develop on different rocks the parent material affects soil formation and has a particularly important influence on the origin of the clay minerals. The porosity, jointing, cleavage, permeability, and water-holding capacity of the parent material affect the concentration of solutions. It is largely responsible for what ions are available to go into solution. Composition of solutions has been used in a number of studies of mineral stability (GARRELS and CHRIST, 1965). This approach has led to

discussion as to whether steady-state or true equilibrium conditions apply in nature but it seems probable that the method gives a general indication, at least, of the trends in weathering and authigenesis. In regard to the construction of stability diagrams the seemingly reasonable suggestion has been made that the composition of soil pore solutions should be used rather than that of groundwater, rivers or springs (FERNANDEZ-MARCOS et al., 1979).

The primary rock-forming minerals differ in their resistance to weathering. Their general order of weathering stability has been deduced from such evidence as the relative frequency of occurrence of minerals in rocks of decreasing age (PETTIJOHN, 1941), mineral stability in different environments, artificial weathering experiments (CORRENS, 1963) and variation plots showing percentage oxides expressed as mole percent on weathering. Pettijohn's series is shown in Table 3.4 and refers to the heavy minerals. The minerals with the highest numbers are the least stable; those with negative numbers are more abundant in older than in more recent sediments perhaps because those minerals may have a tendency to authigenic growth the chances for which become greater with passage of time. GOLDICH (1938, p.56) presented a branched stability series which resembles Bowen's reaction series of the order of crystallization from igneous magmas (Table 3.5). Goldich's series indicates the relative resistance to weathering and does not imply mineral interaction to form those lower in the series as is believed to occur in a cooling igneous magma. Minerals higher in the series crystallize at higher temperatures. It has been inferred from the order of the series that, in general, weathering stability increases with decreasing difference between the temperature of formation and the temperature of the near-surface environment so that minerals which crystallized at higher temperatures are less resistant to weathering than those which crystallized at lower temperatures.

JACKSON and SHERMAN (1953, p.235) deduced a weathering sequence consisting of thirteen stages which is mainly applicable to particles in the clay-size range (Table 3.6). Many other schemes, including ones based on mineral assemblages and facies, have been proposed to define weathering stages. Many agree except for matters of detail and where there are disagreements it is probable that in many cases they are due to differences in composition between different samples of the same mineral and differences in the type of weathering and composition of the active solutions. Differences between minerals may result from such factors as the presence or absence of twinning, lattice strain, inclusions, cleavage and composition. The concept that defects are sites of weakness where attack on minerals by weathering commences has been supported by various investigators who have used electron microscopic techniques (EGGLETON and BUSECK, 1980). The order of persistence of minerals shows that in general minerals with a high Si:Al ratio show greater resistance

to weathering than minerals in which more Si^{4+} ions are replaced. For example, alkali plagioclase, in which only one quarter of the Si^{4+} ions are replaced by Al^{3+} ions shows greater resistance to weathering than calcic plagioclase in which half the Si^{4+} ions are replaced. Other factors are evidently also involved since Na-plagioclase tends to break-down more readily than K-feldspar.

TABLE 3.4

ORDER OF PERSISTENCE OF MINERALS ON WEATHERING¹
(After PETTIJOHN, 1941, P.618).

| | | | |
|-----|------------|------|-------------|
| (3) | Anatase | (10) | Kyanite |
| (2) | Muscovite | (11) | Epidote |
| (1) | Rutile | (12) | Hornblende |
| (1) | Zircon | (13) | Andalusite |
| (2) | Tourmaline | (14) | Topaz |
| (3) | Monazite | (15) | Sphene |
| (4) | Garnet | (16) | Zoisite |
| (5) | Biotite | (17) | Augite |
| (6) | Apatite | (18) | Sillimanite |
| (7) | Ilmenite | (19) | Hypersthene |
| (8) | Magnetite | (20) | Diopside |
| (9) | Staurolite | (21) | Actinolite |
| | | (22) | Olivine |

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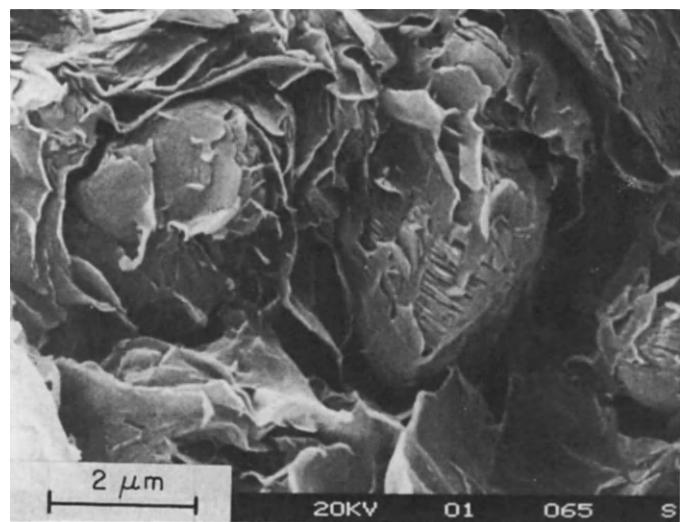
TABLE 3.5

STABILITY OF MINERALS IN WEATHERING¹

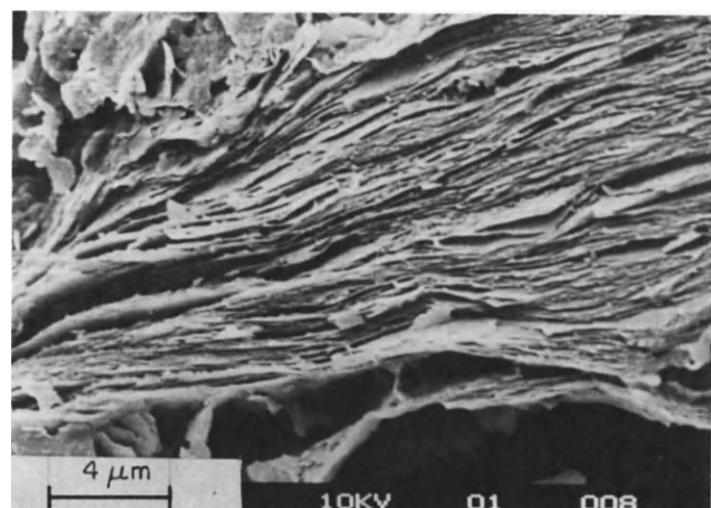
| | |
|------------|---------------------------|
| Olivine | Calcic plagioclase |
| Augite | Calci-alkalic plagioclase |
| Hornblende | Alkali-calcic plagioclase |
| | Alkali plagioclase |
| Biotite | Potash feldspar |
| | Muscovite |
| | Quartz |

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When igneous rocks are the parent material the relatively unchanged minerals inherited by the soil are those which are most resistant to the weathering regime of the local environment. Zircon, rutile, corundum and others are some of the most stable minerals in this category. Chemical weathering of less stable primary minerals often leads to formation of clay minerals. Sometimes the alteration takes place in a spheroidal fashion producing an onion-skin texture (Fig. 3.2A). Igneous and metamorphic rocks may contribute to the soil primary micas and chlorites - minerals which require relatively little



A. Onion-skin texture. S. Sumatra



B. Layer silicate showing exfoliation, Trinidad

Figure 3.2. Scanning Electron Micrographs of Weathering Textures

structural change to be converted into clay minerals. Sedimentary parent rocks very frequently contain detrital clay minerals which weathering releases to the soil. Nearly any sort of parent rock may contain varying amounts of authigenic clay minerals which may be contributed to the soil together with the older minerals.

Edges of mica-type minerals are susceptible to attack by weathering (BOYLE et al., 1967) and splitting, separation of layers, major exfoliation (Fig. 3.2B) and cracking have been beautifully illustrated in scanning electron micrographs by TARZI and PROTZ (1978). Loss of interlayer cations is believed to result in formation of mixed-layer and expanding lattice minerals. Biotite appears to be more susceptible to this sort of alteration than muscovite and this has been linked to differences in the orientation of the hydroxyl ions, decrease in layer charge and other factors. In dioctahedral micas the proton of the hydroxyl group is oriented towards the unoccupied cation site in the octahedral layer and so it is farther from the interlayer potassium. Hence it is thought that the interlayer bonding is stronger in dioctahedral minerals than in trioctahedral minerals containing structural hydroxyl ions. This may therefore explain why biotite, being trioctahedral, is apparently more susceptible to alteration to an expandable mineral than muscovite (GILKES et al., 1972). Another somewhat similar reaction involves removal of the hydroxide interlayers from chlorite. Expandable minerals formed by this sort of process may lose their ability to expand by subsequent uptake of cations with reversion to the original mineral or to a related mixed-layer mineral.

Cation fixation and interlayer precipitation of positively charged hydroxides of aluminium, other sesquioxides and magnesium, as gibbsite-like and brucite-like layers, involves build-up of the lattices of the clay minerals. The properties of such minerals are often intermediate or "intergradient" between those of swelling and non-swelling minerals (JACKSON, 1963, p.33; NORRISH, 1973). Formation of intergrade minerals by degradation processes rather than as a product of the build-up of pre-existing smectites by interlayer precipitation has also been described. Transformation of plagioclase and amphibole into beidellite with formation of an intergrade mineral as an intermediate stage is an example of this type of reaction (PROUST and VELDE, 1978).

It has been observed that there are certain conditions which generally favour development of particular clay minerals. Much work has shown for example that acid conditions favour the formation of kaolinite though laboratory syntheses suggest that under appropriate conditions kaolinite may be precipitated from gels over a considerable pH range. A relatively high Al:Si ratio (1:1) and absence or removal of other metal cations is also required. Equilibrium diagrams for aluminium hydroxide and kaolinite taking gels into

account have been developed (IGLESIA and OOSTERWYCK-GASTUCHE, 1978). Granites often alter to kaolin minerals due to the chemical control of the parent material. Montmorillonite is widely distributed in soils. A tentative map of

TABLE 3.6

WEATHERING STABILITY OF LESS THAN 2 μm SIZED MINERAL PARTICLES¹
(After JACKSON and SHERMAN, 1953, p.235).

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-
- | | |
|------|--|
| (1) | Gypsum (also halite, sodium nitrate, ammonium chloride, etc.) |
| (2) | Calcite (also dolomite, aragonite, apatite, etc.) |
| (3) | Olivine-hornblende (also pyroxenes, diopside, etc.) |
| (4) | Biotite (also glauconite, Mg-chlorite, antigorite, nontronite, etc.) |
| (5) | Albite (also anorthite, stilbite, microcline, orthoclase, etc.) |
| (6) | Quartz (also cristobalite, etc.) |
| (7) | Muscovite (also 10A zones of sericite, illite, etc.) |
| (8) | Interstratified 2:1 layer silicates and vermiculite (including partially expanded hydrous micas, randomly interstratified 2:1 layer silicates with no basal spacings, and regularly interstratified 2:1 layer silicates) |
| (9) | Montmorillonite (also beidellite, saponite, etc.) |
| (10) | Kaolinite (also halloysite, etc.) |
| (11) | Gibbsite (also boehmite, allophane etc.) |
| (12) | Hematite (also goethite, limonite, etc.) |
| (13) | Anatase (also zircon, rutile, ilmenite, leucoxene, corundum, etc.) |
-

its world-wide distribution shows that there are large areas in temperate and northern regions, as well as in Africa, India, Australia and South America where smectites comprise more than 50 per cent of the soil (GRADUSOV, 1974). Montmorillonite has a lower Al:Si ratio than kaolinite and contains Mg, Fe and Ca. Alkaline conditions with poor drainage and a low potassium content are generally favourable for montmorillonite formation. Basic igneous rocks which contain calcic feldspars and ferro-magnesian minerals often provide suitable parent material. Such rocks may weather to kaolinite rather than montmorillonite, however, if the Ca, Mg and Fe are removed by thorough leaching. Conditions which favour formation of the mica minerals are less well defined.

The wide range of chemical composition within a group of clay minerals makes it possible for related species to form from basic and felsic parent materials. For example, iron- and magnesium - poor montmorillonite together with zeolites have been reported as alteration products of felsic volcanics (SHEPPARD and GUDE, 1973; WHITE et al., 1980) whereas iron - and magnesium - rich smectites have been reported from basalts (BENSON and TEAGUE, 1982). Allophane, imogolite and related non-crystalline minerals when present are most

often found in relatively recent soils formed by weathering of volcanic ash. A range in pH of 5 to 7 seems to favour their formation. They occur in regions of recent volcanism - particularly the countries of the Pacific rim (WADA and HARWARD, 1974) - and elsewhere (VIOLANTE and TAIT, 1979).

Chemical processes at elevated temperatures

Reactions which involve water-vapour pressures in excess of 1 atm. and take place above 100°C are termed hydrothermal. They occur in association with igneous and metamorphic action. Hydrothermal conditions differ from those in the zone of weathering with respect to temperature; the concentration and nature of ions in the system is also often different. The physico-chemical conditions which favour development of the different clay minerals are, however, generally comparable with those found in weathering. Most of the clay minerals have been identified in a hydrothermal association. Commonly more than one clay mineral is present but occasionally hydrothermal deposits are composed largely of a single clay mineral. The kaolin deposits associated with the granites of southwestern England are of this type.

TABLE 3.7

MINERALOGICAL ALTERATION ADJACENT TO INTRUSIVE VEIN¹
(Data from SALES and MEYER, 1948, pp.12-13.)

| Vein | Zone of Alteration | | Argillized Zone | | Unaltered Quartz Monzonite |
|------|--------------------|--|----------------------|----------------------------|----------------------------|
| | Sericite Zone | | Kaolinite Subzone | Montmorillonite Subzone | |
| | | | Kaolinite Subzone | Montmorillonite Subzone | Unaltered Quartz Monzonite |

¹ Published by permission of AIME, Society of Mining Engineers.

A zoned distribution of clay minerals suggesting a sequential development due to progressive alteration and evidently connected with the direction of migration of active solutions and vapours is a common feature in many hydrothermal deposits (Table 3.7). Mixed-layer minerals are commonly encountered in transitional zones between zones of discrete clay minerals. Amorphous minerals such as allophane also are sometimes found in this type of association. The possibility that there is a definite type of clay mineral association with particular varieties of economic mineralization and ore genesis has given impetus to detailed investigations.

The character of the alteration depends upon the nature of the solutions,

the composition of the host rock and the duration and intensity of the alteration. The composition and temperature of the solutions have a dominant effect on the clay minerals developed if the hydrothermal action is long continued. The composition of the original rock may be completely changed due to selective leaching and removal of original elements and the introduction of new elements from the hydrothermal solutions. When the alteration is not too great the character of the host rocks has a significant effect. For example, hydrothermal alteration of tholeiites (silica oversaturated-quartz normative) in Iceland and Ireland led to formation of quartz, chalcedony, celadonite and zeolites whereas in olivine basalts the secondary minerals consisted of a suite of zeolites with no quartz and chalcedony (WALKER, 1960a, b). Secondary minerals formed by weathering are sometimes distinctly different from those formed by hydrothermal alteration of related rocks. Weathering of tholeiitic basalts in the Columbia Plateau led to formation of nontronite (Fe-rich smectite), clinoptilolite and silica minerals rather than the minerals described above which resulted from hydrothermal alteration of the Irish and Icelandic tholeiites (BENSON and TEAGUE, 1982). In outer zones of intense alteration and in zones where hydrothermal effects have only been slight pseudomorphs and relics of the pre-existing minerals showing varying amounts of replacement are commonly found and alteration via intermediate minerals is also known. For example EXLEY (1976) showed that Na-plagioclase altered hydrothermally to kaolinite via mica and montmorillonite which formed as intermediate products - kaolinite behaved antipathetically towards both mica and montmorillonite.

Clays formed by hydrothermal action often have fabrics which are distinctly different from mineralogically similar clays formed by weathering or sedimentary processes (SERGEYEV, et al., 1980). Hydrothermal kaolin has been found to be composed of small-sized, tightly packed, platy or elongate crystals in which flakes and packets were interlocked giving the material a low porosity and high bulk density. Weathering formed large flakes, expanded books and elongates of kaolinite sometimes with ragged edges; deposits had high porosity and low bulk density (KELLER and HANSON, 1975; KELLER, 1976). The formation of the related serpentine minerals from olivine, pyroxenes, amphiboles and chlorites is another example. This transformation generally occurs below 200°C, at pressures of a few kilobars, in alkaline fluids ($\text{pH} > 10$) deficient in CO_2 and Mg (WICKS and WHITTAKER, 1977; WICKS, 1979). If the reaction is accompanied by uptake of water an increase of solid volume is implied but microscopic evidence of perfect pseudomorphous replacement shows that the change sometimes occurs at constant volume. Indeed this is apparently not uncommon in transformations of this sort and delicate textural details may be preserved; possibly the depth and pressure at which the reactions occur determines whether they take place at

constant volume or with volume increase.

In addition to its scientific interest hydrothermal studies have considerable social and economic importance. For example if high level radioactive waste is disposed of by burial in the ground the nuclear decay processes may generate high temperatures of 200° to 400°C so that the rock may be exposed to hydrothermal conditions. Because of the toxicity and solubility of some ions such as Cs¹³⁷ the sorption capacity of clays for ions of this sort could be extremely important. KOMARNENI and ROY (1980) showed that while hydrothermal heating caused a decrease of the Cs-sorption capacity of several clay minerals it led to an increase of Cs-fixation by Cs-sorbed and Cs-saturated clays. Interlayer collapse in montmorillonite fixed Cs on cation-exchange sites and Cs-aluminosilicates and other minerals were formed (KOMARNENI and WHITE, 1981). Other situations where hydrothermal studies have engineering importance concern geothermal wells, some techniques of enhanced oil recovery in which high temperature steam is injected into formations and proposed methods of in situ extraction of heavy oil deposits. Under some conditions experiments suggest that smectites may be synthesized (BAYLISS and LEVINSON, 1971; BOON, 1971; PERRY and GILLOTT, 1979). Clay minerals and smectites in particular are prone to disperse and migrate and experiments have shown that such movements may cause significant reductions in permeability of rocks (WALDORF, 1965). Mineral transformations may be used as indicators of temperatures attained (PERRY and GILLOTT, 1982). Details of hydrothermal action are discussed in texts dealing with metamorphism and many papers have been published on the formation of clays by hydrothermal action (PETERSON et al., 1946; SALES and MEYER, 1948; KERR, 1955; KRISTMANNSDOTTIR, 1975; VELDE, 1977).

CLAY MINERALS IN THE SEDIMENTARY CYCLE

Clay minerals react to changes in environment such as accompany erosion, transportation and deposition. Such reactions may involve ion exchange, reconstruction of degraded minerals and formation of one type of clay mineral from another or from simpler substances. Care is required in interpreting lateral or environmental differences in mineralogy as evidence of mineralogical change since such differences may result from other causes such as sorting and selective transportation. For example illite and expandable clays have been reported to be selectively transported from soils (RHOTON et al., 1979).

Exchange reactions are governed by physico-chemical laws and depend upon the clay mineral, the nature and ion population of the exchange sites and on the concentration and composition of the solution. River waters tend to be relatively rich in Ca²⁺ ions compared to the sea (Tables 2.2, 2.3). Many cation-exchange sites are therefore likely to be occupied by Ca²⁺ ions during

river transport of land-derived clays. On entering the marine environment a rapid exchange reaction probably takes place. Its nature has been investigated experimentally and on the basis of field observations. The general conclusion is that Ca^{2+} ions are replaced by Mg^{2+} and K^+ ions (GRANT WHITEHOUSE and McCARTER, 1958; KELLER, 1964, p.47).

An increase in salinity such as occurs when clays enter the sea has commonly been reported to be accompanied by a decrease in total exchange capacity; this has generally been attributed to the fixation of ions, particularly potassium. This explanation has been questioned and the possibility suggested that the apparent decrease in exchange capacity may be an artifact introduced by the analytical procedure (NEAL, 1977). The selective sorption of potassium by clay minerals seems however to be a reasonable explanation for the relatively high Na^+ to K^+ ratio (47 times, molar) of sea-water compared to igneous rocks in which these elements are present in approximately equal proportions (compare Table 2.3 with Table 3.1). EBERL (1980) concluded that a better understanding of selective adsorption and fixation (see Ch. 5) can be obtained if the crystal chemistry of the clay minerals is considered when exchange free energies are calculated. Interlayer water content and layer charge appear to be particularly important.

Weathering of mica-type clay minerals often results in replacement of interlayer K^+ by hydrated ions and may lead to formation of mixed-layer clay minerals and "degraded" illites. The mineral is sometimes expansive and it may resemble montmorillonite. It is thought that when such degraded material reaches the sea it readily picks up potassium and becomes better crystallized or rejuvenated. In this respect it differs from those expanding lattice minerals in which the negative charge is located in the octahedral layer and which will not readily sorb potassium (WEAVER, 1958; JOHNS and GRIM, 1958). Some authors consider that clay minerals undergo more fundamental changes than those which involve ion exchange and many such reactions have been proposed. Formation of glauconite may involve this sort of process. Glauconite is essentially an Fe-illite and is believed to form under conditions of slow sedimentation in the marine environment from degraded material by uptake of potassium and iron. Living organisms may play a role in its formation (BURST, 1958, HOWER, 1961; OJAKANGAS and KELLER, 1964). Laboratory studies have shown that microbial action may also decrease the percentage of mica, expandable clays and vermiculite relative to that of quartz and chlorite (WALL et al., 1974). Weathering may remove interlayer aluminium from chlorite which may then be converted to illite by uptake of potassium under fluvial conditions (MURAD and FISCHER, 1978). Conversely chlorite may form under marine conditions by uptake of magnesium and development of brucite interlayers in an altered trioctahedral structure; iron may possibly act as a catalyst (TOWE and GRIM,

1963, p.852). Degraded alumino-silicates may also take up dissolved silica in the ocean (MACKENZIE et al., 1967). In active ocean ridges it appears that chemical interaction takes place between basaltic rocks and ocean water undergoing convective circulation. Mg^{2+} is removed from the sea-water and montmorillonite is formed (ELDERFIELD, 1977).

A sedimentary basin may be supplied with different suites of clay minerals depending on conditions of weathering, parent material, etc., in the surrounding source areas. It has been found that there is often a correlation in the distribution of clay minerals between soils on continents and recent sediments in adjoining oceanic basins into which weathering and erosion products are carried by agents of transportation. For example kaolinite is found in significant amounts in soils on continents and in recent oceanic sediments in low latitude regions of the earth. Chlorite, illite and smectite are also reported to have a terrigenous source in parts of the Atlantic Ocean (BISCAYE, 1965; GRIFFIN et al., 1968; LISITZIN, 1972). The distribution of the clay minerals in the sedimentary deposits is affected by sorting. This is brought about by waves and currents. There are differences between the clay minerals in their settling rate either as units or aggregations which result from size differences in the individual minerals and differences in their tendency to flocculate in the presence of electrolytes and organic materials (MURRAY and HARRISON, 1956; GRANT WHITEHOUSE et al., 1960; PRYOR and GLASS, 1961, p.503; GRIFFIN, 1962; SENGUPTA, 1975; KRANCK, 1975; GIBBS, 1977). Sorting can produce a distribution of clay minerals in a sediment which may be erroneously interpreted as the result of mineralogical transformations. A clear means of distinguishing between the effects of the two processes would greatly increase the usefulness of clay minerals as indices of the depositional environment.

Marine sediments generally have a higher boron content than comparable fresh-water sediments. Clays contain much of this boron. Illite and to a lesser extent kaolinite and montmorillonite sorb boron in proportion both to the amount present and to the salinity of the water (FREDERICKSON and REYNOLDS, 1960; FLEET, 1965; LERMAN, 1966; ALEKSINA, 1972). The boron is strongly held and it is thought to migrate relatively rapidly from surface sites to positions within the crystal structure possibly proxying for silicon or aluminium in tetrahedral sites. As the amount of boron taken up increases with increase in salinity the boron content has been used as a measure of the salinity of the water in which illitic sediments were deposited (ADAMS et al., 1965). The total boron content of a sediment is affected by many factors. Among these are the amount of boron already present in detrital clay minerals, rate of sedimentation which affects the time for which a clay mineral is in contact with the boron-containing solution, and the presence of other boron-containing

minerals such as tourmaline. Studies of the mechanism of adsorption of boron by clay minerals and the influence of factors such as boron concentration and pH have shown that an adsorption maximum occurs at about pH 9.0 to 9.7. This value is significantly higher than that of ocean water in which the pH is a little above 8 near the surface and has a value of about 7.7 at depth. The adsorption maximum was attributed to a stronger affinity of clays for $B(OH)_4^-$ than for $B(OH)_3$ (KEREN and MEZUMAN, 1981). There are other geochemical methods for deducing whether sediments were deposited under freshwater or marine conditions. For example the ratio of pyrite-to-"FeS" (acid-volatile iron monosulphides) has been found to be greater than 10.0 in modern marine sediments whereas in sediments which were deposited under brackish estuarine or freshwater conditions the ratio is generally less than one (BERNER et al., 1979). When geochemical data are used to deduce palaeosalinities supportive evidence should also be obtained from the sedimentary geology.

POST-DEPOSITIONAL CHANGES IN CLAYS

It was formerly believed that at the time of deposition many clays have a natural water content which is close to the liquid limit. More recent work (W. HARRISON et al., 1964, p.742) has shown, however, that the water content actually exceeds the liquid limit at the time of sedimentation. On burial the water content decreases together with the void ratio due to the increase in load; syneresis may also play a part (TERZAGHI, 1955, p.563). The process of void ratio reduction is termed "compaction" by geologists and "consolidation" by engineers. The term "compaction" as used in sedimentology has been defined as the "Reduction in bulk volume or thickness of, or the pore space within a body of fine-grained sediments in response to the increasing weight of overlying material that is continually being deposited or to the pressures resulting from earth movements within the crust. It is expressed as a decrease in porosity brought about by a tighter packing of the sediment particles." (BATES and JACKSON, 1980). BARKER (1981) defines "consolidation" as, "The gradual compression of a cohesive soil, due to a mass acting on it, which occurs as water is driven out of the voids in the soil. Consolidation occurs only with clays, or other soils, of low permeability. It is not the same as compaction which is an artificial mechanical process." Overburden pressure is commonly calculated approximately as the product of hydrostatic pressure (which is taken as about 10 bars/100 metres) and 2.65 (an approximate average specific gravity for rock).

The importance of settlement and differential settlement to the stability of all kinds of structures founded on non-lithified deposits has led to detailed theoretical and experimental studies by engineers into the process of consolidation. Particular attention has been focussed upon plastic soils and

sediments affected by relatively small loads in the pressure range up to about (5 MPa) (approximately 50 tons/sq.ft.). This corresponds to burial under a depth of about 750 m (2,500 ft.) of overburden or less. More limited investigations have been made in the range of pressures which are transitional between those corresponding to shallow loading and those found under metamorphic conditions.

Consolidation is accompanied by structural, physical, chemical and mineralogical changes in the sediment and in its contained pore solutions. The nature of these changes has been scientifically investigated at least from the time of SORBY (1908, pp.227-231).

PRINCIPLES OF CONSOLIDATION THEORY

The theory of consolidation, developed by TERZAGHI (1925) and others, is intended to enable engineers to calculate rate and amount of settlement of structures founded on non-lithified sediments and soils. The principles are also applicable to the consolidation of sedimentary layers on burial by younger strata (RIEKE and CHILINGARIAN, 1974). The theory is based on a consideration of the mechanics of void ratio reduction on loading. The process may be illustrated by reference to a model analogy (Fig. 3.3). The model consists of a frictionless piston fitting closely into a cylinder and supported by a spring on the bottom of the cylinder. The cylinder below the piston is filled with water. When a load is applied to the piston it is at first carried by the water as the spring is much more compressible and the stopcock is closed. When this is opened water escapes until the load is gradually transferred to the spring and the piston eventually comes to rest when equilibrium has been attained. The transient excess pressure in the water due to the load increment is termed the hydrostatic excess pressure. The difference between the load and the hydrostatic pressure is termed the effective pressure. The time for equilibrium to be established is directly proportional to the volume of water and inversely proportional to the velocity at which it flows out through the stopcock. In a loaded sediment water is squeezed out at a rate which depends upon the permeability and in TERZAGHI'S treatment the rate was calculated by application of Darcy's law which states that the velocity of flow is proportional to the hydraulic gradient. The constant of proportionality is known as the coefficient of permeability or the hydraulic conductivity. The equilibrium condition represented in the model by transference of the load to the spring corresponds in a sediment to transference of the load from the pore water to the mineral particles of which the soil structure is composed. In clays in which permeability is low consolidation is a slow process.

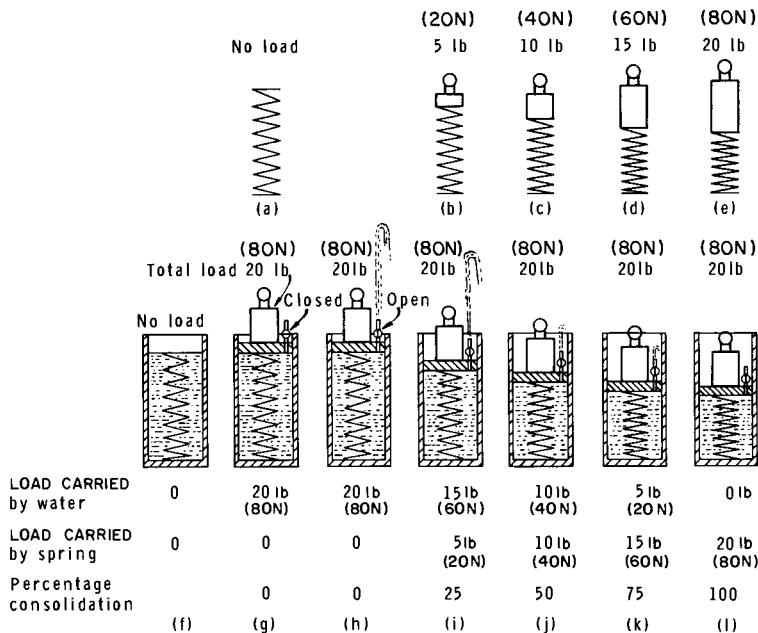


Fig. 3.3. Model analogy of consolidation. (Adapted from TAYLOR, 1948, p.223).

There are a number of simplifying assumptions in Terzaghi's theory. The chief ones are:

- (1) The material is completely saturated and homogeneous.
- (2) The pore water and mineral particles are incompressible.
- (3) Darcy's law is valid.
- (4) Consolidation is one dimensional and is due entirely to change in the water content.
- (5) Constant values are assumed for certain soil properties such as the coefficient of permeability and coefficient of consolidation.

In fact many of these assumptions are known to be erroneous or are open to question and are responsible for difficulties sometimes encountered in applying the theory quantitatively to predict settlement on the basis of laboratory data. Other mathematical models have been developed in which fewer simplifications are made. These employ non-linear springs and dashpots (BARDEN, 1968), Bingham viscoplastic models (ZIENKIEWIZ et al., 1975) or other combinations of elements. Due probably to the complexity of their application none appears to have been widely accepted.

Pore volume is a function of particle-size distribution, grain shape, and packing geometry. These factors depend upon the provenance, erosion history and nature of the minerals, the environment of deposition and the post-

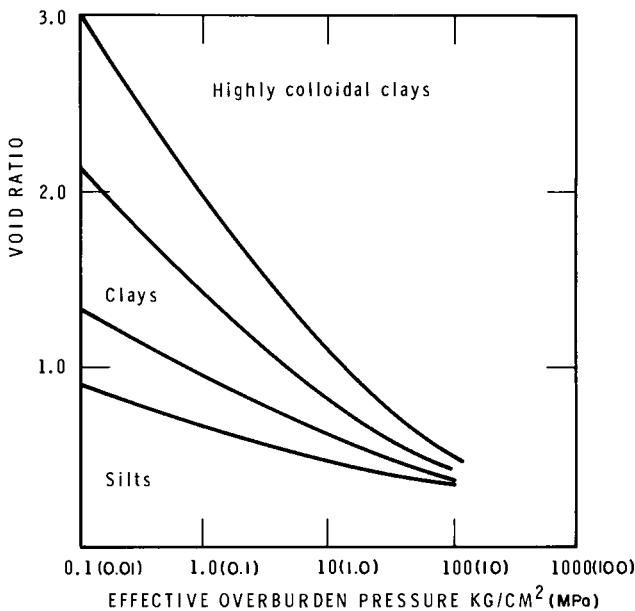


Fig. 3.4. Approximate relation between void ratio and overburden pressure (Adapted from SKEMPTON, 1953, p.55. Reproduced by permission of the Council of the Yorkshire Geological Society.)

depositional history. Particle size is also important since it determines the relative importance of surface, physico-chemical, or gravitational forces. MEADE (1964) reviewed factors responsible for the removal of water from clayey sediments on compaction and concluded that particle size exerted a dominant influence throughout a wide range of pressures. Other factors considered significant were nature of exchange ion, interstitial electrolyte concentration, acidity, temperature, organic content and the arrangement of particles at the onset of compaction. Physico-chemical factors of importance in understanding the compressibility of clays have been discussed by BOLT (1956) and others.

Decrease in void ratio may be plotted against increase in effective pressure for field or laboratory samples which have been consolidated. A comparison of void ratio versus effective pressure data for different sorts of sediment subjected to consolidation in the field and in the laboratory has been made by SKEMPTON (1953, pp.52-55) (Fig. 3.4). He found fairly close agreement between the field and laboratory results in the pressure range up to about 100 kg/cm² (10 MPa) which corresponds to a depth of burial of about 4,000 ft. (1200 m). Samples obtained in the field from greater depths showed a more rapid decrease in void ratio than did samples tested in the laboratory at corresponding pressures. This was believed to indicate "the development of molecular forces

between the particles" in the sediments consolidated in nature. On the basis of soil mechanics tests on deep-sea sediments and an analysis of seismic data HAMILTON (1959, p.1407) also concluded that chemical effects induced by pressure become important in lithification when burial reaches depths of the order of 500-2,300 ft. (150-700m); clay was believed to become converted to shale by cementation between grains.

If a soil or sediment is confined at a certain pressure under such conditions that drainage is possible it consolidates to an equilibrium state with respect to void ratio. Under these conditions consolidation results in a gain in strength since the increase in density, contact area between particles and friction increase the shear resistance of the soil. Rate of consolidation decreases with time under constant load so application of load in increments can significantly decrease the time required for complete consolidation. This principle can be used to optimize consolidation rate to achieve a required gain in strength. If the material has been subjected only to an increase of pressure it is described as "normally consolidated". If consolidation is less than that which is normal for the existing overburden the sediment is said to be "underconsolidated"; such deposits commonly have high water contents. They are associated with rapid sedimentation which results in an increase in overburden pressure at a rate which is too fast for normal drainage of pore water; load is partly supported by trapped fluid. If the pressure has been reduced below the maximum say by removal of overburden by erosion the volume of the material will increase. On unloading to a pressure p , however, it has been found that a clay has a lower void ratio than at pressure p during the loading cycle owing to a hysteresis effect (Fig.12.11). Sediments which have been loaded to a maximum pressure and which are then unloaded to a lower confining pressure are said to have been "pre-consolidated" or "over-consolidated". A similar phenomenon, known as quasi-preconsolidation, has been observed in normally consolidated clays (BJERRUM, 1967). This is caused by the creep of clay particles into a stable configuration under constant effective stress (or secondary consolidation in engineering terminology) and is predicted by the non-linear rheological models mentioned previously.

When a saturated clay dries it shrinks due to the forces associated with soil moisture suction. These forces can reach a magnitude of several thousands of atmospheres (Fig.6.3). Clays which have been dried and then subsequently re-saturated have similar properties to clays which have been pre-consolidated under load. Desiccated layers and pre-consolidated clays have great importance in foundation engineering owing to the physical differences in their properties from those of normally consolidated non-dried clays. Under loads which are less than the pre-consolidation load a pre-consolidated soil is less compressible than a normally consolidated soil. Its compressibility at loads

which exceed the pre-consolidation pressure, however, is comparable to that of the same soil in the normally consolidated condition. A pre-consolidated soil has a higher shearing resistance than a normally consolidated soil when both are under the same load (Fig. 3.5).

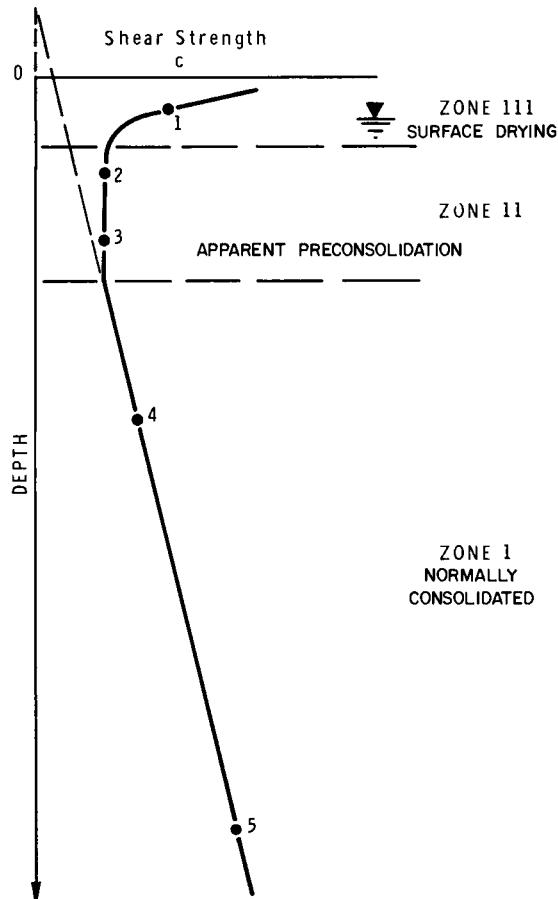


Fig. 3.5. Change in shear strength due to drying (zone III) and increasing overburden pressure in normally consolidated soil. (After SKEMPTON and NORTHEY, 1952. Reprinted from Geotechnique by permission of the Institution of Civil Engineers.)

There are well established engineering test procedures for the recognition of pre-consolidation and for the estimation of the pre-consolidation load in such soils (see Chapter 12: Engineering Analysis). These techniques have been applied in attempts to estimate the maximum depth of burial of sedimentary rocks (ALTSCHAEFL and HARRISON, 1959) and the former thickness of Pleistocene glaciers (W. HARRISON, 1958). These methods have also been used in the investigation of dried crusts formed in subaqueously deposited sediments due to such causes as drainage of lakes (ROMINGER and RUTLEDGE, 1952) and changes in

the relative position of land and sea (KENNEY 1964). Most confidence can be placed in the results of the engineering tests when they agree with the geological evidence.

OTHER PHYSICAL CHANGES

In addition to the decrease in void ratio there are other changes of a physical nature which affect clays after deposition. Joints are developed in a great many clays. SKEMPTON and NORTHEY (1952, p.39) found that clay which had been remoulded at its liquid limit and then stored under water for 1 year developed a fissured structure. The water content of the clay close to the fissures was slightly lower than that of the clay in bulk. They suggested that the fissures developed as a result of syneresis, the de-watering of gels, which results from a drawing together of the colloidal particles. Shrinkage cracks in clay kept submerged have also been produced experimentally by BURST (1965) (Fig. 3.6) and it seems likely that some joints in clays may form as a result of this process.

Sediments quite frequently show structures which are interpreted as evidence of lateral and vertical movements shortly after deposition. Slump and slide structures due to lateral movement of sediments have been described from rocks of a variety of geographical locations and geological periods. Subaqueous mass movements of this sort have been attributed to seismic shocks and other causes of liquefaction and fluidization which accompany consolidation (LOWE, 1976). It has also been suggested that mass movements may result from release of large amounts of water and light hydrocarbons from gas hydrates (MCIVER, 1982). Decomposition of gas hydrates may result from a decrease in pressure or an increase in temperature. Recently it has been reported that gas hydrate decomposition produced a measured, "volumetric expansion of 20:1 of gas volume to pore-fluid volume" - an expansion which exceeded by a factor of four the volume of gas that could be released from solution in pore water under similar conditions (SHERIDAN, et al., 1982). It seems possible that if such processes occur naturally on a sufficient scale mass movements may well result from this cause as suggested above. Structures associated with vertical movements due to uneven compaction include load pockets, load waves, load casts, antidunes (Fig. 3.7), and ball-and-pillow structures. These structures have recently been reviewed by POTTER and PETTIJOHN (1963, pp. 143-172) and terminology has been discussed by SULLWOLD (1959, 1960). They generally occur in sandstone or siltstone interbedded with argillaceous layers which were in a water saturated and plastic condition at the time the structure was formed. Either differences in compaction characteristics between the beds or changes in consistency due to some form of disturbance may be responsible for their formation.

Clay sediments in which there is a strong planar orientation of clay

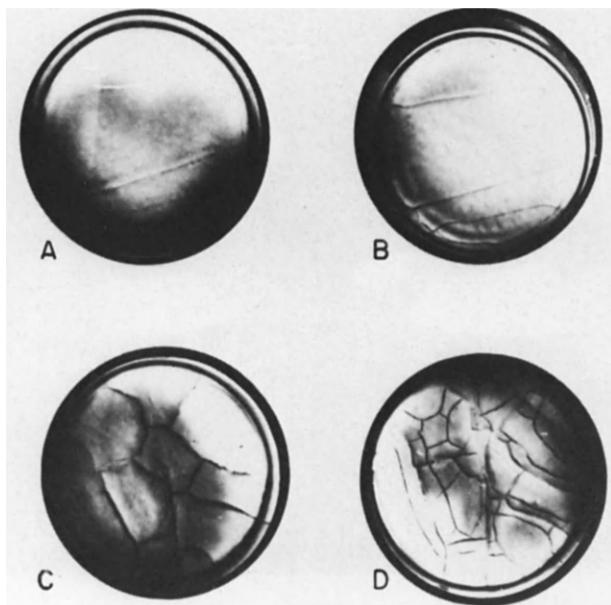


Fig. 3.6. Subaqueously formed shrinkage cracks in kaolinite with major additions of bentonite (After BURST, 1965, p.351, reproduced by permission of the Editor, Journal of Sedimentary Petrology).
A. February 21, 1963; 90% kaolinite, 10% bentonite. B. February 27, 1963; 90% kaolinite, 10% bentonite. C. February 27, 1963, 75% kaolinite, 25% bentonite. D. March 11, 1963; 75% kaolinite, 25% bentonite.

minerals may result from deposition of well-dispersed platelets (LOUGHNAN, 1978). It seems probable however that in many cases parent suspensions were flocculated and that strong preferred orientation results from unidirectional consolidation and compaction strain (WILLIAMSON, 1980; CURTIS et al., 1980). When clays are compacted the platy clay minerals tend to assume a parallel orientation normal to the pressure but in general there is no systematic correlation between depth of burial and degree of preferred orientation (MEADE, 1961, p.D91) or fissility (WHITE, 1961). Shales occur in close proximity to mudstones in deposits which range in age from at least Carboniferous to Eocene (BOSWELL, 1961, p.15). In pressure ranges up to about 100 kg/cm^2 (10MPa) degree of orientation is influenced to a considerable extent by conditions at the time of sedimentation. Either adsorption of the clay platelets on irregular detrital particles or flocculation of the clay minerals favours an imperfectly oriented or random arrangement. Disturbance of sediment by organisms living on the sea-bottom (benthos) may be a factor. Extent of fissility is probably also influenced by the nature of the cementing agent (INGRAM, 1953).

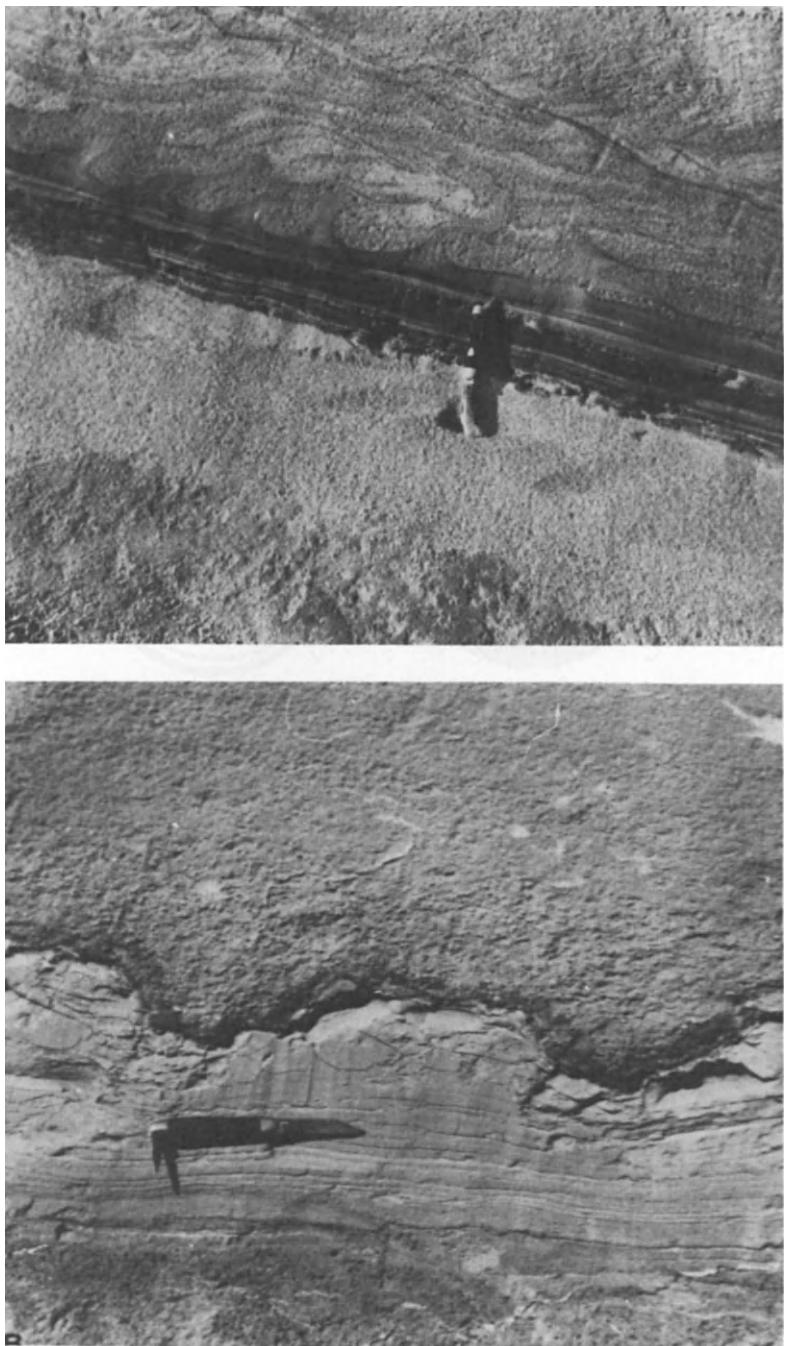


Figure 3.7 Load folds in shale. (After Sullwold, 1960, p.442; by permission of The American Association of Petroleum Geologists.)

MINERALOGICAL CHANGES

The dividing line between mineralogical changes caused by metamorphic processes and those due only to increased overburden pressure is gradational and somewhat arbitrary. The term diagenesis is often used for reactions which occur following burial but prior to metamorphism though changes before burial in the marine environment are sometimes included; there is no universally accepted definition of the term (BATES and JACKSON, 1980). The importance of reactions of this sort was emphasized by some authors at a relatively early date (CUMMINS, 1962; CARRIGY and MELON, 1964; MILLOT, 1970). In the lower temperature ranges of regional metamorphism the mineralogical changes are generally in response to an increase of shear stress as well as to rise in temperature. Shear is apparently necessary for certain seemingly minor transformations which affect clay minerals. For example WEAVER (1959, p.181) concluded that without shear a one-layer monoclinic (1M) mica lattice cannot be transformed into a two-layer monoclinic (2M) structure.

Normal pressures however can have important effects and increase in depth of burial has frequently been reported to cause an improvement in crystallinity of clay minerals. Evidence for the formation of illite from smectite during burial has been documented for over 20 years and continues to accumulate (ESLINGER and SELLARS, 1981). In the depth interval from 2000 to 3,700 metres interlayered illite/smectite has been found to be converted from less than 20 per cent to about 80 per cent illite layers after which the proportion of illite layers shows little further increase (HOWER et al., 1976). The transformation probably involves replacement of Al by Mg and Fe in the octahedral layers and substitution of Al for Si in the tetrahedral layers. The change is accompanied by an increase in K₂O, Al₂O₃ and layer charge together with a decrease in SiO₂ - content and expulsion of a relatively large amount of water from the mineral. Suggested associated changes include decomposition of potash feldspar, mica and kaolin together with formation of chlorite; calcite disappears in the same depth interval. HOWER et al (1976) concluded that the shale studied acted as a closed system for all components except H₂O, CaO, Na₂O and CO₂ while BLATT (1979) thought it possible that a small amount of soluble silica migrates out of mudrocks as a result of such mineralogical changes. On the other hand some workers have linked these transformations with the deposition of significant amounts of silica or carbonate cements in adjacent sandstones (POWELL et al., 1978; BOLES and FRANKS, 1979).

Some mineralogical transformations result from reaction with pore solutions. Such changes depend on permeability as well as on the nature of the clay and concentration of the solution. Water may vary from fresh to hypersaline. There is much support from laboratory experiments that the composition of pore solutions influences diagenetic changes. Heating

experiments led HELLER-KALLAI (1975) to speculate that conversion of montmorillonite to illite may depend in part upon reaction between the smectite and alkali halides or other proton acceptors. High salinities occur in evaporite basins such as the Dead Sea but are also known elsewhere as in the Orca Basin in the northwest Gulf of Mexico. There, increase in content of smectite, apparently at the expense of illite, kaolinite and chlorite, occurred below 300 cm and was related to the abnormally high concentration of Na^+ and Ca^{++} together with the very high water content of the sediments (TOMPKINS and SHEPARD, 1979). It has frequently been reported that the clay mineral content of sandstones is different from that of nearby shales. It seems very probable that this difference has in some cases resulted from the greater permeability of the sandstones and consequent greater accessibility to reactive solutions of the clay within the rock (WEAVER, 1959, pp. 172-174). The presence of authigenic clay in sandstones and other sediments is now widely recognized (CURTIS, 1975; FOSCOLOS et al., 1982).

Criteria by which authigenic clays can be distinguished from those of alloogenetic (detrital) origin have been discussed by WILSON and PITTMAN (1977). They consider the most reliable criteria to be (a) delicacy of clay morphology, (b) occurrence of clay as pore linings absent only at grain contacts and (c) composition radically different from associated alloogenetic clays. Distinctive morphologies for the major clay mineral groups were also recognized and which though not entirely reliable serve as a first approximation in identification. Smectite has a wrinkled appearance, illite occurs as flakes from which highly elongate laths or whiskers extend, chlorite often has a pseudohexagonal morphology with a cardhouse or rosette arrangement and kaolinite and dickite develop books of stacked pseudohexagonal flakes. Numerous scanning electron micrographs of authigenic clays displaying features of this sort have been published (Figs. 4.19 A to F) (Gillott, 1980). Authigenic clays have important engineering significance particularly in reservoir engineering as blockage of pore throats due to clay expansion or movement due to flow may significantly decrease permeability.

Increase in depth of burial is evidently associated with a general improvement in the crystallinity of clay minerals and with a tendency for expansive clays to lose their swelling capability. The extent of mineralogical change is probably also affected by the permeability of the rock. Care has to be exerted in reaching such conclusions owing to the possibility of a change with time in the type of material which was deposited at the time of sedimentation.

CHANGES IN CONTENT AND COMPOSITION OF PORE SOLUTIONS

The amount of interstitial water in a sediment generally decreases with

burial but at depths below about 3000 metres overpressured zones are sometimes found in which density decreases and volume of argillaceous and other sediments increases. These effects may result from increase in the amount or pressure of pore water. They have been attributed to a number of causes including expansion of water due to temperature increase on burial, release of water due to mineralogical changes such as the conversion of montmorillonite to illite, faulting, earth movements, etc., (BURST 1976; FERTL and CHILINGARIAN, 1977). If the solutions are unable to escape due to an overlying impermeable layer, as in a stratigraphic trap, or because of structural or other causes, excess or abnormally high fluid pressures will be encountered. It has also been postulated that fluid migration due to generation of high hydraulic pressures at depth may transport hydrocarbons formed diagenetically in shale into reservoir rocks.

It has been commonly observed that the salt content of water in rocks from deep bore holes shows a steady increase with depth. Below about 1,500 ft. many sediments contain water which has a higher salt content than sea-water. On the other hand water of low salinity is known from depths of the order of 10,000 - 20,000 ft. (3,000 - 6,000 m) (YODER, 1955, p. 509). Experimental studies have been made of the change in chemistry of solutions forced out of clay pastes when compressed. The clay paste is generally confined in a cylinder and compressed by a piston which incorporates some system by which pore water may be squeezed out of the sample and collected for analysis.

Changes in the composition of pore solutions in muds made with pure montmorillonite and kaolinite in solutions of CaCl_2 up to 1.2N and in solutions of NaCl up to 4.6N were studied by VON ENGELHARDT and GAIDA (1963). They found no change in the composition of the pore solutions on compaction of the kaolinite muds. Montmorillonite pore solutions showed a decrease in the concentration of salt up to 800 atm. With further increase in pressure, at which the pore ratio was reduced below 0.5, an increase in the concentration of the pore solution was detected. These results were regarded as evidence for an exchange type of reaction involving the clay minerals and permeability changes were attributed to changes in the texture of the clay. Decrease in concentration of pore fluids expelled on compaction at 40°C of montmorillonite clay has been reported to be related exponentially to the effective axial pressures (ROSENBAUM, 1976). The stage involving the decrease in salt content with increased pressure was observed at an early date by KRYUKOV et al. (1962). The pressure at which the change became marked varied with the nature of the clay and pore solutions. The results were regarded as offering an explanation for the commonly "observed lower salinity of pore solutions in argillites as compared with the interbedded sandstones." The exchange reaction was believed governed by the Donnan equilibrium and equations have been derived

to follow changes in the chemistry of the solutions. Activity coefficients in the suspension and negative adsorption by the clay minerals are thought to affect the electrolyte concentration of the expelled solution (APPELO, 1977). Significant depletions in salinity and chlorinity of interstitial water have been found to be associated with gas hydrates in sediment cores obtained in the Deep Sea Drilling Project (SHERIDAN, et al., 1982). Gas hydrates are known to exclude salt during crystallization (HAND, et al., 1974).

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CHAPTER 4

COMPOSITION AND FABRIC OF CLAYS

Clays are multicomponent systems in which solid, liquid, and gaseous phases are commonly present. The solid phase is polycrystalline and sometimes also polyamorphous. The crystalline components are inorganic minerals and the amorphous constituents may be either inorganic or organic. The inorganic minerals generally make up over 90% of the solids but this fraction may fall to as little as 5% in organic deposits such as peat. The composition is summarized in Fig. 4.1. Near the earth's surface the solids generally comprise about 50% of a soils total volume.

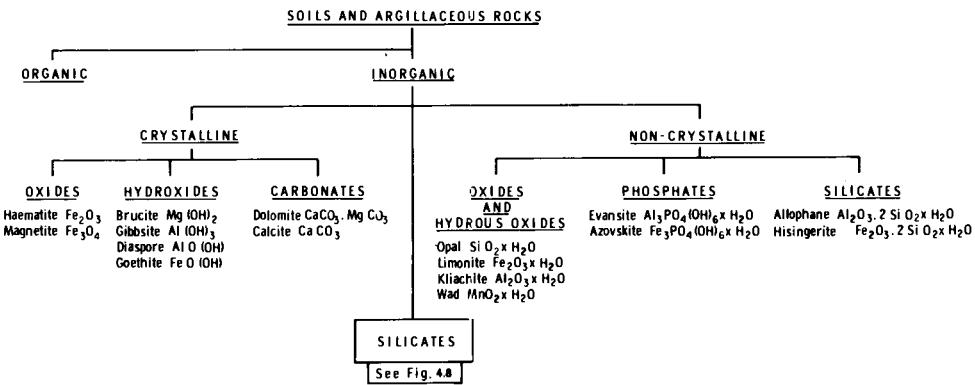


Fig. 4.1 Composition of soils and argillaceous rocks.

The remaining volume is occupied by the soil atmosphere and soil solutions. The composition of the soil atmosphere deviates with depth and poor conditions of aeration from that of the normal atmosphere. In the temperate zone the oxygen content may drop from the normal value of about 20% near the surface to as little as 3% at a depth of 70 cm and the CO₂ content may increase from the surface value of about 0.03% to reach 10% or even 20% under frozen soil horizons (MOHR and VAN BAREN, 1954, p. 86; JACKSON, 1964, p. 72). The composition and the arrangement and state of aggregation of the solid constituents of a clay result from its genesis and history.

THE COMPOSITION

In clays the largest proportion of the inorganic components is crystalline. The crystalline minerals are defined by the crystal chemistry; the amorphous minerals are defined by the elemental composition.

The most important crystalline components in clays are the secondary clay minerals. These are hydrous aluminosilicates which have distinctive properties due to their structure, shape and very small particle size. These minerals are responsible for most of the qualities which characterize clay. In addition to the clay minerals clay may contain any of the rock-forming minerals which have been reduced by attrition or chemical processes to the appropriate particle size range. The frequency with which primary minerals occur in clays varies with the stability of the minerals. Carbonates, oxides, hydrous compounds and silicates occur but the latter are by far the most important. Calcite and dolomite are the commonest carbonates, haematite and magnetite are important oxides and goethite, diaspore and brucite are hydroxy compounds.

CRYSTALLOGRAPHY

The plane faces and external symmetry of crystals has long attracted scientific attention. The external properties result from the regularity of internal arrangement. The atoms of which a crystal is composed are packed together in an orderly arrangement in three dimensions. The resulting pattern may be represented by a

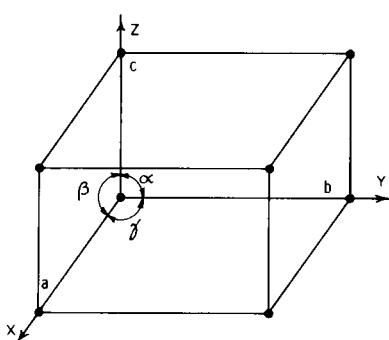


Fig. 4.2 The unit cell. α, β, γ = interaxial angles; XYZ = crystallographic axes; abc = repeat distances.

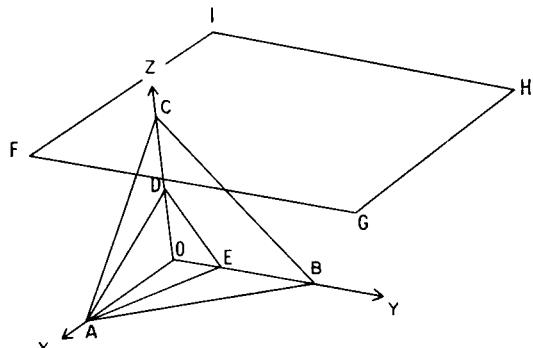


Fig. 4.3 Designation of crystal faces by Miller indices. ABC = parametral plane; crystallographic parameters: OA = a, OB = b, OC = c. AED = crystal face;

intercepts $\frac{a}{1} : \frac{b}{3} : \frac{c}{2}$; indices (132).

FGHI = crystal face; intercepts

$\frac{a}{\infty} : \frac{b}{\infty} : \frac{c}{1}$; indices (001).

set of points termed a space lattice. The regularity of packing in a crystal is such that order is not confined to the nearest neighbours of an atom but extends indefinitely in space. Subdivision of the structure into the smallest unit which retains all the properties and attributes of the crystal as a whole forms what is termed the unit cell. This is defined by reference to axes taken from some point chosen as origin in terms of the inter-axial angles and in terms of the repeat distance along each of the axes (Fig. 4.2). These values are the lattice constants or lattice parameters of the unit cell.

Planes in the lattice are defined by reference to the intercept made on the axes of the unit cell. Each plane is assigned a set of indices. The most popular system is based on work of the English crystallographer Miller and the indices are known as Miller indices. If a plane intercepts all three axes the Miller indices of the plane are the reciprocals of the fractional intercepts on the three axes. If the lengths of the axes of the unit cell are designated a , b , c any plane which cuts each of these axes makes intercepts of a/h , b/k , c/l . As the lengths a , b , and c , are unit lengths on each axis the plane makes fractional intercepts on each axis of $1/h$, $1/k$, $1/l$, and the Miller indices of the plane are (hkl) (Fig. 4.3). If a plane is parallel to an axis it is assigned the symbol zero relative to that axis, rather than infinity, the appearance of which in the indices is avoided by the device of employing reciprocals.

A plane which makes unit intercept on the X-axis and is parallel to the Y- and Z-axes has Miller indices (100) ; a similar plane parallel to the X- and Z-axes is the (010) plane and a comparable basal plane which cuts the Z-axis is assigned the symbol (001) . When a plane is referred to, the indices are enclosed in curved brackets. The spacing between the basal planes of layer lattice clay minerals is of considerable importance in clay mineral classification and in identification by X-ray diffraction.

BONDING AND STRUCTURE

The unit particles of which a crystal is composed may be molecules, atoms or ions. The forces between the units are electrical in nature. Attractive forces are of longer range than repulsive forces but these increase more rapidly as particles come close together. There are two chief types of attractive forces. Coulomb forces which exist between oppositely charged particles and exchange forces which result from electron sharing between neighbouring atoms. When the forces holding atoms together are mainly coulombic the bonding is described as ionic. When exchange forces dominate the bonding is described as covalent. In addition to ionic and covalent bonds there are weaker forces such as the hydrogen bond and even weaker van der Waals bond. The water molecule also plays an important structural role as it is a permanent dipole. It may become oriented in the structure and sometimes is strongly attached particularly to small highly charged cations.

Ionic bonds are dominant in inorganic minerals though the silicon-oxygen bond is probably partly covalent. To a first approximation the structure of ionic solids is determined by geometrical considerations which arise from the way in which spheres of different radius and charge may be packed. Cations being generally smaller may be regarded as fitted into the interstices between the larger anion spheres. In detail such a view is probably inaccurate but serves the useful purpose of allowing a qualitative understanding of the general features of ionic structures. There is a limit to the number of anions which can surround a cation to form a stable group. This limit may be deduced from the ratio of the radius of the cation to the radius of the anion; the value of this ratio is termed the coordination number. When the coordination number reaches its lower limiting value the anions approach contact and there is a rapid increase in repulsion between the negatively charged spheres and a different grouping becomes more stable (Fig. 4.4). Repulsive forces play a large role in determining the particular kind of crystal structure.

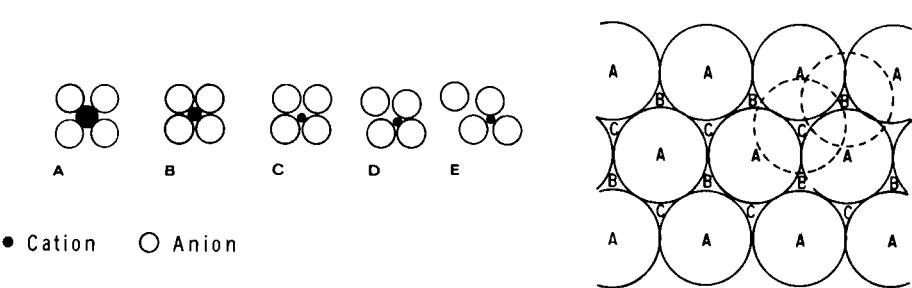
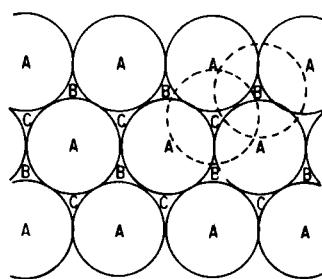


Fig. 4.4 Affect of cation to anion radius ratio on stable coordination. A,B,E : stable
C, D : unstable - repulsion between anions favours decrease in coordination.

Fig. 4.5 Close packed spheres



In many compounds the anions are arranged in an approximately close packed configuration. There are two types of close packing designated cubic close packing and hexagonal close packing. There are also more open types of packing. In the close packed arrangement succeeding sheets of spheres are set in the cusps between the spheres of the sheet below. The third sheet of spheres may occupy a different position relative to the first set as in the cubic arrangement or may fall in the same relative position as the first set of spheres as in the hexagonal scheme (Fig. 4.5). If each layer in a stack is given the symbol A, B, or C depending on the coordinates of its sphere centres with respect to the origin of the unit cell the cubic close packed arrangement may be represented symbolically as ABCABCABC... while the hexagonal arrangement is expressed in the same notation as ABABAB...

Chemically related substances are said to be isomorphous if they develop crystals which are similar in form. Polymorphs are different crystalline modifications of the same chemical substance. The chemical composition of polymorphic modifications is the same but the physical properties are different. Polymorphic modification generally results from differences in conditions such as temperature or pressure at the time of crystallization and the unit particles (atoms, ions, molecules) have different structural arrangements. Calcite and aragonite are well known examples but the majority of crystals show the phenomenon.

Polytypism is a special form of polymorphism. The only modification to the structure involves a difference in stacking arrangement of identical sheets. Two dimensions of the unit cell are the same and the modifications differ from one another only in the direction normal to the plane of the sheets and this lattice constant is altered by an integral multiple of the dimension of a single layer. The unit layer may be composed of only one sort of atom or may have a complex structure involving many sorts of atoms as in the clay minerals. Polytypism differs from polymorphism however in a number of important respects. VERMA and KRISHNA (1966, pp. 62-64) illustrate this point by reference to SiC in which the phenomenon was first recognised. Many polytypic modifications seem to form under essentially the same conditions of temperature and pressure and have very nearly identical physical properties. The atoms have the same arrangement of nearest and next nearest neighbours and differences are only found when more distant neighbours are considered. Hence the internal energy of different polytypes is nearly the same. Polytypes may be represented symbolically in the same notation as employed to represent cubic and hexagonal close packing. For example the hexagonal sequence ABABAB...may be changed to the polytype represented by ABACABAC...and the cubic close packed stacking sequence ABCABCABCABC...may be changed to ABCACBABCACB...which is the 6-layered hexagonal (6H) polytypic modification. Many combinations of hexagonal and cubic stacking are known and some have very long repeat distances. Irregular or random changes in stacking sequence are also known and this generates one dimensional disorder in the crystalline structure.

As an alternative to considering the packing of spheres the structure of ionic solids may be pictured as composed of polyhedral groups of anions enclosing cations. The polyhedra are linked together by sharing corners, edges, or more rarely faces. There are general principles, known as Pauling's Rules (PAULING, 1960, pp. 543-562), which apply to the manner in which such polyhedral elements may be packed. These rules have proved very useful in interpreting the structure of the silicates, many of which can be regarded as linked tetrahedral and octahedral groups. The cation to oxygen radius ratio is compatible with a tetrahedral grouping of oxygens about a silicon, with an octahedral grouping of oxygens about magnesium and with either an octahedral or tetrahedral grouping of oxygens about aluminium.

| COMBINATION OF TETRAHEDRA | DIAGRAMMATIC REPRESENTATION OF STRUCTURE | Si - O Group and Negative Charge | Oxygen to Silicon Ratio | EXAMPLE |
|---------------------------|--|-------------------------------------|-------------------------|------------|
| INDEPENDENT | | $(\text{Si}_4\text{O}_4)^{4-}$ | 4:1 | OLIVINES |
| DOUBLE | | $(\text{Si}_2\text{O}_7)^{6-}$ | 7:2 | AKERMANITE |
| RINGS | | $(\text{Si}_3\text{O}_9)^{6-}$ | 3:1 | BENITOITE |
| | | $(\text{Si}_6\text{O}_{18})^{12-}$ | | BERYL |
| CHAINS | | $(\text{Si}_4\text{O}_3)_n^{2-}$ | 3:1 | PYROXENES |
| BANDS | | $(\text{Si}_4\text{O}_{11})_n^{6-}$ | 11:4 | AMPHIBOLES |

Fig. 4.6 (Legend see p. 97)

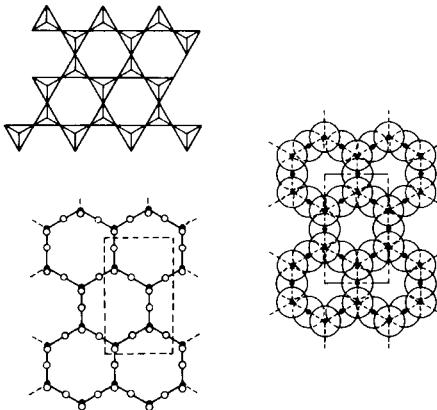
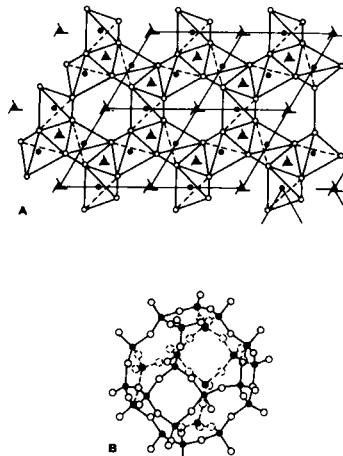
| COMBINATION OF TETRAHEDRA | DIAGRAMMATIC REPRESENTATION OF STRUCTURE | Si - O Group and Negative Charge | Oxygen to Silicon Ratio | EXAMPLE |
|---------------------------------|--|--|-------------------------------|---------|
| SHEETS |  | $(\text{Si}_4\text{O}_{10})_n^{4-}$ | 5:2 | MICAS |
| FRAMEWORKS |  | $(\text{Si}_2\text{O}_5)_n^0$ | 2:1 | QUARTZ |

Fig. 4.6. Chief varieties of structural combination in silicates.
A. After DEER et al. (1963, 4: 184). B. After WINCHELL (1951, p.240).

CRYSTAL CHEMISTRY OF SILICATES

In silicates the silicon ions are surrounded by a tetrahedral group of four oxygen ions. Two silicons may be joined to the same oxygen by bonds of equal strength. Such equal sharing makes possible polymerization or repeated linkage of the silicon ions via common oxygens. The extent and type of polymerization is made the basis for classification of the silicates.

When adjacent silica tetrahedra share no oxygen the $(\text{SiO}_4)^{4-}$ groups are separate (Fig. 4.6). Minerals with this type of structure are classified as nesosilicates (Greek neso, island). The olivines, garnets, and zircon are minerals in which the $(\text{SiO}_4)^{4-}$ tetrahedral groups are independent. In the sorosilicates (Greek soro, group) two tetrahedra share a common oxygen, the group $(\text{Si}_2\text{O}_7)^{6-}$ is formed, and the structure is that of a double tetrahedron (Fig. 4.6). Three-fold and six-fold rings are formed by $(\text{Si}_3\text{O}_9)^{6-}$ and $(\text{Si}_6\text{O}_{18})^{12-}$ groups respectively as in the minerals benitoite and beryl. Silicates with ring structures are classed as cyclosilicates (Greek cyclo, ring). When each tetrahedron shares two corners with a neighbour infinite chains form of composition $(\text{SiO}_3)_n^{2-}$ and there are many structural possibilities (Fig. 4.7) depending on the arrangement of the linked tetrahedra (BELOV, 1963). Differences in the relative positions of neighbouring chains give subdivisions among the pyroxenes (Fig. 4.7b; $[\text{Si}_2\text{O}_6]_\infty$) which are important minerals in igneous rocks. A somewhat analogous arrangement occurs in the amphiboles but in this mineral group two neighbouring chains are cross-linked to form a band with a characteristic $(\text{Si}_4\text{O}_{11})^{6-}$ grouping (Fig. 4.6). Silicates with chain and bandlike internal structural arrangement of the atoms are classed as inosilicates (Greek ino, thread). This arrangement commonly results in a fibrous external morphology in these minerals. This is best shown by certain forms of asbestos which belong to the amphibole group. Palygorskite and sepiolite are fibrous clay minerals with tetrahedral sheets arranged in bands. They have affinities with the chain silicates but are considered more closely related to the layer silicates. The name "hormites" has been rejected and they are considered to be a subdivision of a category of pseudo-layer silicates (BAILEY et al, 1971). Structural analyses have been made by X-ray diffraction and more recently by selected area electron diffraction (RAUTUREAU and TEHOUBAR, 1976).

Layer structures (Phyllosilicates, Greek phyllo, sheet) are formed by polymerization in two directions which leads to the characteristic grouping $(\text{Si}_4\text{O}_{10})^{4-}$ (Fig. 4.6). The micas, chlorites, serpentines, and most clay minerals belong to this family. The internal arrangement is generally reflected externally in the platy habit of these minerals. The layers are held together by different forces in different minerals but the interlayer bonding is weaker than that within the layers. This gives phyllosilicates a pronounced cleavage in the plane parallel to the sheets.

Three-dimensional framework structures (tektosilicates, Greek *tektos*, framework) result when each oxygen is shared between two silicones (Fig. 4.6). The silica minerals, feldspars and zeolites have structures based upon this plan. The classification of silicates according to these principles is illustrated in Fig. 4.8.

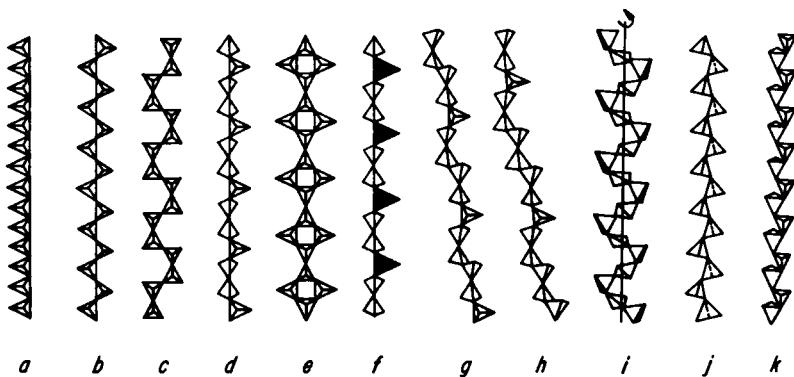


Fig. 4.7 Structural arrangements of linked tetrahedra in infinite chains. (After BELOV, 1963, p. A8; reproduced by permission from Acta Crystallographica.)

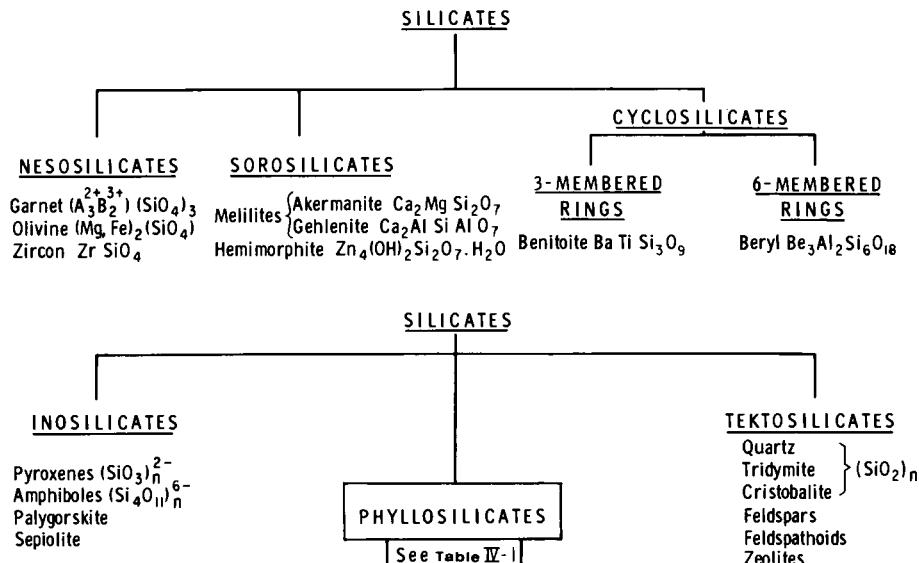


Fig. 4.8 Classification of silicates.

One ion may sometimes replace another in the structure without altering the form of the crystal; this is referred to as isomorphous substitution. It occurs with considerable facility in silicates and many minerals show no constancy of chemical composition when a comparison is made between different samples. When the sizes of the ions involved do not differ greatly the minerals, though different chemically, may show few or no external distinguishing features though changes in the dimensions of the unit cell occur which are related to extent of isomorphous substitution and ionic radii (RUSSELL and CLARK, 1978). The limits of such ionic substitution may be partial or may allow complete replacement of one ion by another. Cations often proxy for one another and hydroxyl and fluorine may enter the structure as substitutes for oxygen. The ratio of the radii of aluminium to oxygen is about 0.43 which is very close to the value of 0.414 which is the boundary value for transition from 6-fold to 4-fold coordination. Because of this aluminium can occupy sites which are either octahedrally or tetrahedrally co-ordinated by oxygen and in silicates aluminium frequently occupies both types of site in the same structure. LOEWENSTEIN (1954) has suggested rules which govern the disposition and arrangement of aluminium and silicon in tetrahedral co-ordination. It is believed that when a common oxygen links two adjacent tetrahedra only one can be occupied by aluminium. If two aluminium ions are neighbours to a common oxygen at least one of the aluminium ions must have a co-ordination number larger than four. These rules explain the 50% limit to substitution of aluminium for silicon observed in structures with polymerized tetrahedra apart from the clintonites (xanthophyllites). The increase in negative charge on the tetrahedron which results from the substitution of aluminium for silicon is compensated elsewhere in the structure by some corresponding change such as replacement of a univalent by a divalent cation.

PHYLLOSILICATES

The minerals which are of most importance in clays have layer structures and are classified as phyllosilicates. They have in common the same two types of structural element. These are the SiO_4 silica tetrahedron polymerized into sheets and the Mg(OH)_2 brucite-like, or Al(OH)_3 gibbsite-like, octahedral element both of which form sheet or layer structures (Fig. 4.9).

In the silica sheets the individual tetrahedra share three corners in the same plane with neighbouring tetrahedra. Open hexagonal rings indefinitely repeated in two dimensions result from this arrangement. Such a simple network is possible as it is a geometrical property of the hexagon to fill space.

In the brucite or gibbsite sheets the cation is co-ordinated by six hydroxyls arranged in the form of an octahedron. Edges are shared between neighbouring octahedral groups so that hexagonal units extended in the form of a sheet once more result. In the brucite arrangement the cations form a sheet sandwiched between

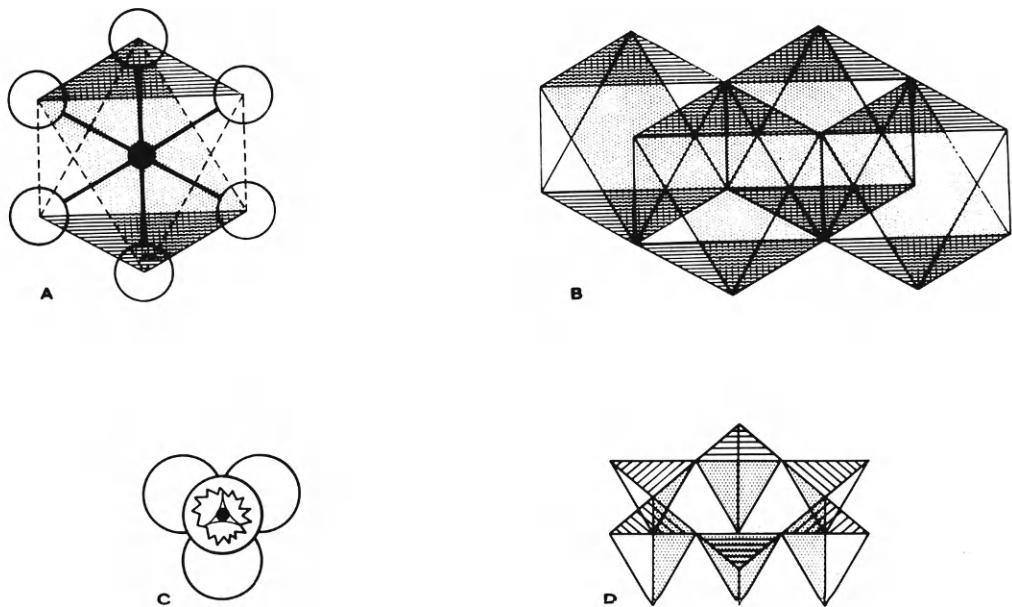


Fig. 4.9 Octahedral and tetrahedral groups. A. Octahedral group. B. Linked octahedra. C. Tetrahedral group. D. Linked tetrahedra.

two sheets of hydroxyls. Each cation has three hydroxyl neighbours in the sheet above and three in the hydroxyl sheet below. The lower group of hydroxyls is rotated relative to the upper group of three hydroxyls through an angle of 60° about an axis normal to the sheets. This therefore results in an approximately hexagonal close packed arrangement of the two hydroxyl sheets. In the brucite arrangement all the available octahedral sites are occupied by divalent cations. In the gibbsite arrangement only two thirds of these positions are filled by trivalent cations. The smaller more highly charged cations such as aluminium exert a strong deforming or polarizing effect upon the anions with development of surface hydrogen bonds and shortening of the b-axis.

The general structural scheme of the layer silicate minerals is generated by the combination of sheets of articulated tetrahedral and octahedral elements. Two thirds of the hydroxyls in one plane of the octahedral sheet are replaced by the apical oxygens of the tetrahedral sheet. The remaining OH^- ions in this sheet are in the centres of the hexagons formed by the oxygens of the tetrahedral sheet. A combination of one octahedral and one tetrahedral sheet in the manner described generates a 1:1 unit or unit of structure (Fig. 4.10). This is the basic structural plan of the kaolinite-serpentine group of minerals (Table IV-1).

When a second tetrahedral layer is added in a similar manner with replacement of hydroxyls in the sheet on the opposite side of the octahedral cation a 2:1 type of layer structure results. In this arrangement two tetrahedral sheets sandwich a

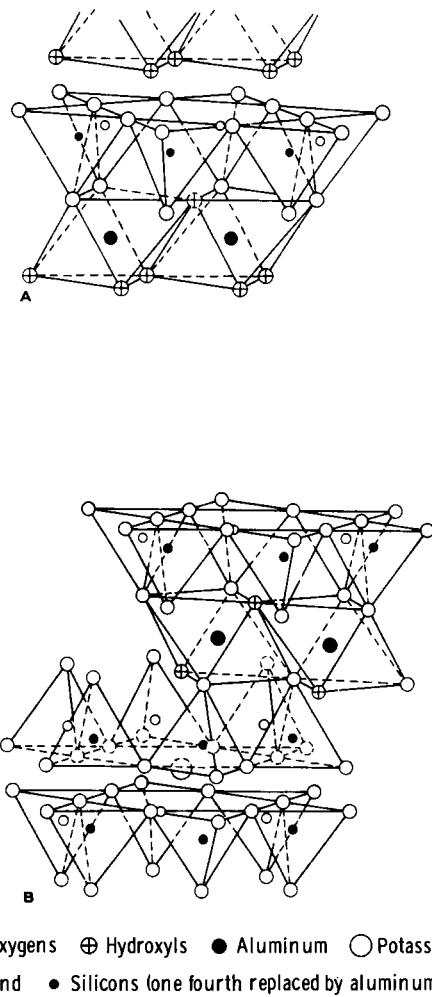


Fig. 4.10 Diagrammatic illustration of 1:1 and 2:1 layer lattice. (After GRIM, 1953, by permission of McGraw-Hill Book Co.) A. Kaolinite structure. B. Muscovite structure.

central octahedral sheet (Fig. 4.10). This arrangement is found in the pyrophyllite-talc group, the smectites, the vermiculites and the mica groups (Table IV-1).

There is a slight difference in the dimensions of the octahedral and tetrahedral sheets so when these are combined there is a small misfit. This and other causes are likely to lead to internal stress in silicate structures relief from which may be sought internally either by ionic substitution or by rotation of tetrahedra or externally by change in shape. Attempts have been made to relate postulated residual stress to properties of the layer silicate minerals such as ob-

served lattice dimensions, (RADOSLOVICH, 1962; RADOSLOVICH and NORRISH, 1962), external morphology, (BATES, 1959; RADOSLOVICH, 1963a; HOPE and KITTRICK, 1964) stability to weathering, frequency of occurrence and the known limits of solid solution in the various minerals (RADOSLOVICH, 1963b; RADOSLOVICH, 1963c).

In the chlorite minerals there is an additional octahedral layer which is located between successive 2:1 units. The fundamental unit structure of the chlorites therefore contains a 2:1 layer plus an interlayer hydroxide sheet.

TABLE IV-1 CLASSIFICATION SCHEME FOR PHYLLOSILICATES RELATED TO CLAY MINERALS

| LAYER TYPE | GROUP (x = CHARGE PER FORMULA UNIT) | SUBGROUP | SPECIES * |
|------------|--|---|---|
| 1:1 | KAOLINITE - SERPENTINE x ~ 0 | KAOLINITE SERPENTINE | KAOLINITE, DICKITE, HALLOYSITE CHRYSOTILE, LIZARDITE, AMESITE |
| | PYROPHYLLITE - TALC x ~ 0 | PYROPHYLLITE TALC | PYROPHYLLITE TALC |
| | SMECTITE x ~ 0.2 - 0.6 | DIOCTAHEDRAL SMECTITE TRIOCTAHEDRAL SMECTITE | MONTMORILLONITE, BEIDELLINE SAPONITE, HECTORITE, SAUCONITE |
| | VERMICULITE x ~ 0.6 - 0.9 | DIOCTAHEDRAL VERMICULITE TRIOCTAHEDRAL VERMICULITE | DIOCTAHEDRAL VERMICULITE TRIOCTAHEDRAL VERMICULITE |
| | MICA x ~ 1 | DIOCTAHEDRAL MICA TRIOCTAHEDRAL MICA | MUSCOVITE, PARAGONITE PHLOGOPITE, BIOTITE, LEPIDOLITE |
| | BRITTLE MICA x ~ 2 | DIOCTAHEDRAL BRITTLE MICA TRIOCTAHEDRAL BRITTLE MICA | MARGARITE CLINTONITE, ANANDITE |
| | CHLORITE x VARIABLE | DIOCTAHEDRAL CHLORITE DI, TRIOCTAHEDRAL CHLORITE TRIOCTAHEDRAL CHLORITE | DONBASSITE COOKEITE, SUDOITE CLINOCHLORE, CHAMOSITE, NIMITE |

* ONLY A FEW EXAMPLES ARE GIVEN. # THE STATUS OF ILLITE (OR HYDROMICA), SERICITE, ETC. MUST BE LEFT OPEN AT PRESENT, BECAUSE IT IS NOT CLEAR WHETHER OR AT WHAT LEVEL THEY WOULD ENTER THE TABLE. MANY MATERIALS SO DESIGNATED MAY BE INTERSTRATIFIED.

PERMISSION TO REPRODUCE TABLE IV-1 FROM S.W. BAILEY, 1980, THE CANADIAN MINERALOGIST, 18, p144 IS GRATEFULLY ACKNOWLEDGED TO THE MINERALOGICAL ASSOCIATION OF CANADA.

The 1:1 layer silicates have a dimension of about 7\AA normal to the sheet whereas in the 2:1 layer structures this dimension is about 10\AA . In the chlorites the thickness of the unit layer is about 14\AA so minerals with this type of structural scheme are sometimes described as "14A minerals". A difference in basal spacing is readily detected by X-ray diffraction analysis and is the most important criterion used in the classification of the layer silicate minerals into types.

The phyllosilicate types are divided into groups on the basis of charge on the layers (Table IV-1). When there is an exact balance of positive and negative for-

ces within the sheets the charge is zero and the layers are held together either by van der Waals forces as in the case of pyrophyllite and talc or by hydrogen bonds as in kaolinite. A net negative charge results from unbalanced isomorphous substitutions in the layers. Apart from the chlorites this is neutralized by cations in the interlayer positions. The location and magnitude of the negative charge within the layer influences the tightness of interlayer bond. In smectite the layer charge per formula unit has a value of 0.2 to 0.6, in vermiculite the charge is 0.6 to 0.9, in mica it is about 1 and in brittle mica it is about 2. In chlorite the net negative charge on the 2:1 layer is balanced in the additional octahedral layer by a positive charge which results from such substitutions as replacement of some of the divalent magnesium by trivalent aluminium cations. A unit or unit structure contains one or more chemical formula units. A unit of kaolinite, for example, consists of a 1:1 layer. In vermiculite the unit structure includes the interlayer hydrated cations together with the 2:1 layer (BAILEY, et al., 1971).

The distribution of cations within the octahedral layer is used as a basis of subdivision of groups into subgroups (Table IV-1). When trivalent aluminium is the dominant cation in this layer only two thirds of the available octahedral sites are occupied. Such a structure is described as dioctahedral and there are two octahedral cations per half unit cell. When a divalent ion such as magnesium is dominant in the octahedral layer all the available sites are filled. In this type of structure there are three octahedral cations per half unit cell and the structure is described as trioctahedral. The distinction between the two structural arrangements can generally be made quite readily by X-ray diffraction. In a dioctahedral mineral the (060)^o planes have a spacing close to 1.50 \AA whereas this spacing has a value of about 1.53 \AA to 1.55 \AA in a trioctahedral mineral. There are a few minerals which are exceptions in this regard. In Ba- and lysine-vermiculite it has been found that the 061 reflections are influenced by translations between the layers caused by the interlayer cations. Hence some caution is suggested in measurement of the 060 reflection to establish chemical composition and other properties (TELLERIA, et al., 1977).

Mineral species within each subgroup result from isomorphous substitutions in the structure and from differences in the stacking arrangement of sheets which are identical in two dimensions (polytypism). The classification of the principal groups of phyllosilicates is illustrated in Table IV-1 and is the outcome of international discussions summarized by MACKENZIE (1965), BRINDLEY (1966) and BAILEY (1971, 1979). Recommendations from various national groups of clay scientists to do with nomenclature and classification are considered every three years by the Nomenclature Committee of AIPEA. In the recommended terminology it is considered correct to refer to "planes" of atoms, "sheets" for combinations of planes and "layers" for combinations of sheets.

The kaolinite-serpentine group

The members of this group are 1:1 layer silicates. The theoretical composition of the dioctahedral subgroup is $\text{Al}_4\text{Si}_4\text{O}_{10}(\text{OH})_8$ and the species show little chemical variation as isomorphous substitution is very limited. In this respect the kaolinites differ from most other clay minerals. The mineral species are kaolinite, nacrite, dickite and halloysite. Nomenclature is the subject of discussion (DOUILLET and NICOLAS, 1969) and since the first three bear a polytypic relation to each other it has been suggested that they be given a single name followed by symbols expressing the stacking sequences. Halloysite is more hydrous and evidence supports the view that it is a distinct species (KIRKMAN, 1977). The mineral anauxite has been discredited (BAILEY et al., 1971). The layers have little charge unbalance and are held together by bent hydrogen bonds though electrostatic bonding and coupling between hydroxyls have also been considered (WIECKOWSKI and WIEWIORA, 1976; GIESE, 1973; CRUZ, 1972). The hydroxyls occupy four types of position in the structure. On edges, on exposed surfaces, in inner surface positions between bonded 1:1 layers and in the inner plane common to the tetrahedral and octahedral sheet of a 1:1 layer. The infrared spectrum shows a band at about 3620 cm^{-1} which is thought to arise from vibrations of the inner hydroxyl whereas bands at 3695 , 3670 and 3650 cm^{-1} are attributed to hydroxyls in the other positions (LEDOUX and WHITE, 1964, 1966a,b). The base exchange capacity of these minerals is lower than most other clay minerals commonly being $< 10 \text{ meq}/100 \text{ g}$ (milliequivalents per 100 g) dry clay; halloysite has a cation exchange capacity of about $40 \text{ meq}/100 \text{ g}$ dry clay. The exact value depends on particle size and other factors such as the presence of internal pores, micaceous occlusions and interstratification with smectite or other clay mineral layers (DIXON and MCKEE, 1974; LEE et al., 1975).

Kaolinite, nacrite and dickite have a platy morphology but halloysite is often spheroidal or tubular perhaps due to rolling-up on drying. In halloysite the tetrahedral silica layer faces the external skin of the tubes whereas in chrysotile, which is a tubular mineral belonging to the serpentine subgroup, the octahedral layer is external. The relationships between morphology and structural order in kaolinite and halloysite have been discussed by SANTOS et al (1965). Recent work with the scanning electron microscope has shown that two or more kaolin minerals, including plates and elongates, are frequently intermixed in specimens from "classic areas" even when the deposits are residual. It is suggested that departures from the ideal in crystallinity, chemical composition, behaviour in industrial use, etc., may result from these variations on the micro-scale (KELLER and HAENNI, 1978).

Kaolinite formation at the expense of primary minerals is favoured by acid conditions under both weathering and hydrothermal action. Dickite and nacrite have commonly been regarded as of hydrothermal origin. Low temperature occurrences of

dickite have been listed by BAYLISS et al (1965). Halloysite seems to form as an alteration product of porous volcanic deposits changing to kaolinite as duration of weathering increases.

The serpentines are trioctahedral analogues of the kaolinites and have a 1:1 layer structure. The name serpentine applies to a group of three minerals, chrysotile, lizardite, and antigorite, in which the composition departs little from that represented by the formula $Mg_6Si_4O_{10}(OH)_8$ (WHITTAKER and ZUSSMAN, 1956). X-ray diffraction studies have shown that the three minerals differ structurally and attempts have been made to correlate infrared spectra with structural features (YARIV and HELLER-KALLAI, 1975). Serpentines occur in the form of fibres, tubes, laths and plates.

In older literature the name "septechlorite" was used for some minerals which are structurally related to the serpentines and kaolinites but which are compositionally related to the chlorites (NELSON and ROY, 1954, p. 344). Minerals of this sort are amesite, berthierine (chamosite), greenalite and cronstedtite. Amesite is related to serpentine by replacement of part of the magnesium and part of the silica by aluminium; in berthierine the magnesium is replaced by ferrous iron. Cronstedtite is similar in composition to chamosite but the aluminium is replaced by ferric iron.

Serpentines are found in altered ultrabasic rocks. Synthetic studies have suggested that they are formed below about 450°C whereas chlorites form above about 500°C. Serpentine mineralogy, petrology and paragenesis was the subject of a symposium published by the Canadian Mineralogist (1979).

The pyrophyllite-talc group

The pyrophyllite-talc group has a 2:1 type of layer structure. In structure pyrophyllite and talc may be looked upon as the parents respectively of the dioctahedral and trioctahedral subgroups of the 2:1 layer silicates.

In pyrophyllite two thirds of the octahedral sites are occupied by Al and the mineral is dioctahedral. There is little or no substitution of Si^{4+} by Al^{3+} and there is no net negative charge on the sheets so no interlayer cations are required to give electrical neutrality. Sheets are held together by weak van der Waals forces and the nature of the structure makes polytypic modification possible by displacement of successive layers. Crystals are commonly disordered. The composition is given by the formula $Al_4(Si_8O_{20})(OH)_4$ and individual samples show little chemical variation. Pyrophyllite is not a very common mineral; it occurs in metamorphic rocks in hydrothermal associations. Pyrophyllite-like layers regularly intergrown with montmorillonite-like layers occur in rectorite.

Talc is similar in structure to pyrophyllite but the octahedral sites are occupied by Mg ions and all the sites are filled. The mineral is trioctahedral and there is little or no charge on the layers. There is structural disorder similar

to that found in pyrophyllite. The chemical composition is expressed by the formula $Mg_6(Si_8O_{20})(OH)_4$ and there is not much chemical variation between samples. The mineral minnesotaite is similar to talc but the magnesium is replaced by ferrous iron. Like pyrophyllite, talc occurs under conditions of low-grade thermal metamorphism generally in hydrothermal associations.

The smectite group

The smectites are 2:1 layer silicates with a layer charge of 0.2 to 0.6 per formula unit. Ionic substitutions in the 2:1 layers result in the negative charge which may be located in either the tetrahedral or octahedral sheet. From the viewpoint of properties and analytical recognition the most distinctive feature of the smectites is that water and organic liquids may penetrate between the layers so that the basal spacing is variable. Water uptake is accompanied by a big increase in volume and large swelling pressures are generated.

There is a considerable range in composition and there are both dioctahedral and trioctahedral members of the group. Study of synthetic compounds indicates that there is an incomplete range of solid solution between dioctahedral and trioctahedral members (MUMPTON and ROY, 1956, p.337). Montmorillonite and beidellite are important dioctahedral minerals, montmorillonite having an octahedral charge arising from some substitution of Mg for Al in the octahedral layer and beidellite being aluminium-rich. In nontronite Fe^{3+} may completely fill the octahedral sites and there may also be extensive replacement of Si by Fe^{3+} (GOODMAN et al., 1976). Saponite, hectorite and saucnite are trioctahedral. In the classical formulae saponite contains Mg as the principal octahedral cation and there is some substitution of Al for Si in the tetrahedral sheet; hectorite contains no Al but has some replacement of Mg by Li; and Zn is present in significant amounts in the octahedral sheet of saucnite. The relationships of members of the group have been reviewed by ROSS (1960).

The layer charge is balanced by exchangeable interlayer cations. The total negative charge per unit area of the 2:1 layer is less than in the micas so that the concentration of interlayer cations is lower. Calcium is the commonest interlayer ion but when sodium is the exchange ion the mineral swells more when placed in contact with water. The cation exchange capacity ranges from 80 to 150 meq/100 g.

When the interlayer cation is replaced by potassium montmorillonite resembles illite in composition but does not lose its ability to take-up water between the 2:1 layers. There are two factors which probably account for this difference. In montmorillonite the largest proportion of the negative charge is located in the octahedral layer, whereas in illite most of the negative charge is seated nearer the surface in the tetrahedral layer. In montmorillonite therefore, the negative

charge is separated by a greater distance from the balancing positive charge which in both cases is located in the interlayer cations. Hence, the interlayer bonding in montmorillonite is probably less strong than in illite. The second factor is that owing to the smaller negative charge on the 2:1 layer there are fewer interlayer bonding cations per unit of surface.

In many beidellites it has now been concluded that there are charged sites in the octahedral as well as in the tetrahedral sheets (GLAESER, et al., 1967; SCHULTZ, 1969). In saponites the charge, located in the tetrahedral sheet, has recently been associated with crystallographic order normal to the layers. Relatively rigid links are thought to form between layers via water molecules bonded by dipole interaction to interlayer cations and by hydrogen bonds to negatively charged surface oxygens. In the monolayer hydrate infrared spectroscopy indicates no intermolecular hydrogen bond (SUQUET et al., 1975; 1977a). Saponites have been synthesized with a layer charge varying between 0.33 and 1.0 so that the basis for separating smectites as phyllosilicates with a charge density of < .6 from transformed micas with a layer charge above that value seems unsound. Similarly the difference between high charged saponite and low charged vermiculite is questioned (SUQUET et al., 1977b).

Smectites form complexes with polar organic compounds; the complexes formed with glycol and glycerol have a stable basal spacing so they are of use in X-ray analysis. The structural arrangement of the ethylene glycol molecules in the interlamellar region has been worked out by Fourier methods (REYNOLDS, 1965).

The vermiculite group

Vermiculite occurs as large crystals as well as in the clay size range. The large crystals are trioctahedral and are found in the sand- or silt-size fractions of soils (ALEXIADES et al., 1973); clay grade material may be either trioctahedral or dioctahedral. The fundamental structure is similar to that of the other 2:1 phyllosilicate minerals. There is a negative charge of 0.6 to 0.9 per formula unit which is balanced by interlayer cations. Vermiculite has a cation exchange capacity of 100 to 260 meq/100 g of dry clay. A value of 159 meq/100 g for trioctahedral vermiculite was given by ALEXIADES and JACKSON (1965). Vermiculite is of more widespread occurrence in soils than was once thought. Most authorities consider that it forms as an alteration product of muscovite, biotite or other phyllosilicates. In weathering environments it not infrequently contains hydrated and hydroxy interlayer precipitates.

In magnesium-vermiculite the interlayer magnesium ions are surrounded by two sheets of water molecules. The water and magnesium ions are oriented but there is also water present which is not attached to an adjoining cation. This water is readily expelled when the mineral is heated and the basal spacing decreases due to

dehydration. Provided the heating has not been too severe, rehydration occurs readily on exposure to damp air or moisture. The structure and dehydration mechanism have been discussed by MATHIESON and WALKER (1954), MATHIESON (1958) and WALKER (1956). More recent studies of vermiculite saturated with Li^+ , Na^+ , Ca^{2+} , Mg^{2+} and Ba^{2+} ions have indicated that four layer stacking types exist. A three-dimensionally ordered structure was found for one of the types (V_{III}) whereas the other three types (V_{I} , V_{V} and V_{VII}) had semi-ordered structures (CALLE, et al., 1978).

The variable basal spacing links vermiculite with the smectites though the bonding of adjacent 2:1 layers via a sheet of partially ordered water and magnesium ions is reminiscent of the chlorites. The dividing line between smectite and vermiculite based upon charge density is to some extent arbitrary as it is possible that there is a continuous series with no sharp boundary. On the other hand attempts to synthesize smectites with a cation exchange capacity intermediate between those of smectite and vermiculite were unsuccessful suggesting discontinuity (HARWARD and BRINDLEY, 1964). WALKER (1958) showed that vermiculite will take up one or two layers of glycerol between the layers depending on the exchangeable cation. When exchange sites were saturated by Mg^{2+} however vermiculite took up only one layer developing a basal spacing of 14.5\AA whereas Mg - montmorillonite took up two layers of glycerol and expanded to 17.8\AA . Swelling behaviour in glycerol of the Mg - saturated mineral has commonly been used as the criterion for distinguishing vermiculites from smectites. Work with synthetic saponites has shown that there are difficulties in distinguishing saponites from vermiculites. Discontinuities exist in physico-chemical behaviour such as swelling properties in water, glycol and glycerol but these seem dependent upon cation exchange capacity, solvation liquid and charge density rather than upon type of mineral (SUQUET et al., 1977). It has been suggested that the strengths of interlayer bonds may be more useful than layer charge to the understanding of behaviour and recent calculations lend support to this idea (GIESE, 1978). In general smectites differ from vermiculite in that the layer charge is usually lower, ionic substitutions are less well ordered and the layer charge originates in the tetrahedral sheet of vermiculite but in the octahedral, tetrahedral or both sheets of smectites.

The mica group

The basic structure of these minerals consists of a 2:1 layer made up of two inwardly directed sheets of silicon-oxygen tetrahedra which sandwich an octahedral sheet. There is a negative charge on the 2:1 layer of about 1 per formula unit. The charge is neutralized by cations which are located in the interlayer region. There are dioctahedral and trioctahedral micas. Interlayer bond energies of dioctahedral micas have been calculated to be higher than those of trioctahedral micas even when layer charge is the same. This has been linked with the occupancy of

the octahedral sites. This factor appears to contribute as much to the difference in energy as difference in orientation of hydroxyls even though the latter are much closer to the interlayer cations (GIESE, 1977).

Muscovite is dioctahedral and the chemical composition is expressed by the formula $KAl_2(Si_3AlO_{10})(OH)_2$. In muscovite there are six oxygen ions located close to the interlayer potassium ion and a further group of six oxygen ions at a greater distance (RADOSLOVICH, 1960, p. 929). In the ideal structural arrangement the potassium ion would be co-ordinated by 12 equidistant oxygen ions of which 6 would be located in the 2:1 layer above the potassium and 6 located in the 2:1 layer below the potassium. In the real structure there is distortion from this ideal arrangement. The majority of micas are polytypic and possible stacking arrangements and stabilities have been described (SMITH and YODER, 1956, p. 217; VELDE, 1965). In the laboratory a one layer monoclinic polytype (1 Md) formed under low temperature conditions, at higher temperatures and with longer periods of synthesis a 1 M polytype developed and at even higher temperatures a 2 M polytype. The polytypism is based on the displacement of 1/3 the length of the a-axis inherent in the hexagonal close packing of the octahedral layer together with the open hexagonal arrangement of the oxygen ions in the surface of the 2:1 layers. Relative shifts in succeeding layers lead to differences in occupancy of octahedral cation sites. Among dioctahedral micas it seems that the 2M₁ variety is the most common with 1M and 3T polytypes being less frequently found. Among trioctahedral micas the most common type seems to be 1M.

Other dioctahedral micas are paragonite, phengite, leucophyllite and celadonite. In paragonite the interlayer K⁺ is replaced by Na⁺. In phengite the Si:Al ratio exceeds 3:1 and Mg²⁺ or Fe²⁺ substitute for Al³⁺ in the octahedral sheet. Leucophyllite is the compositional end-member in which the Al³⁺ ions in the tetrahedral sheet are completely replaced by Si⁴⁺ and half the octahedral Al³⁺ is replaced by Mg²⁺. The layer charge is located in the octahedral sheet. Celadonite has a "composition KMgFe³⁺Si₄O₁₀(OH)₂ with a tetrahedral Al (or Fe³⁺) range of 0.0 to about 0.2 atoms. Substantial octahedral variations from this formula can be described by adjectival modifiers, such as aluminian celadonite or ferroan celadonite. Further characteristics of celadonite are $d(060) < 1.510 \text{ \AA}$ and sharp infrared spectra, as described by BUCKLEY et al (1978). There is an area of potential overlap of celadonite and glauconite analyses between about $Al^{IV} = 0.17$ to 0.20" (BAILEY et al., 1979). Trioctahedral micas include biotite, phlogopite, lepidolite and taeniolite.

The commonest mineral in argillaceous deposits is of the potash mica-type and is commonly identified as "illite" as a first approximation. Many illites are mixed-layer minerals and it is by no means certain that illites constitute a valid group which is distinct from the micas (YODER and EUGSTER, 1955, BRINDLEY, 1966, p. 30). Nonetheless most workers consider that illite is useful as a gener-

al term (GAUDETTE et al., 1966, p. 33) for clay-grade micas and it is likely to continue to be used in that capacity until the nature of the mineral becomes better defined by further research. For the present the status of the mineral is left open (BAILEY et al., 1971).

Most commonly the illite found in clays is dioctahedral and is closely related to muscovite though it contains less potassium and more water and shows structural variability. Trioctahedral mica-type minerals of clay-size grade are known but are much less common. The extent of solid solution between di- and trioctahedral illites is not known with certainty but is thought to be limited. The commonest illite polytype is disordered and has a one-layer monoclinic cell (1Md). Such minerals differ in composition from ideal muscovite and this is probably connected with the apparent differences in stability of the polytypic modifications.

Illites have a cation exchange capacity of 10 to 40 meq/100 g which exceeds that of the kaolinite-serpentine group but is less than that of the smectites and vermiculites. Most of the potassium ions are not exchangeable. Water and organic liquids are unable to penetrate between the layers though loss of potassium due to weathering may result in partial hydration. Glauconite has been defined as, "an Fe-rich dioctahedral mica with tetrahedral Al (or Fe^{3+}) usually greater than 0.2 atoms per formula unit and octahedral R^{3+} correspondingly greater than 1.2 atoms. A generalized formula is $\text{K}(\text{R}_{1.33}\text{Fe}_{0.67})(\text{Si}_{3.67}\text{Al}_{0.33})_{10}(\text{OH})_2$. Further characteristics of glauconite are $d(060) > 1.510 \text{ \AA}$ and (usually) broader infrared spectra than celadonite, as described by BUCKLEY et al., (1978). The species glauconite is single-phase and ideally is non-interstratified. Mixtures containing an iron-rich mica as a major component can be called glauconitic. Specimens with expandable layers can be described as randomly interstratified glauconite-smectite. Mode of origin is not a criterion, and a green fecal pellet in a marine sediment that meets the definition for celadonite should be called celadonite." (BAILEY, et al., 1979). Glauconites are compositionally heterogeneous but there is little or no overlap between glauconite and celadonite. The compositional variation found in sedimentary glauconite pellets has been described by BURST (1958) and the nature of glauconite further discussed by VELDE and ODIN (1975) and THOMPSON and HOWER (1975).

The brittle mica group

The brittle micas have a 2:1 layer structure and a charge per formula unit of about 2. Margarite is a dioctahedral species and clintonite is a trioctahedral Li-poor, Ba-poor species (FORMAN et al., 1967; BAILEY et al., 1971). In structure these minerals are similar to the more common micas but the interlayer ion is Ca^{2+} and there is an unusually large replacement of Si^{4+} by Al^{3+} in the tetrahedral layer. They occur in rocks which have been altered by metamorphic and metasomatic processes.

The chlorite group

In these minerals the alumino-silicate layer structure is similar to that found in the earlier described minerals which are 2:1 layer silicates. In the chlorites however, the 2:1 layers are regularly intergrown with a sheet of cations which are octahedrally co-ordinated by hydroxyls. There is no sharing of anions between the interlayer hydroxide sheet and the 2:1 layer. Magnesium or aluminium are generally the dominant cations though isomorphous replacement by other cations is common in the chlorites. The 2:1 layer carries a negative charge due mainly to some replacement of Si^{4+} by trivalent cations in the tetrahedral sheet. This negative charge is balanced by a positive charge on the interlayer hydroxide sheet due to replacement of divalent by trivalent cations. Chlorites have a cation-exchange capacity of 10-40 meq/100 g.

Chlorites differ from vermiculite in that interlayer magnesium ions are co-ordinated by hydroxyl ions rather than water molecules so the hydroxide sheet is more complete and better formed. Most chlorites are trioctahedral though dioctahedral chlorite is known to occur (BRYDON, et al., 1961). It has been suggested that the chlorites be subdivided into dioctahedral, di, trioctahedral and trioctahedral sub-groups (Table IV-1). Dioctahedral chlorite is dioctahedral in both the 2:1 layer and in the interlayer hydroxide sheet. A di, trioctahedral chlorite is dioctahedral in the 2:1 layer but trioctahedral in the interlayer hydroxide sheet. Trioctahedral chlorites are named according to the dominant divalent cation in the octahedral sheet. Names recommended are clinochlore for the Mg-dominant mineral [end member: $(\text{Mg}_5\text{Al})(\text{Si}_3\text{Al})_0\text{O}_{10}(\text{OH})_8$], chamosite for the Fe^{2+} -dominant mineral [end member: $(\text{Fe}_5\text{Al})(\text{Si}_3\text{Al})_0\text{O}_{10}(\text{OH})_8$], nimite for the Ni-dominant mineral [end member: $(\text{Ni}_5\text{Al})(\text{Si}_3\text{Al})_0\text{O}_{10}(\text{OH})_8$] and pennantite for the Mn^{2+} -dominant mineral [end member: $(\text{Mn}_5\text{Al})(\text{Si}_3\text{Al})_0\text{O}_{10}(\text{OH})_8$]. All other species and varietal names should be discarded according to this recommendation (BAILEY et al., 1979; BAYLISS, 1975). Earlier schemes of classification have been described by FOSTER (1962), BROWN and BAILEY (1962) and SCHIROZU and BAILEY (1965).

Chlorites normally have a stable 14A basal spacing though hydrated chlorite termed "swelling chlorite" which shows an increase in basal spacing on treatment with glycerol has been described (STEPHEN and MACEWAN, 1950). The 14A chlorites are also related to 7A minerals which were termed septechlorites in early literature (NELSON and ROY, 1954, p. 344) and which are reported to be the low-temperature form. These minerals are sometimes classed as serpentines. Chlorites occur in igneous, metamorphic and sedimentary rocks and they may be either detrital or authigenic in sediments.

Interstratified clay minerals

The basic structure of many of the clay minerals is so similar that intergrowths of more than one type are common. Minerals with such interstratifications are

known as mixed-layer minerals. The intergrowth may be regular or irregular. Clay minerals with irregular interstratifications of this type are said to be among those most frequently found in sediments (WEAVER, 1956). Segregation of layers into zones also occurs and if the numbers of layers is sufficient diffraction effects similar to those from separate phases are recorded.

NON-CRYSTALLINE SOLIDS

Materials of this type lack long-range order on the atomic scale. The nearest neighbours of a particular atom may be essentially the same as in a crystal of the same chemical composition but there is no regularly repeated periodic pattern in the disposition of next nearest and more distant neighbours. Such solids are sometimes described as amorphous. This term does not have absolute meaning as there is no sharp dividing line between the crystalline and non-crystalline states. Ambiguity can be avoided by referring to the analytical method employed as in the phrase "amorphous to X-rays" though the term non-crystalline is considered preferable.

Glasses and gels are the commonest materials of this type encountered in nature. Such materials diffract X-rays as the atomic arrangement is not completely random. The diffraction maxima occur in more or less diffuse halos. There are gradations between the diffraction effects produced by crystalline and non-crystalline materials which are dependent on the orderliness of atomic arrangement. The structure of glasses based on silica was discussed by ZACHARIASEN (1932) who concluded that silicon-oxygen tetrahedra, similar to those in crystalline silicates, were present but that the network is not periodic and symmetrically repeated as in crystals (Fig. 4.11). Gel-like materials commonly have an internal network of very fine pores which result in a high specific surface area. They often have interesting surface chemical properties and frequently contain variable quantities of water and other substances. These may be incorporated in the structure or held by surface forces of various kinds.

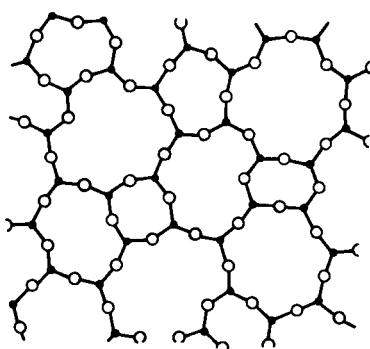


Fig. 4.11 Atomic configuration of silica glass. (After ZACHARIASEN, 1932, p. 3846; reprinted by permission of the American Chemical Society.)

Non-crystalline compounds which occur in clays may be classified as oxides, silicates and phosphates (BROWN, 1955). Included are such minerals as allophane, imogolite, kliachite, opal and other siliceous gels, limonite, hisingerite and wad. Allophane is a hydrous aluminosilicate of variable composition and imogolite has a chemical composition intermediate between that of allophane and kliachite (YOSHINAGA and AOMINE, 1962). Hisingerite is a comparable hydrous iron silicate. Kliachite is hydrous aluminium-oxide and limonite is a term employed for comparable iron compounds. Opal is an impure, microporous, disordered form of cristobalite containing non-essential water and probably also hydroxyl groups in the structure (FRONDEL, 1962, pp. 287-306). Wad is a non-crystalline hydrous manganese dioxide. Evansite is a hydrous aluminium phosphate and azovskite is a similar compound in which iron takes the place of the aluminium.

FABRIC OF CLAY SOILS

The engineering properties of clay soils are sometimes decisively influenced by the fabric. This term is defined as, "the physical nature of a soil according to the spatial arrangement of its particles and voids" (BATES and JACKSON, 1980, p.220). Primary fabric forms on deposition and secondary fabric develops later. When fabric elements display a mutual parallelism they are said to possess a preferred orientation. This may result from deposition, growth or deformation. The term "microstructure" is often used in soils engineering when the effects of interparticle forces as well as fabric are being considered. Fabric may be determined with the optical microscope, the scanning electron microscope or by x-ray diffraction though other physical methods have also been used.

Primary fabric develops in response to gravitational and magnetic forces, to flow in the depositional medium and to colloid chemical processes when particles are sufficiently fine. Sediments deposited by a flowing medium such as water are likely to show monoclinic symmetry of fabric; when deposition takes place from a static medium the fabric may be expected to display axial symmetry (PHILLIPS, 1960, p.661). Schematic representations of the appearance of these two sorts of fabric when plotted on a pole figure diagram are shown in Fig. 4.12. The composition of the fluid phase determines the flocculation state of clay minerals - whether the settling units are single crystals or aggregations. It is also thought that living organisms have an effect by digesting settling units and excreting them in the form of organic-rich agglomerations and pellets (Fig.4.13a).

Single crystal clay mineral platelets may associate in an edge-to-edge, edge-to-face, face-to-face or random type of arrangement depending on the interparticle balance between the forces of attraction and repulsion and the amount or absence of turbulence in the water. If a deflocculated system remains undisturbed the particles slowly settle out. As repulsive forces exist between the clay particles

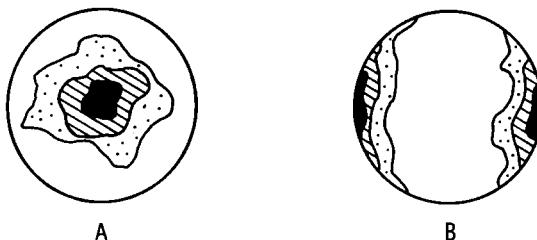
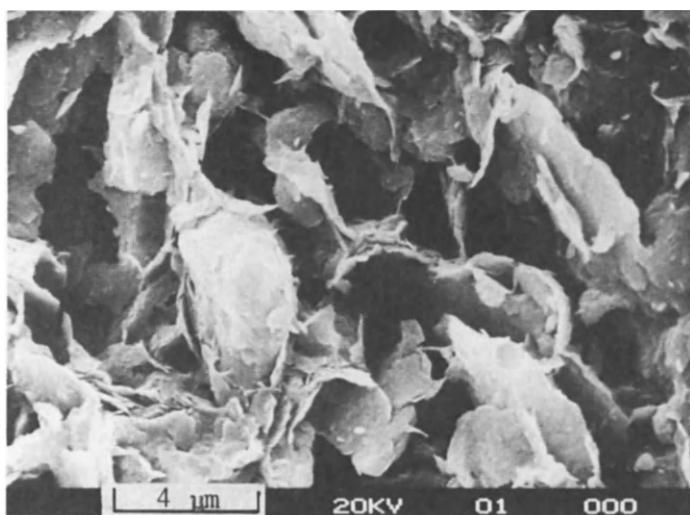


Fig. 4.12 Contoured equal area projections to illustrate symmetry. A. Axial symmetry. B. Monoclinic symmetry.

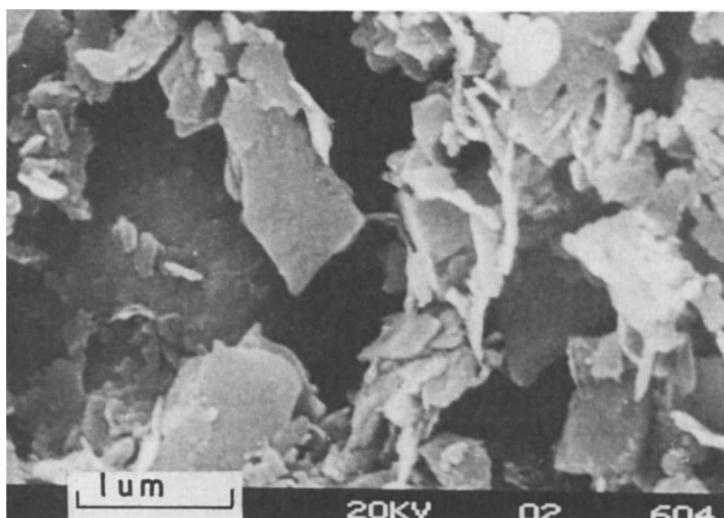
they should assume a more or less parallel close-packed type of orientation. This type of fabric would be expected in a clay deposited from the fresh quiet waters of an ice-covered lake in winter although interestingly the clay layer in varves has been variously reported to have an open flocculated structure (Fig. 4.14c); the silt layer also has an open fabric (Fig. 4.14d). Clay flocculates rapidly in water with a moderate electrolyte content as attractive forces become dominant between the particles, which should bond in both an edge-to-edge and edge-to-face type of association. The particles should assume a more or less open arrangement giving the deposit a loose texture. A secondary fabric develops in response to deformation - consolidation (compaction) and shear, crystal growth, moisture movements and the effects of living organisms including bacteria.

At an early date TERZAGHI (1925) suggested that some sediments or soils were composed of individual grains of silt and flocculated clay arranged in an arching skeleton enclosing large voids. This arrangement has been termed honeycomb structure, and it has been illustrated diagrammatically by CASAGRANDE (1940, p. 85) (Fig. 4.15). A structure described as "cardhouse" was postulated by GOLDSCHMIDT (1920) and these ideas were later developed by LAMBE (1953, 1958). He predicted a parallel type of arrangement of clay particles for fresh water deposits and a flocculated arrangement for marine deposits (Fig. 4.16). Arrangements of clay minerals which resemble some of the proposed fabrics do exist in soils (Fig. 4.13b) but in recent work it has been suggested that clay minerals are more often deposited as aggregations than as single crystals.

In early experimental work the optical microscope was used by MITCHELL (1956) to study the orientation of clay minerals in North American soils. ROSENQVIST (1962) studied Norwegian marine clays with the transmission electron microscope and RAITBURD (1960) used X-ray methods. Studies of swelling behaviour of various types of clays led AYLMORE and QUIRK (1960, pp. 1046-1048; 1962, p. 126) to sug-

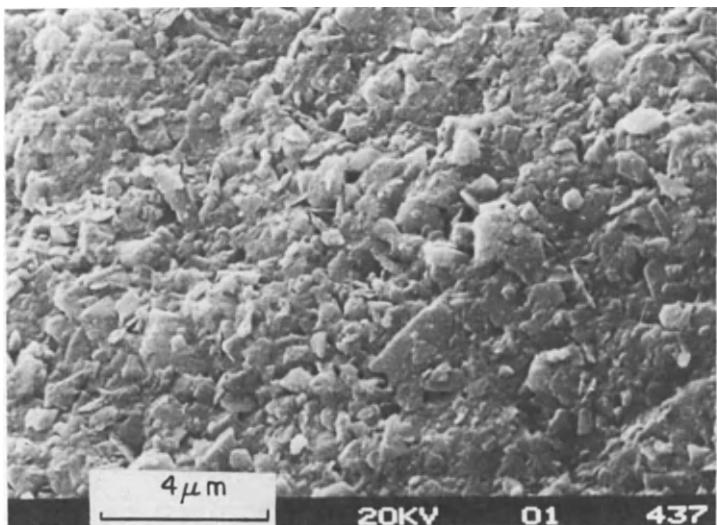


A. Open fabric with pellet or clay-coated silt
Grain - Trinidad.

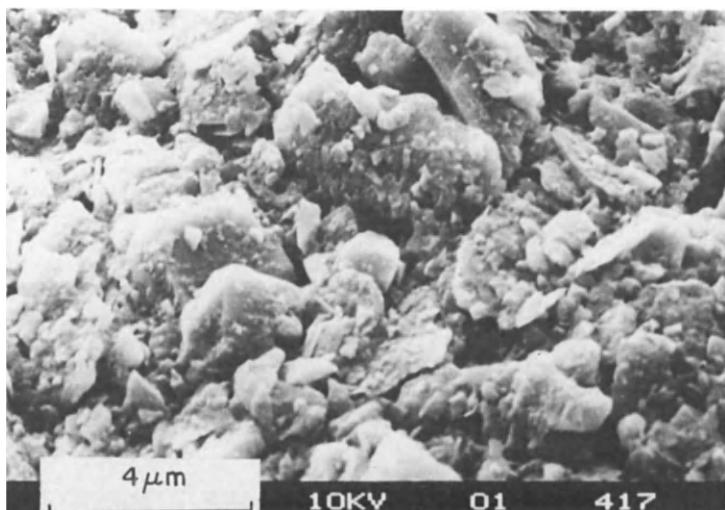


B. Open fabric in sensitive soil - Kars Bridge,
Ontario.

Fig. 4.13 Scanning electron micrographs of soil fabric.

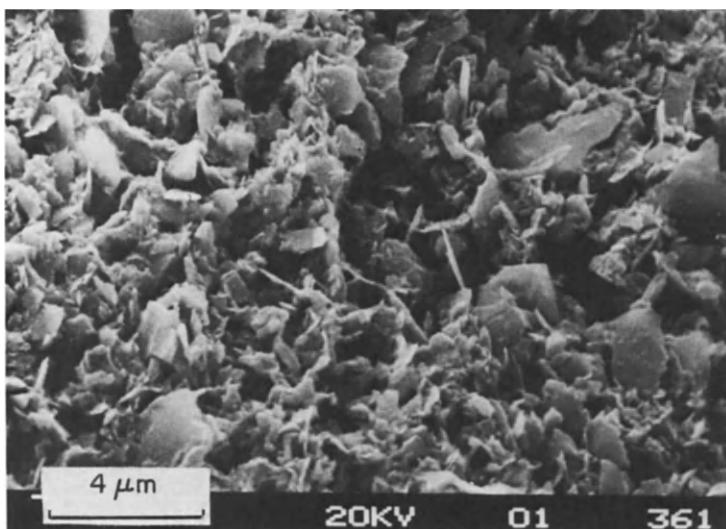


A. Fabric of clay layer in varve - Olga, N. Quebec.
(Air dried)

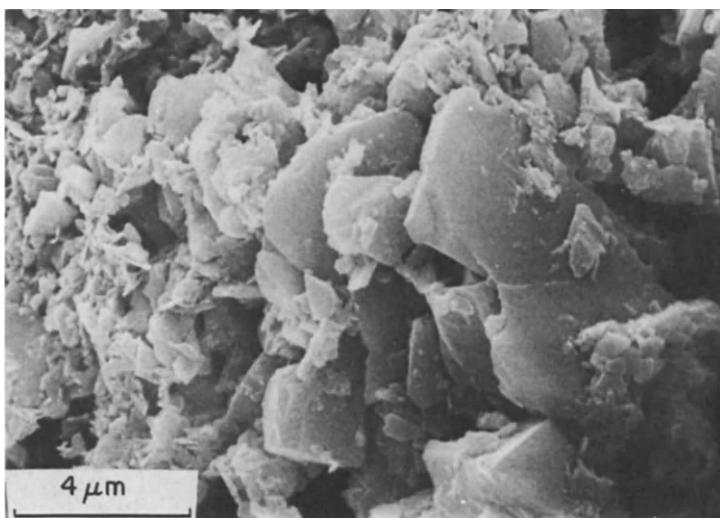


B. Fabric of silt layer in varve - Olga, N.Quebec.
(Air dried)

Fig. 4.14 Scanning electron micrographs of soil fabric.



C. Fabric of clay layer in varve - Olga, N. Quebec.
(Freeze dried)



D. Fabric of silt layer in varve - Olga, N.Quebec.
(Freeze dried)

Fig. 4.14 Scanning electron micrographs of soil fabric.

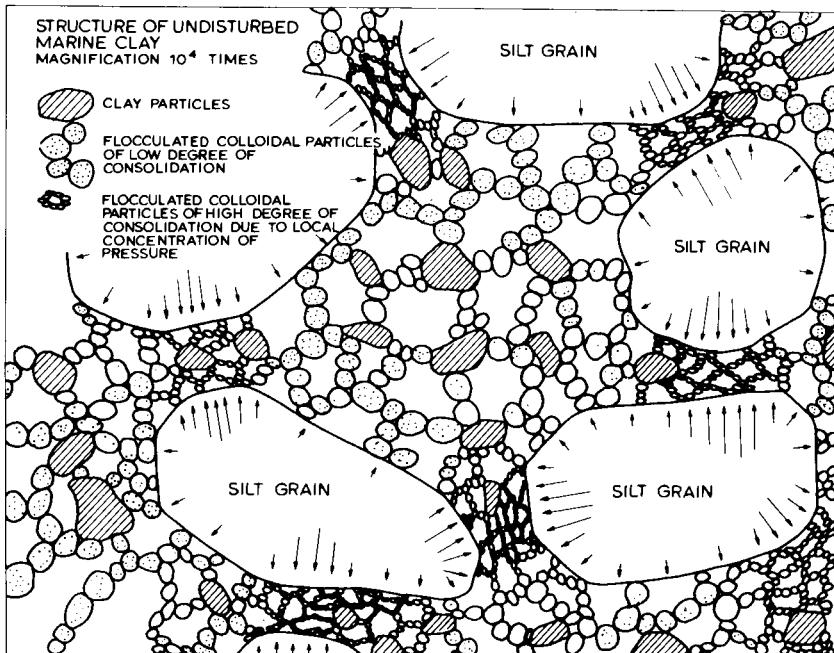


Fig. 4.15 Proposed fabric of clay soils. Honeycomb structure in flocculated soil. (After CASAGRANDE, 1940, p. 85).

gest that clays may develop a domain structure termed turbostratic. In this arrangement the clay mineral platelets have a preferred orientation within aggregates but between the aggregates themselves the orientation is random. Deposition of more or less well cemented particles composed of oriented aggregates of clay platelets could lead to this sort of fabric in a sediment. VAN OLPHEN (1977) suggested modes of particle association based on the proposal that clay minerals may acquire a reversible positive edge charge under certain conditions while faces retain a negative charge (Fig. 5.5). Most studies have been of a qualitative nature but quantitative methods have been developed not only for estimation of particle arrangement but also for analysis of shape and texture of particles (FOSTER and EVANS, 1971; TOVEY and WONG, 1974; BENNET et al., 1977; GILLOTT, 1980).

The scanning electron microscope has been used for more than a decade in the study of fabric (SMART, 1967; GILLOTT, 1969; TOVEY, 1970; GRABOWSKIEJ-OLSZEWSKIEJ, 1980). Partly because of the relative ease of sample preparation, the almost 3-dimensional quality of the image and the possibility of using auxiliary stages (SERGEYEV et al., 1980) and other analytical attachments fabric studies have become much more common.

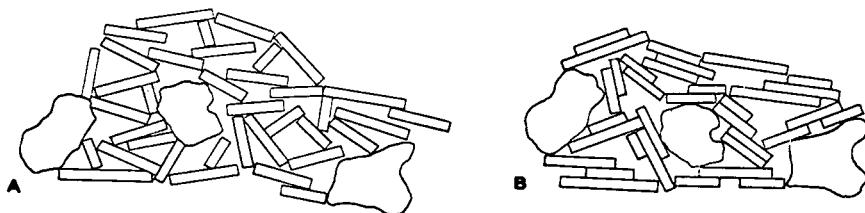


Fig. 4.16. Proposed fabric of clay soils. (After LAMBE, 1953, p.38.) A. Undisturbed salt water deposit. B. Undisturbed fresh water deposit.

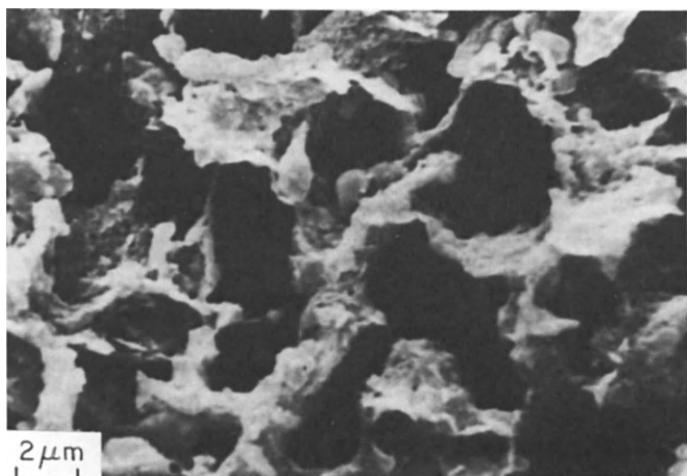
Workers in the Soviet Union and Poland suggest that types of contact between fabric elements may be linked with behaviour of soil in engineering tests. They propose that relatively weak bonds form when there is a film of water between particles which are not in physical contact; these bonds break and re-form readily when stressed. Contacts of this sort are termed "coagulation". Strong brittle bonds form when there is a significant contact area between particles. Such contacts are termed "phase". When the physical contact area is small and the bond is partly due to interpenetration of surface layers of adsorbed water the contacts are termed "transitional". Five principal types of microstructure are recognized in sedimentary clay soils termed honeycomb, skeletal, matrix, turbulent and laminar (Fig. 4.17); eluvial and hydrothermal deposits were found to have distinctively different microstructures (OSIPOV, 1975, 1978; OSIPOV and SOKOLOV, 1978; SERGEYEV et al., 1978, 1980).

Many new terms to describe microstructures have appeared such as packets or books (SLOANE and KELL, 1966), stepped face-to-face (SMALLEY and CABRERA, 1969), cornflake (O'BRIEN, 1970), microblocks (BOCHKO, 1973), connectors (COLLINS and McGOWN, 1974) and crumbs (YONG and WARKENTIN, 1975). This work has led to models of soil structure in which it is proposed that aggregations of clay minerals and silt- or sand-sized particles are linked together by short or long chains (Fig. 4.18). Minerals linking aggregations are said to be bonded in stepped face-to-face or edge-to-edge fashion. Within and between aggregations there are pores the shapes of which change with increase in overburden pressure (BENNETT et al., 1977). Pores have a great influence on flow so pore fabric has a marked effect on permeability (SMART, 1975). Better agreement was obtained between observed and calculated flow-rates when differences in pore structure between and within aggregations were considered (OLSEN, 1962).

Much of the clay in sediments is known to be detrital but diagenetic reactions have received increased attention from sedimentologists and others in recent years. Indirect evidence had long indicated that recrystallization, reconstitution and synthesis of new minerals took place in sediments and these ideas have

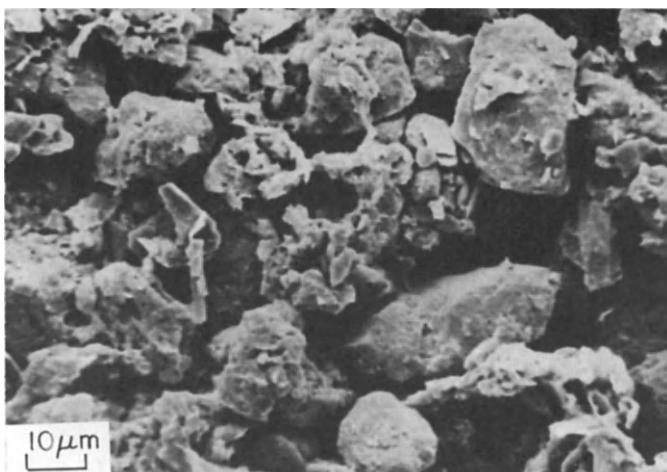


A. Honeycomb. Marine silt, Black Sea, U.S.S.R.



B. Honeycomb. Marine silt, Black Sea, U.S.S.R.

Fig. 4.17 Scanning electron micrographs of soils showing some types of microstructure recognized by Soviet scientists [Photographs supplied by courtesy of Professors V.N. Sokolov and V.I. Osipov, Moscow State University, U.S.S.R. Reproduced by permission of Journal of Microscopy, Vol.120, 3, pp. 237-260 (1980).]



C. Skeletal. Loess, Minusinsk, U.S.S.R.

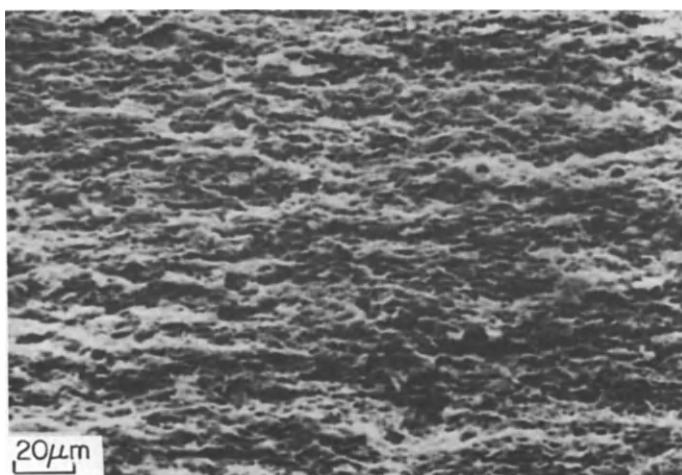


D. Matrix. Glacial loam, Moscow, U.S.S.R.

Fig. 4.17 Scanning electron micrographs of soils showing some types of microstructure recognized by Soviet scientists [Photographs supplied by courtesy of Professors V.N. Sokolov and V.I. Osipov, Moscow State University, U.S.S.R. Reproduced by permission of Journal of Microscopy, Vol.120, 3, pp. 237-260 (1980).]



E. Turbulent. Marine clay, Leningrad, U.S.S.R.



F. Laminar. Varved clay, Novgorod, U.S.S.R.

Fig. 4.17 Scanning electron micrographs of soils showing some types of microstructure recognized by Soviet scientists [Photographs supplied by courtesy of Professors V.N. Sokolov and V.I. Osipov, Moscow State University, U.S.S.R. Reproduced by permission of Journal of Microscopy, Vol.120, 3, pp. 237-260 (1980).]



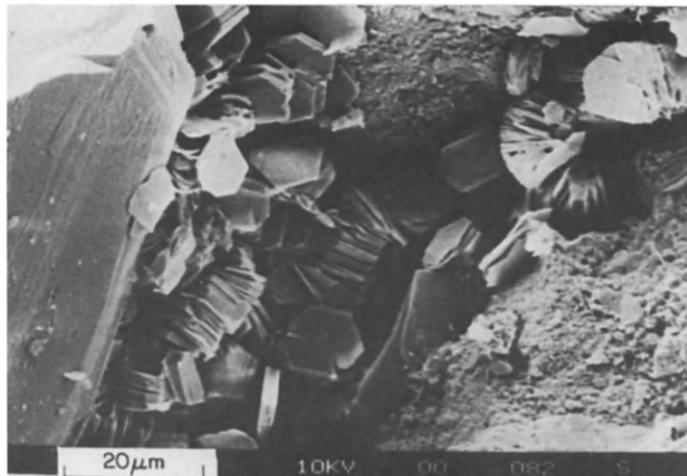
Fig. 4.18 Mosaic of scanning electron micrographs of soil from Oakville, Ontario showing aggregations, connectors and inter- and intra-agglomerate pores.

been convincingly demonstrated by the fragile appearance, position and almost perfect morphology of some clay minerals observed by scanning electron microscopy (Fig. 4.19). Fabric relations and the geochemical reactions implied are not only of theoretical interest but are of significance to the practicing engineer. Hydrocarbon formation and transportation, permeability of oil reservoirs and aquifers and reactions between clay minerals and connate waters or injected aqueous solutions, steam or other media are involved (WILSON and PITTMAN, 1977; PITTMAN and THOMAS, 1978; FAROUQ ALI and MELDAU, 1978; CZARNECKA and GILLOTT, 1979; PERRY and GILLOTT, 1979).

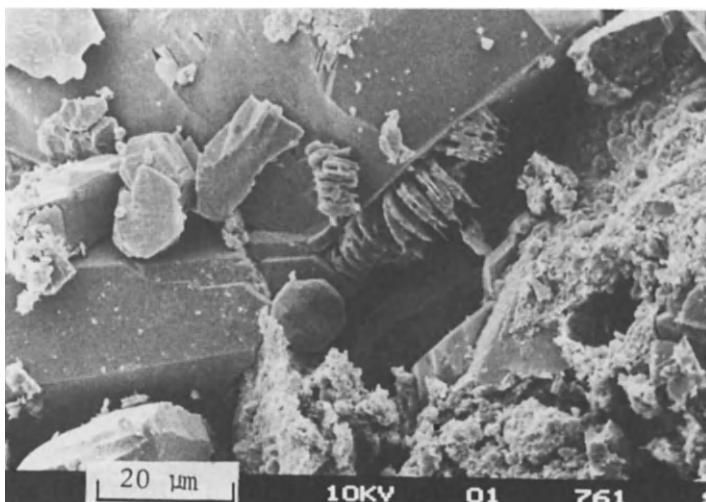
Sediments exposed to subaerial weathering show changes with depth of a morphological nature. Of these the most important is probably the division of the soil profile into horizons (Fig. 4.20) which reflect compositional and fabric differences. These are caused by changes in the chemical and physical environment and by the migration of soluble salts, fine-grained clay minerals and other colloids. The chief transporting agencies are percolating solutions and frost action, though living organisms also play a role in fabric evolution. Cracks, pore spaces, mineral grains and other fabric elements are often coated with clay which is sometimes oriented parallel to the surfaces of deposition; layering has been observed suggesting cyclical sedimentation.

Weathering frequently produces changes of importance to the engineer; in addition to chemical and physical processes biological agencies are sometimes involved. An interesting reaction of this sort, causing heave and also acid contamination of ground-water and streams by drainage from certain mine tips involves micro-organisms. Autotrophic bacteria play a part in the oxidation of pyrite which leads to production of sulphuric acid - one of the most important reactions in weathering (CURTIS, 1977). In black pyritic shales this reaction has been associated with heave of lightly loaded structures. Gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) and jarosite $[\text{KFe}_3(\text{SO}_4)_2(\text{OH})_6]$ are important products of the biogeochemical transformations (Fig. 4.21). The growth of such minerals, with unit cells larger than the reactants, has been held responsible for the heave pressures developed. The fabric relations between the new minerals and rock structure observed by scanning electron microscopy have been used as evidence in attempts to understand the heave mechanism (PENNER et al., 1970; QUIGLEY and VOGAN, 1970; GILLOTT et al., 1974; GRATTAN-BELLEW and EDEN, 1975; COVENEY and PARIZEK, 1977; GILLOTT, 1980).

Seasonal freezing and thawing of saturated soil has the effect of promoting sorting with the fines at the bottom and the coarse grains at the top. A secondary effect is that sorting promotes the tendency for a soil to form ice lenses by segregating the grains which are of an appropriate size range (CORTE, 1961, 1962). Sorting and segregation tend to produce striped or polygonal patterns in the soil (Fig. 4.22). These patterns have been reviewed and classified by WASHBURN (1956).

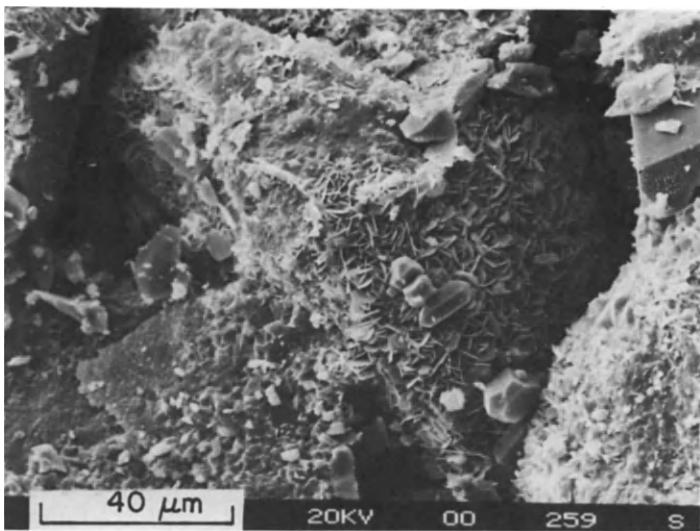


A. Kaolinite. Bluesky formation, Cretaceous.
N.W. Alberta, Canada.

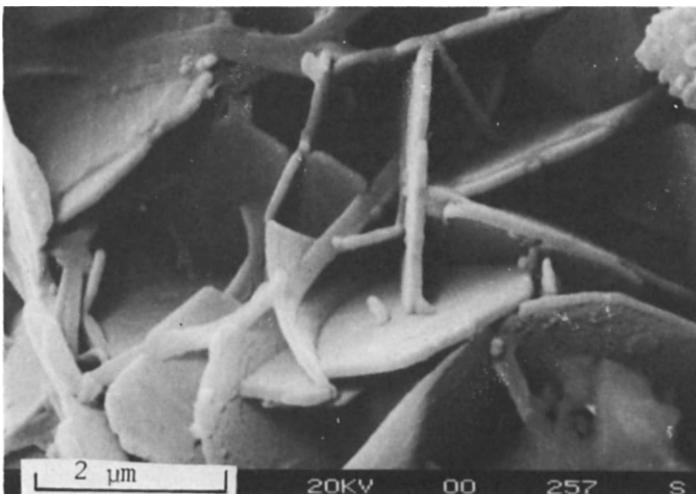


B. Kaolinite altering to illite. Gething
formation, Cretaceous.

Fig. 4.19 Scanning electron micrographs of
authigenic minerals.

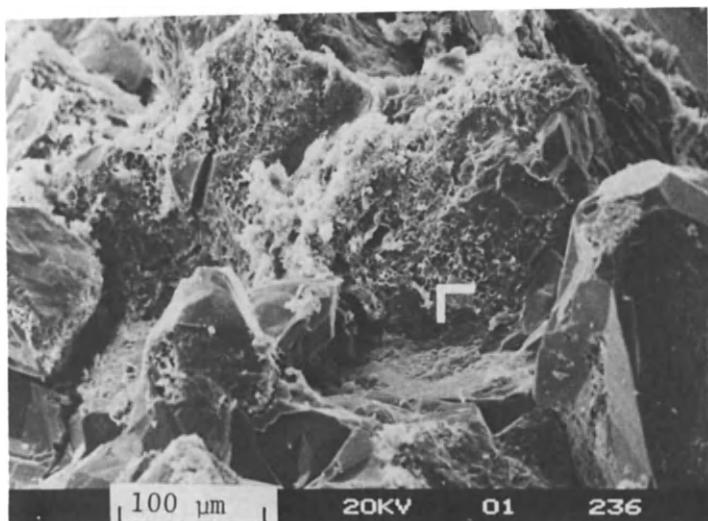


C. Chlorite and quartz in pores between sand grains. Falher formation, Cretaceous.
N.W. Alberta, Canada.

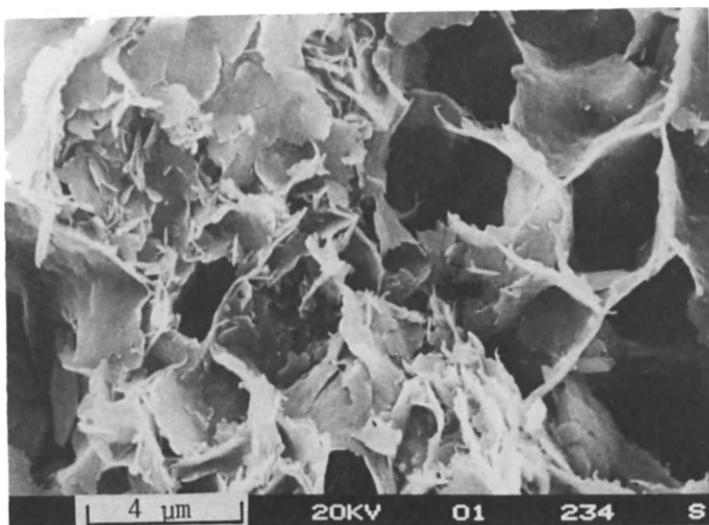


D. Chlorite. Falher formation, Cretaceous.
N.W. Alberta, Canada.

Fig. 4.19 Scanning electron micrographs of authigenic minerals.



E. Quartz overgrowths on sand grains and authigenic clay. Nikanassin formation, Cretaceous.



F. Authigenic illite. Nikanassin Formation, Cretaceous.

Fig. 4.19 Scanning electron micrographs of authigenic minerals.

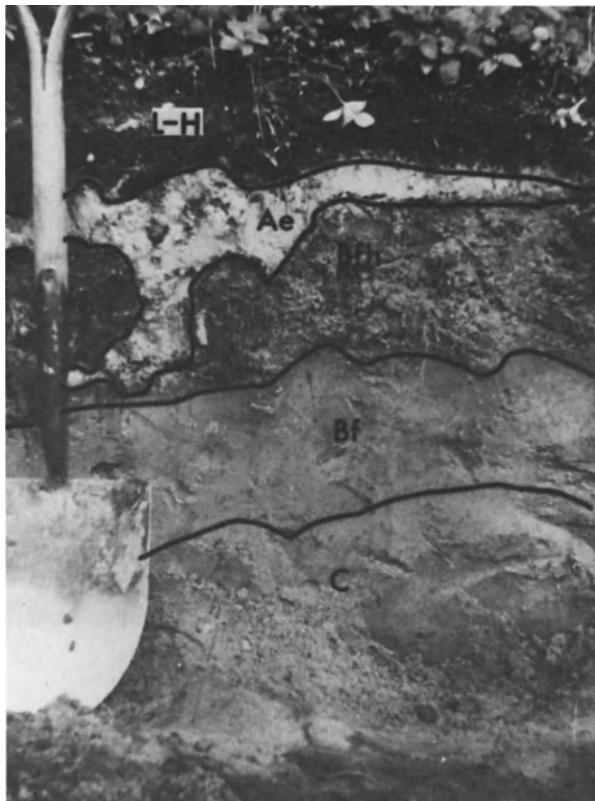
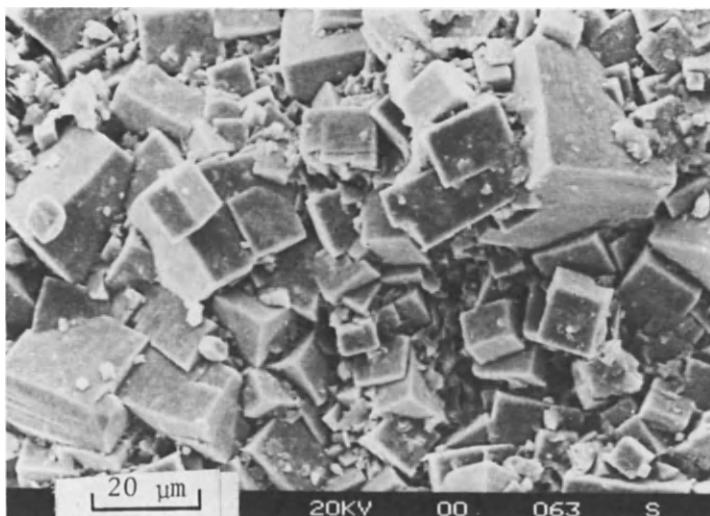


Fig. 4.20 A representative soil profile (podzol) showing the leaf-mat accumulation (LH-horizon), the horizon of eluviation (Ae), the horizons of accumulation (Bfh and Bf) and the parent material (c). (Photograph supplied by Research Branch, Canada, Agriculture).

Freezing and thawing, wetting and drying and pressure effects are thought responsible for development of cracks, cleavages and fissures. These agencies also promote formation of aggregations which are made more stable by the bonding action of compounds with cementitious properties such as sesquioxides and hydroxides, organic matter and clay minerals themselves. Experimental evidence has been obtained that an increase in clay content is accompanied by an increase in the stability of aggregations (KEMPER, 1966) and earlier work indicated a correlation with the surface area of the clay minerals present. The U.S. Soil Survey classifies such structural elements into four classes termed platelike, prismlike, blocklike, and spheroids (Fig. 4.23). The extent and direction of cleavage and state and stability of aggregations of primary particles have an important effect on the physical properties of a soil such as its porosity, aeration, permeability, water holding capacity, resistance to erosion and stability.



A. Pyrite.

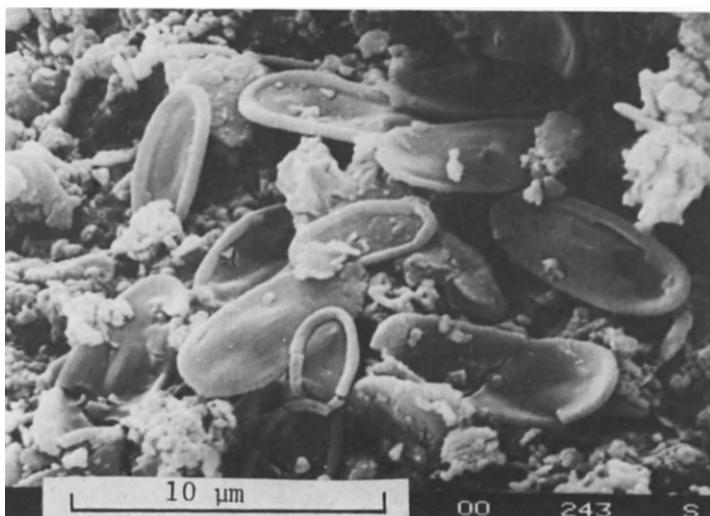
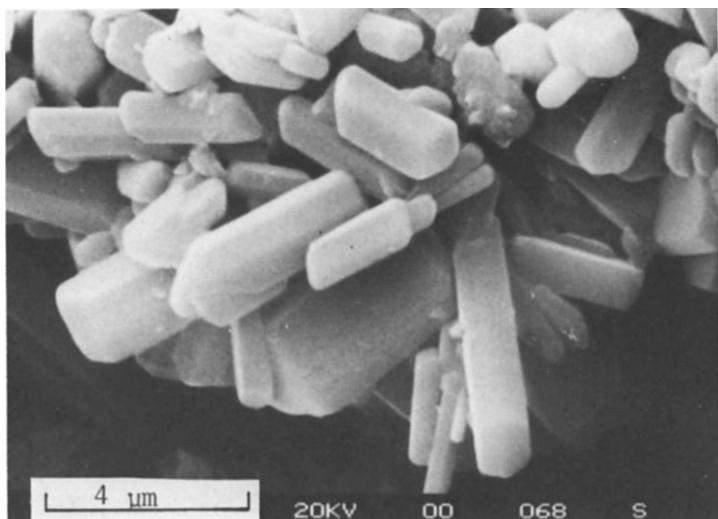
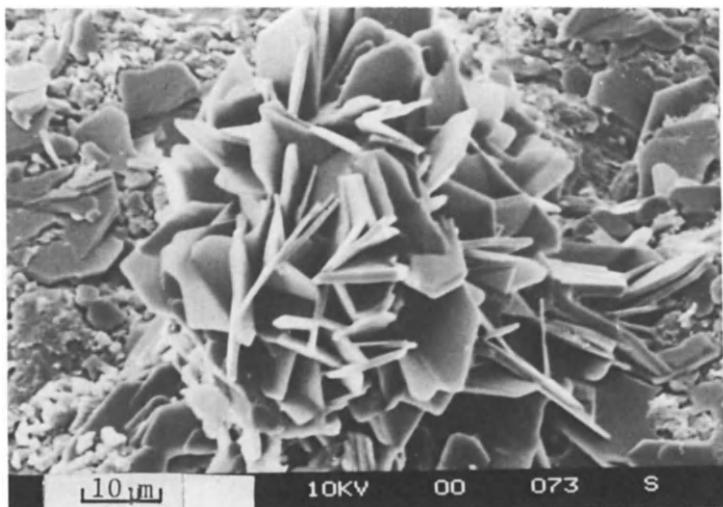


Fig. 4.21 Scanning electron micrographs of minerals in black shale subject to biogeochemical alteration.

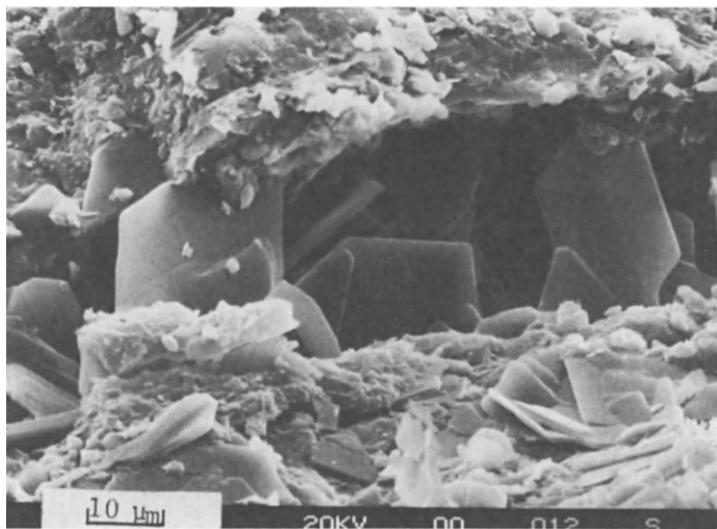


C. Lath-like gypsum.

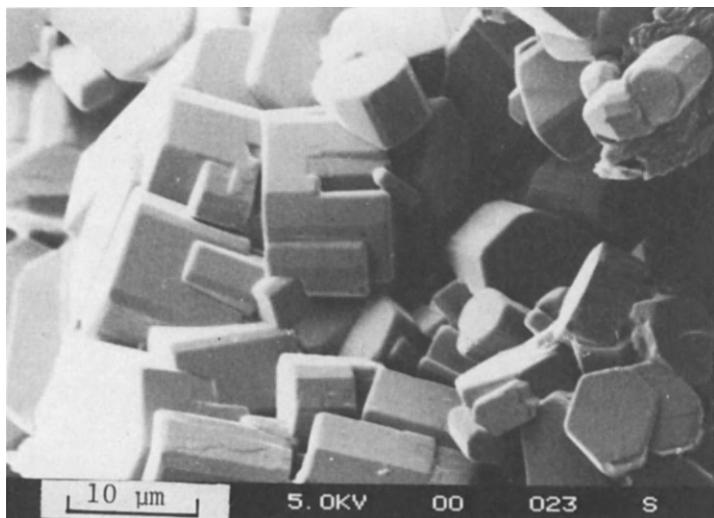


D. Radiating gypsum.

Fig. 21 Scanning electron micrographs of minerals in black shale subject to biogeochemical alteration.



E. Gypsum in shale parting.



F. Jarosite.

Fig. 4.21 Scanning electron micrographs of minerals in black shale subject to biogeochemical alteration.



Fig. 4.22 Sorting due to seasonal freezing and thawing. (Photographs supplied by A.L. Washburn, Yale University, New Haven, Connecticut).

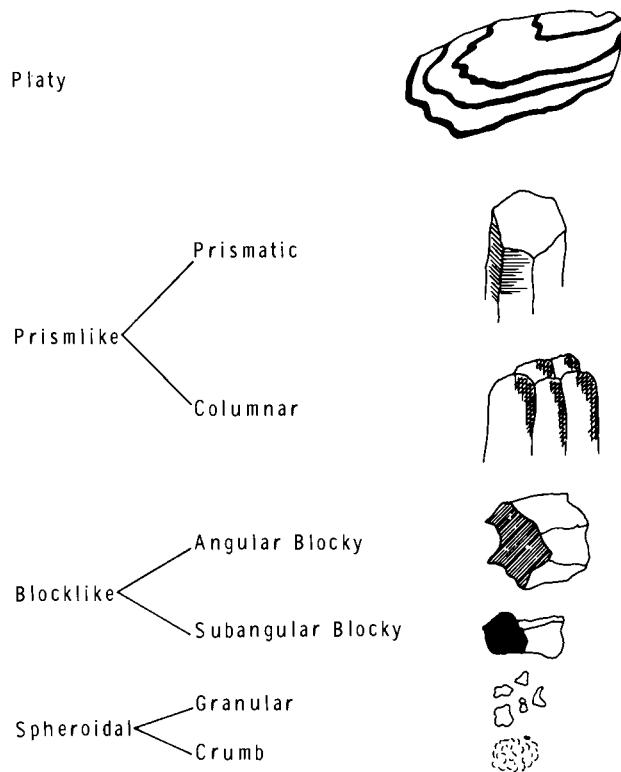


Fig. 4.23 Some of the types of soil structure. (After U.S. Dept. Agriculture, 1951, p.227).

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CHAPTER 5

PHYSICAL CHEMISTRY OF CLAYS

Clays have unusual physico-chemical properties chiefly because of the combined influence of two factors. These are the high specific surface⁺ and the electrical charge in the silicate structure of the clay minerals. The high specific surface results from the small particle size and platy or elongate morphology of the minerals and the negative charge from ionic substitutions in the crystal structure. The charge is now thought to occur as discrete charges rather than as a uniform distribution over the surface. By definition clays are composed of particles smaller than 2 micrometres (equivalent spherical diameter) which places them within the limits of the colloidal state.

PROPERTIES OF COLLOIDAL PARTICLES

Particles exhibit properties characteristic of the colloidal state when they have sizes within the range of about 50 to 2000 Å (GLASSTONE, 1948). Particle size is generally expressed in terms of equivalent spherical diameter and may be found by application of Stokes' Law to data obtained in sedimentation experiments. The size limits of the colloidal state are to some extent arbitrary but have a basis which has been discussed by KRUYT (1952, p.5). A colloidal silicate was defined by ILER (1955, p.181) "as any water-insoluble silicate, either amorphous or crystalline, having a specific surface area greater than about 25 square meters per gram" (25,000 m²/kg).

The surfaces of materials have distinctive physico-chemical properties. In the interior of a solid, liquid or gas there is no imbalance in the forces acting on the atoms which are surrounded on all sides by a similar configuration of other atoms. The surface atoms of a solid or liquid however are pulled by attractive forces most strongly on the side facing inwards. Hence the surface atoms are in a state of strain. It was postulated by HABER (1914, p.521) and LANGMUIR (1918, p. 1362) that surface atoms possess residual forces of the type involved in chemical bonding on their outer side which are responsible for adsorption. Langmuir proposed an equation for the equilibrium state based on the law of mass action. Surface tension phenomena in liquids and the high chemical reactivity often shown by surface atoms in solids result from the special nature of the surface environment.

WEYL (1953) has discussed the atomic structure of surfaces in terms of crystal chemical principles. He attributes considerable importance to the polarization of

⁺ Surface area per unit weight, commonly expressed in m²/kg.

ions. This is likely to have a maximum effect on ions exposed at surfaces (Fig. 5.1). In his view many surface phenomena to do with solid surface-liquid interaction can be accounted for in terms of screening of cations. Small highly charged cations are relatively insensitive to polarization whereas large anions are readily deformable. He postulates that in the surface atomic layers there is structural distortion the effects of which extend to considerable depths. There is little doubt that surface atoms differ energetically from those in interior locations. It is also fairly well established that in crystals there is distortion of the regularity of the atomic arrangement at a surface though the depth to which the effect extends is a subject for discussion.

Clay minerals have a small size and platy or fibrous morphology. Unit weight of any material when composed of small particles has a larger surface area than unit weight of the same material when composed of larger particles. The result of decreasing the size of spherical or cubic particles by 10 times is to increase the specific surface by the same factor. If plates and fibres which have a thickness to size ratio of say 1:10 are considered, the surface area per gm. of four shapes of comparable sizes is in the following ratio: sphere: cube: plate: fibre: 3: 3: 12: 21 (SEARLE and GRIMSHAW, 1959, p.472). Hence, clay minerals have a high specific surface area due to the additive effect of both size and shape (Fig. 5.2).

In the layer lattice silicates the area of the sheet surface (001 crystal faces) is much larger than that of the edge surface (crystal faces parallel to the Z-crystallographic axis). In kaolinite however the edges of the crystals make up about 10 to 20 per cent of the surface area, $(15-40) \cdot 10^3 \text{m}^2 \text{kg}^{-1}$, whereas in smectites edges commonly account for only 2 to 3 per cent of the total (internal and external) surface area, of about $760 \cdot 10^3 \text{m}^2 \text{kg}^{-1}$. In proportion to the surface available edge effects are therefore much more significant in kaolinites than in smectites. In the 1:1 layer structure minerals one sheet surface consists of a network of oxygen ions linked to tetrahedrally co-ordinated silicons (siloxane surface) whereas the opposite sheet surface consists of hydroxyl groups linked to octahedrally co-ordinated cations. In the 2:1 layer lattice minerals there is a siloxane surface on both outer faces of the sheet. The edges are composed of alternate rows of silicon and aluminium ions (in dioctahedral minerals) linked to oxygen or hydroxyl ions. Hence the sheet surfaces differ from the edge surfaces and have distinctive properties.

Quartz is common in the clay size grade and is sometimes fine enough to have colloidal properties. It is believed that the surface of quartz crystals is covered by a hydrated monolayer (RUFF and HIRSCH, 1928). It is now also fairly certain that colloidal quartz crystals are surrounded by an amorphous or crystallographically disturbed layer of the order of 0.5 microns thick (DEMPSTER and RITCHIE, 1953; GIBB, 1953).

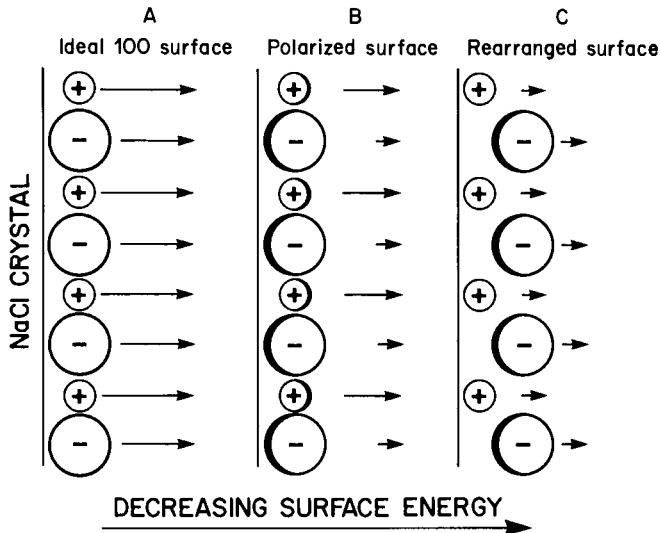


Fig. 5.1. Deformation of surface ions due to assymetrical force field.
(After Weyl, 1953, p.153.)

Amorphous compounds are also sometimes present in clays. According to ILER (1955, p.234) the surface of amorphous silica is normally covered by a monolayer of hydroxyl groups termed a "silanol" surface. These hydroxyl groups are believed to be the sites of adsorption for water, other polar compounds, and cations. In alkaline suspension silica particles acquire a negative surface charge which increases with rise of pH due to adsorption of hydroxyl ions or dissociation of surface hydroxyl groups.

COLLOIDAL SOLUTIONS

Two-phase systems may be obtained in which colloidal sized particles (known as the disperse phase) remain stabley suspended in the dispersion medium. The phases may be either liquid, gaseous or solid. It is possible to form colloidal suspensions in which the clay minerals themselves and other colloid sized mineral particles form the disperse phase in very dilute aqueous solutions of a concentration of a few milliequivalents of electrolyte per litre.

A colloidal suspension has properties which are different from those of either a true solution or a suspension of coarser particles. A colloidal suspension will pass through filter paper; it shows interesting electrical effects (MARSHALL, 1964) such as electrophoresis and electro-osmosis; the particles are observable in the ultra-microscope as they scatter light producing the Tyndall effect; the particles may often be caused to precipitate or "flocculate" by the addition of small amounts of electrolytes; the whole system may set forming a gel, the process being known as gelation. When first formed all the water present may be incorporated in

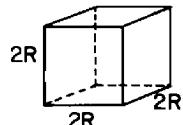
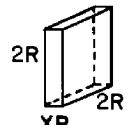
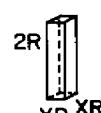
| | SPHERE | CUBE | PLATE | FIBRE |
|------------------------------|---|---|---|---|
| |  |  |  |  |
| VOLUME OF ONE PARTICLE | $\frac{4}{3}\pi R^3$ | $8R^3$ | $2R \times 2R \times XR = 4XR^3$ | $2R \times XR \times XR = 2X^2R^3$ |
| NUMBER OF PARTICLES PER GM. | $\frac{1}{\frac{4}{3}\pi R^3 p}$ | $\frac{1}{8R^3 p}$ | $\frac{1}{4XR^3 p}$ | $\frac{1}{2X^2R^3 p}$ |
| SURFACE AREA OF ONE PARTICLE | $4\pi R^2$ | $6 \times (2R \times 2R) = 24R^2$ | $2(2R)^2 + 4(2R \times XR) = 8R^2 + 8XR^2$ | $4(2R \times XR) + 2(XR)^2 = 8XR^2 + 2X^2R^2$ |
| SURFACE AREA PER GM. | $\frac{4\pi R^2}{\frac{4}{3}\pi R^3 p} = \frac{3}{Rp}$ | $\frac{24R^2}{8R^3 p} = \frac{3}{Rp}$ | $\frac{8R^2(1+X)}{4XR^3 p} = \frac{2(1+X)}{Rp}$ | $\frac{2XR^2(4+X)}{2X^2R^3 p} = \frac{4+X}{Rp}$ |
| p = Density | | | | |

Fig. 5.2. Variation of surface area with different particle shapes. (After Searle and Grimshaw, 1959, p.473.)

a gel but on standing water may be expelled and the process is referred to as syneresis. In an aqueous environment of appropriate composition certain gels show a capacity for taking up or imbibing large volumes of water. A considerable expansive force can be exerted and it has been suggested that a similar mechanism of expansion is involved in such diverse phenomena as heave in certain types of soils and disruption of concrete due to the alkali-silica variety of alkali-aggregate reaction.

Aqueous colloidal systems have been classified as hydrophobic and hydrophilic. Materials which form stable dispersions in water only with difficulty belong to the hydrophobic class and those which disperse readily in water are classed as hydrophilic. The use of these terms has been criticized and hydrophilic systems are now often termed macromolecular colloids. In most respects clays behave like hydrophobic colloids but are not typical due mainly to the permanent negative charge which results from ionic substitutions in the crystal structure.

The stability of colloidal suspensions results from the electric charge associated with the particles. This charge is believed to originate by three principal mechanisms. The charge may result from imperfections such as vacancies or unbalanced ionic substitutions in the crystal structure; from the physical or chemical adsorption of ions at active sites believed often associated with broken bonds; and by the adsorption of ions of the same type as those in the structure of the particle.

When the charge on the colloidal particle results from adsorption the type of ion adsorbed is dependent on the relative ionic concentrations and the pH of the solution. The charge on the particle is sometimes reversible as in the case of aluminium hydroxide which acquires a positive charge due to adsorption of aluminium ions in acid solution and a negative charge due to adsorption of hydroxyl or aluminate ions in alkaline solution. The negative charge carried by colloidal silica particles may also be reversed to positive at low pH by adsorption of very low concentrations of aluminium (BUNGENBERG DE JONG, 1949, p.296).

Clay minerals have a net negative charge associated with ionic substitutions in the structure. It is now generally believed that charge occurs at discrete points rather than as a uniform distribution over the surface. Behavioural differences, such as amount of expansion on interlayer penetration of water and other liquids, result in large measure from differences in charge density. From knowledge of the chemical composition and crystal structure it is possible to calculate the deficiency of charge on the unit cell of a homogeneous clay mineral. Most soils however are heterogeneous and in practice experimental methods are used to obtain the cation exchange capacity which gives a measure of the negative charge. A method using alkylammonium which gives information concerning variations in charge density has been described (LAGALY and WEISS, 1976; LAGALY, 1979.)

VAN OLPHEN (1951, p. 83) has proposed that the negative charge is associated with the flat (001) surfaces whereas the edge surfaces may acquire a positive charge. He points out that where aluminium is the dominant octahedral cation the broken edge of the octahedral sheet is comparable to the surface of a particle of alumina. As mentioned, alumina acquires a positive charge in an acid environment. Van Olphen further suggests that clay crystals may be preferentially fractured where aluminium ions are substituted for silicon in the tetrahedral layer. Hence the exposed edges of the tetrahedral layer may resemble the octahedral layer and may also develop a positive charge (VAN OLPHEN, 1977, p. 94). Experimental evidence cited in support of this view is the anion adsorption capacity shown by kaolinite in acid but not alkaline solution and the edge adsorption of negatively charged colloidal gold observed on kaolinite under the electron microscope (Fig. 5.3)(THIESSEN, 1942). SCHOFIELD and SAMSON, (1954, p. 141) concluded that negatively charged montmorillonite was adsorbed on the positively charged edges of kaolinite crystals. Negatively charged silica particles have been reported to show similar preferential adsorption on the edges of both hectorite (ILLER, 1955, p. 197) and illite but not attapulgite (SIDDIQUI, 1976).

There is thus good evidence that pH-dependent charges are associated with the edges of clay minerals. It is to be expected however that the behaviour of kaolinites will be affected more than that of minerals with 2:1 type structures. This would seem to be implied by the previously mentioned large difference in proportion of total area which the edge surface represents in the two sorts of minerals. The charge on the particles is balanced by ions of opposite charge, known as counter ions, which are situated in the solution surrounding the particle. The concentration of the counter ions falls off with increasing distance from the surface of the colloidal particle. The charge on the surface of the particle together with the charge due to the balancing counter ions is referred to as the electrical double layer or the diffuse double layer. The solution in the double layer is commonly termed the micellar solution. The particle plus double layer solution is sometimes referred to as the colloidal micelle. The solution outside the double layer between colloidal particles is often called the intermicellar solution. The ionic concentration within the double layer is higher than in the intermicellar solution and a gradient develops which is proportional to the difference in concentration.

The nature and extent of the double layer is affected by the concentration and composition of the electrolytic solution, the density of charge on the surface of the colloidal particle and the temperature. The attributes of the double layer have been treated mathematically on the basis of theories proposed by HELMHOLTZ, GOUY-CHAPMAN, STERN, AND DONNAN. Classical colloid chemical treatments, often based on assumed constant surface potential, may apply to edges but platy surfaces are probably better analyzed in terms of a constant surface charge.

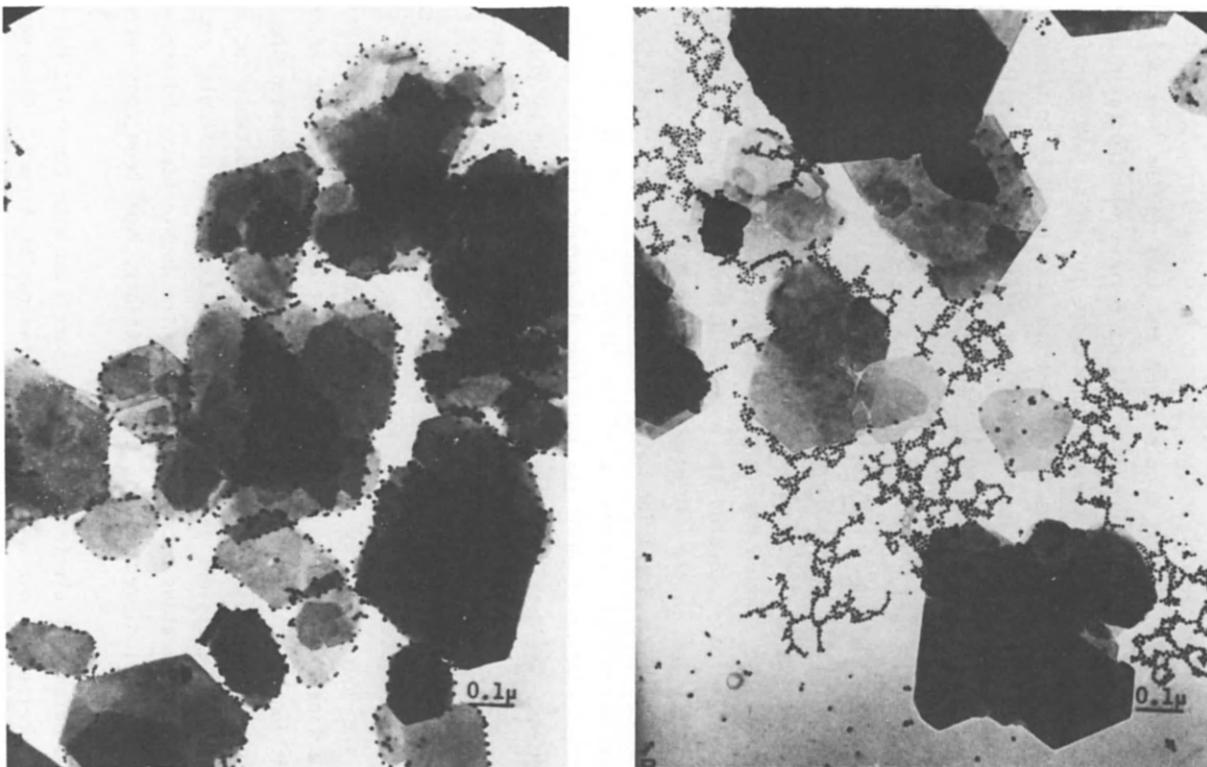


Fig. 5.3. Electron micrographs to show reversal of edge charge on kaolinite. In A the edge charge is positive so negatively charged colloidal Au is strongly attracted and adsorbed; in B the kaolinite is pre-treated with a small amount of sodium pyrophosphate and the edge charge is negative so colloidal Au is not attracted. (Electron micrographs by H.P. Studer, Shell Development Company, Houston, Texas.)

Close to the charged surface there is a high concentration of oppositely charged ions the distribution of which falls off exponentially with increasing distance from the surface. These ions are not rigidly held and there is a continuous interchange between ions within the double layer and ions in the bulk solution. An equilibrium is set up in which there is a balance between electrostatic attraction which tends to hold oppositely charged ions close to the surface of the particle and diffusion by which the ions tend to escape into the bulk solution where the concentration is lower. This cloud of ions with diffuse boundaries is described as forming an atmosphere about the colloidal particle (GOUY, 1917, 1910; CHAPMAN, 1913). Application of the Boltzmann distribution law together with electrostatic theory allows calculations to be made of the change in ionic concentration with distance from the surface of the colloidal particle. Since there is a statistical distribution within the double layer there are ions present with the same polarity as is possessed by the colloid. These ions are sometimes termed coions. Near the particle surface the concentration of similarly charged ions is very small but this increases towards the bulk solution. The general appearance of the ionic distribution in the vicinity of a colloidal particle according to this theory is shown in Fig. 5.4. The mathematical development of this viewpoint leads to the conclusion that the extent of the double layer is affected by the valency of the ions, concentration of the solution, dielectric constant of the medium and temperature. The details of the theory have been presented by VERWEY and OVERBEEK, (1948), WRIGHT and HUNTER (1973 a, b) and VAN OLPHEN (1977). Exceptions to the general conclusions of the theory are known and modifications and refinements have been proposed. In the Gouy theory the size of the ions is not taken into account nor are possible interactions with the solvent molecules. STERN (1924) modified the Gouy theory by introducing the concept of an inner layer in which there is a linear drop in potential. The position of this inner layer is located as a function of ionic size. In addition to interaction between the particle and ions in the solution there are also electrical effects between the polar water molecules and the colloidal particle and between the water molecules and the ions in solution. Interactions between the ions in the double layer and the water molecules of the solvent, disregarded in the Gouy theory, have been considered by BOLT (1955).

Changes in the balance of electrical charges associated with the colloidal particles determine whether or not a stable suspension can be formed. Observations in the ultra-microscope show that colloidal particles are in a state of continuous erratic motion in solution. This is known as Brownian movement and results from bombardment of the particles by ions or molecules in the solution. The continuous fluctuations cause periodic collisions between the particles. These adhere if attractive forces are greater than repulsive forces and the size of the kinetic un-

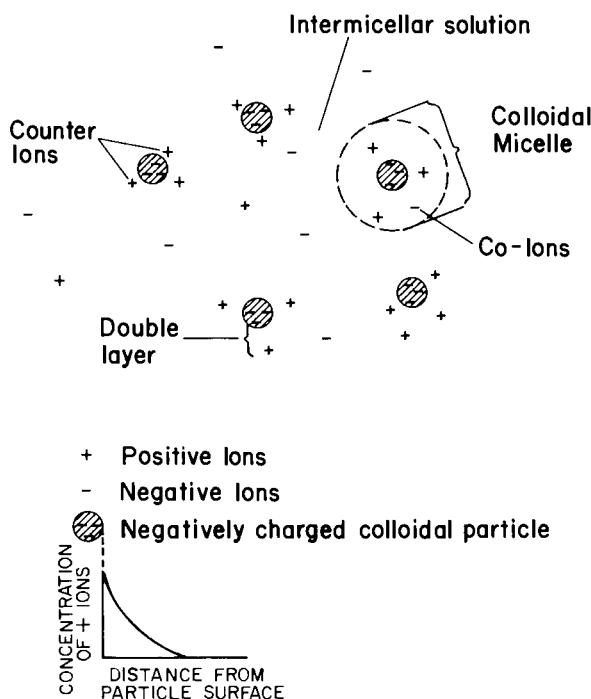


Fig. 5.4. Schematic of colloidal solution.

its rapidly increases. Gravitational forces exert a dominant influence on large particles which soon sediment and the dispersion flocculates. When electrical repulsion exceeds attraction between the particles the dispersion remains stable as particles which come together by chance collisions soon separate and remain in suspension.

Colloidal suspensions which will remain stable for very long periods if the concentration is not changed flocculate readily on addition of a very small quantity of electrolyte. It was found by SCHULZE (1882, 1883) and HARDY (1900, p.115) that the ion which is effective in causing flocculation is the one of opposite charge to that on the colloidal particle. It was also observed that the flocculating power increases rapidly with increasing valence of the ion. These conclusions, known as the Schulze-Hardy rule, serve as a general guide to flocculation phenomena in a variety of colloidal systems.

The susceptibility of hydrophobic colloidal suspensions to flocculation by ions of high valency and opposite sign is accounted for in terms of a balance between attractive and repulsive forces. When the double layers of two particles with the same polarity come in contact repulsion occurs between the like-charges of the

counter ions and perhaps too between oriented water molecules. It is evident that if the particles adhere there must also be attractive forces present which exceed the repulsion of the overlapping double layers. It is believed that van der Waals forces provide the general long-range attraction required to account for particle adhesion when flocculation occurs.

The thickness of the double layer is affected by the nature and concentration of electrolytes in the system. At high electrolyte concentration the extent of the double layer is reduced. Those electrolytes which contain ions of high charge and opposite sign to that on the colloidal particle produce the greatest compression of the double layer. This has the effect of reducing the distance of separation between particles at which repulsive forces begin to operate. The range and extent of van der Waals attraction between particles is however not much affected by changes in the electrolyte concentration. It is believed that in a dilute solution, the double layer extends to a greater distance from the particle surface than the van der Waals attractive forces. Therefore when two particles approach one another by chance diffusion they encounter a net repulsive force which tends to keep them apart due to the interaction of similarly charged ions. This is the condition in a stable hydrophobic sol. In a more concentrated solution however the compression of the double layer limits the extent of the repulsive force and approaching particles first come within the range of van der Waals attraction so that agglomeration ensues.

Colloidal suspensions can also be flocculated by addition of various water soluble organic compounds such as alcohol. It is believed that coagulation results from a lowering of the dielectric constant of the medium. This once more has the effect of compressing the double layers and the sol flocculates by a similar mechanism to that previously described.

The behaviour of colloidal suspensions of clay minerals and the properties of clays in general are affected by the strong likelihood that the edge surfaces may acquire a positive charge while the permanent negative charge is associated with the flat surfaces. Hence in solution a platy clay mineral may have a positive double layer on the edge surfaces while at the same time it has a negative double layer on the flat surfaces (VAN OLPHEN, 1977, p. 93). Thus while the general principles governing the behaviour of colloidal suspensions apply to clay minerals in solution the possible modes of interaction are more than usually complex. Attraction between oppositely charged double layers as well as attraction due to van der Waals forces has to be considered in evaluating the electrical balance of positive and negative charges resulting from changes in the extent of double layers. On flocculation clay platelets may associate in an edge-to-face, face-to-face, or edge-to-edge manner depending on the complex balance between the attractive and repulsive forces involved. Modes of particle association (Fig. 5.5) have been suggested by VAN OLPHEN (1977, p. 97).

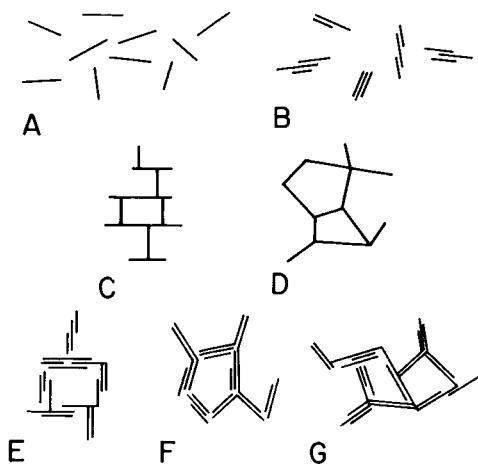


Fig. 5.5. Modes of particle association in clay suspensions, and terminology. (After Van Olphen, 1977, p. 97).

- (A) "Dispersed" and "deflocculated."
- (B) "Aggregated" but "deflocculated" (face-to-face association, or parallel or oriented aggregation).
- (C) Edge-to-face flocculated but "dispersed."
- (D) Edge-to-edge flocculated but "dispersed."
- (E) Edge-to-face flocculated and "aggregated."
- (F) Edge-to-edge flocculated and "aggregated."
- (G) Edge-to-face and edge-to-edge flocculated and "aggregated."

Many seeming anomalies of clay behaviour such as certain of the flowage properties of clay suspensions and properties dependent upon the fabric of sedimentary clay deposits have been accounted for on the basis of the concept of a positive edge negative face charge distribution.

EXCHANGE REACTIONS

The counter ions associated with colloidal particles such as clay minerals are in a state of dynamic equilibrium with the ions in the surrounding solutions. If the composition of the bulk solution changes the ionic content of the diffuse double layers also changes in accordance with the law of mass action.

Exchange reactions are reversible, are stoichiometric and diffusion controlled since the kinetics depend on the rate of diffusion of one ion against another. The diffusion model assumes idealized conditions however which may not be common in nature. Morphology and nature of crystal edges and presence of precipitated coatings may affect reaction rates (TARZI and PROTZ, 1978). Ion selectivity is often shown in exchange reactions the preference being for cations of smaller hydrated radius other things such as ionic charge being equal (HELFFERICH, 1962; CLOOS et al., 1965; GAST, 1969; SAWHNEY, 1972). If an insoluble product forms as

the result of exchange the reaction proceeds to completion. For example, calcium ions may be replaced by sodium ions by use of sodium oxalate as calcium oxalate is insoluble. The back reaction is prevented and calcium originally on the clay is almost completely replaced by sodium.

The extent of ionic replaceability can be determined quantitatively. Comparisons between colloids are normally reported as of pH7 in terms of the cation- or anion- exchange capacity which is generally expressed in milliequivalents (meq) per 100 g of the dry solid. The cation exchange capacity and nature and amount of exchangeable ions have been determined by many methods (BLACK, 1965). The clay may be washed with a salt solution to saturate the exchange sites with an index cation and the exchange ions determined in the leached extract. The index cation may then be displaced by another ion and the amount displaced determined as the cation exchange capacity (JACKSON, 1969). Suitable displacing ions are ones which are strongly held such as Cs^+ , Mg^{2+} , Ca^{2+} or Sr^{2+} (SAWHNEY et al, 1959). Ammonium acetate has also commonly been used. The decrease in ammonium ion concentration at equilibrium or the nitrogen content of the washed clay is determined. Care is required in the use of ions such as NH_4^+ , K^+ , or Cs^+ however since they become fixed by certain minerals such as vermiculite or degraded illites. Radioactive isotopes have also been used as the exchange ions (BEETEM et al, 1962; FRANCIS and GRIGAL, 1971). Attempts have been made to estimate mineral composition from cation exchange capacity (ALEXIADES and JACKSON, 1965; COFFMAN and FANNING, 1974).

Many clay minerals also show an exchange capacity for polar organic compounds and sometimes show specific adsorption phenomena. Ions which are normally exchangeable can become fixed or non-replaceable under certain conditions. The clay minerals themselves are often responsible for the exchange capacity of argillaceous deposits but important contributions to exchange capacity may also be made by colloidal sized particles of other minerals, amorphous constituents like silica gel and by organic matter.

Cation Exchange

Different samples of the same clay mineral give different values for the cation exchange capacity so a range of values exists for the same mineral due to differences in structure and composition between samples. Particle size also has an important effect (JONAS, 1961). Sample pre-treatment requires consideration - for example clays show decreases in cation exchange capacity when heated to temperatures above 100°C (NISHITA and HAUG, 1972). The exchange capacities of the different clay minerals also cover a considerable range of values. There are thought to be four principal mechanisms responsible for cation exchange (BRINDLEY and MAC-EWAN, 1953). Cations are held in exchangeable form on or near the surface of clay minerals by electrostatic forces which result from the net negative charge in the

structure arising from ionic substitutions. This is the chief cause of the cation exchange capacity of the 2:1 layer structure silicates. At edges and corners there are "broken bonds" or unsatisfied valencies to which exchange ions become attached. The number of such sites increases as particle size decreases and fine fractions of many minerals show an increase in exchange capacity. This effect is shown by kaolinite. Edges are believed to play an active role in the exchange phenomena shown by this material (BUTTON and LAWRENCE, 1964). Data from electron spin resonance however do not agree with this suggestion (MCBRIDE, 1976). Small mineral particles and amorphous materials are also thought to derive much of their exchange capacity from broken bonds. Exposed hydroxyl groups may dissociate with the hydrogen ion being replaced by cations. Under certain conditions cations from within the structure may become exchangeable. For example, in an acid environment the aluminium ions move from within the silicate structure of clay minerals into exchange positions.

The exchange sites on kaolinite are believed to have equal value (CARROLL, 1959, p. 760) but it has been shown that for many of the clay minerals there is a wide range in the energy by which single cations are held in exchange reactions (MARSHALL, 1949, p. 118). This arises because in many clay minerals the surface charge density varies with location on the surface. For example the bonding energy in interlayer positions is probably different from that on exposed surfaces or edges. Minerals sometimes show differences in exchange capacity even though the layer charge is the same. In the micas this has been explained in terms of the hydroxyl orientation. In phlogopite, a trioctahedral mica, there is a much shorter hydrogen - interlayer cation distance than in dioctahedral muscovite. This causes a greater repulsion between the silicate layer and the potassium and a weaker interlayer bond (GIESE, 1975). The problem has been investigated experimentally by various techniques such as the clay membrane electrode method developed by MARSHALL (1950). The activity of the ions was determined as a function of other parameters such as concentration and degree of ionisation and saturation. The nature of the surface, the valency of the cations and the nature of other ions present in solution and already present in the exchange position affect the electrochemical properties of clays (MARSHALL, 1954).

It has been established that there is no universally applicable order of replaceability among cations. It appears however that a useful general guide is provided by Wiegner's conclusions. He showed that when ions of the same valency are considered those which are least hydrated (generally those of largest radius in the solid state (Fig. 5.6)) have the greatest power of replacement and once present on clays such weakly hydrated ions are replaced with greatest difficulty (WIEGNER, 1935). Presumably ions of this sort can come closer to the surface from which the negative charge is originating and so the strength of binding is greater.

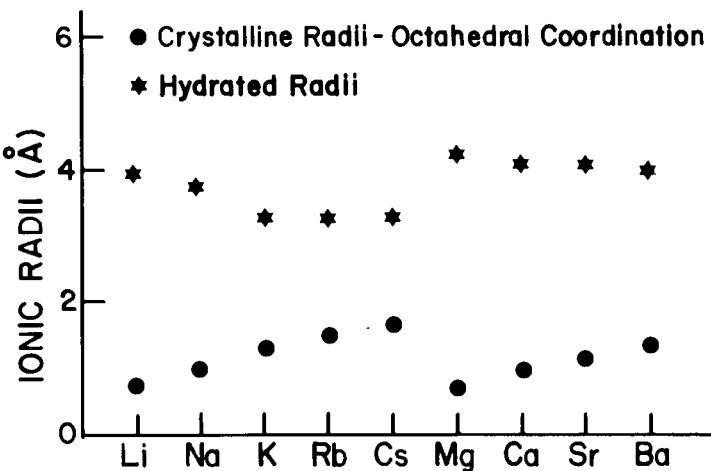


Fig. 5.6. Comparison of ionic radii in hydrated and solid state. (Adapted from Minerals in Soil Environments, p.44, "Surface and Colloid Chemistry", 1977, by permission of, Soil Science Society of America.)

When ions of different valence are present there is a general tendency for the ion of higher valence to be preferentially taken up in exchange reactions. Ions with the highest bonding energy preferentially occupy sites on the surface which have the greatest mean free bonding energy. This is known as Jarusov's rule (JARUSOV, 1937). Cation exchange reactions are generally rapid. Rate is influenced by such factors as ionic diffusion velocity, temperature, concentration, and permeability of natural clays.

Certain ions such as potassium can become fixed or only replaceable with difficulty by the usually employed cation exchange reagents such as ammonium acetate. Fixation is commonly related to the presence of non-crystalline minerals, vermiculite, mixed-layer minerals and degraded illites which lose potassium on weathering but take it in again between the sheets if it becomes available. There is strong preferential adsorption of potassium over other cations and its subsequent replacement is difficult since diffusion, the rate limiting step is very slow (JACOBS, 1963). Potassium fixation is reported to be reduced by exchangeable aluminium (SOMASIRI and HUANG, 1974; NAGASAWA et al., 1974) and increased by oxidation of ferrous iron in the octahedral sheet (KISHK and EL-SHEEMY, 1974). This has been attributed to increased attraction between the layers and interlayer potassium; apparently a change in orientation of the hydroxyl occurs which shifts the proton away from the K^+ so that repulsion between the positive charges is reduced. Treatment with alkalies such as calcium hydroxide and sodium carbonate have been found to increase potassium fixation whereas it is diminished by acid treat-

ment. Potassium-fixation has been related to the proportion of charge in the tetrahedral layer but this is now questioned (KODAMA et al., 1974). The potassium cycle is very important in agriculture (REITEMEIER, 1951; THOMAS and HIPP, 1968). Ammonium is also sometimes fixed probably by illite, vermiculite or chlorite (CARROLL, 1959; RICH and LUTZ, 1965). Interlayer precipitation in vermiculite and smectite of hydroxides of iron, aluminium (WESTFALL, et al., 1973) and magnesium, which sometimes leads to the formation of chlorite-like structures (TOTH, 1964), is a form of cation fixation. Minerals of this sort show an increased capacity for phosphate fixation.

Clay minerals sometimes show a specific affinity or selective sorption as well as fixation of certain cations (SAWHNEY, 1972). These reactions are known to occur when only low concentrations of the specifically adsorbed ion are present in solutions which contain a high concentration of other ions. Purely electrostatic forces are therefore inadequate to account for the mechanism of the process (BOWDEN et al., 1973). Among reactions of this type many of the 10 Å minerals were found to have a high affinity for sorption of cesium (TAMURA and JACOBS, 1960); cobalt and zinc were sorbed by layer structure silicates when present in low concentrations of about 10^{-6} molar in solutions which were 0.1 normal with respect to calcium chloride. The specific sorption in this case was attributed to crystal strain or lattice defects located on the basal surfaces of the minerals caused either by weathering or lattice substitutions (TILLER and HODGSON, 1960; HODGSON and TILLER, 1960). Some montmorillonites show similar selectivity in the sorption of cations (ELIASON, 1960).

When uptake of cations occurs from an electrolyte but the clay has little or no sorption capacity for the anions their concentration in the intermicellar solution rises. This is referred to as negative adsorption. Its significance has been discussed in connection with montmorillonite by EDWARDS and QUIRK (1962).

Organic material can make a large contribution to the cation exchange capacity. This can be reduced by 20-50 per cent if the organic phase is removed even though this may constitute no more than 3 to 5 per cent of the soils mass (TOTH, 1964). The organic compounds are believed to form adsorption complexes with the inorganic compounds. HENDRICKS, (1944) has suggested that in some cases exchange capacity may be reduced by large organic molecules which may blanket more than one exchange site (HENDRICKS, 1944).

Non-crystalline compounds contribute to exchange capacity. A range of values has been published for allophane and imogolite (WADA, 1977). Certain gels such as those of alumina acquire a negative charge at high pH and contribute to the cation exchange capacity; at low pH alumina acquires a positive charge and may add to the anion adsorption capacity. Amorphous compounds of this type are probably of most importance in clays which are undergoing active weathering. They are probably of most direct concern in the layer of the soil which is of greatest interest to ag-

riculture. They are thought to be responsible for the variation in charge shown by soils with change in pH. An increase in the acidity of a soil solution can cause the charge to pass through the point at which positive and negative charges balance (the isoelectric point) so that the soil particles acquire a positive charge.

Ion exchange has been considered quantitatively on the basis of formulas derived in accordance with four chief theories. The principles employed were embodied in the Freundlich adsorption isotherm, the law of mass action, the Donnan membrane theory and the principle of oscillation volumes. The equations developed from the mass action law have been compared by WIKLANDER (1964) with ones derived from the Donnan theory. He concludes that the two theories are only different ways of solving the same problem but fewer assumptions are involved in the Donnan theory.

The oscillation volume theory was developed by JENNY (1936). Exchangeable cations are regarded as having a mean oscillation volume about the centre of electric charge. When oscillation volumes overlap exchange becomes a possibility which occurs when a replacing ion comes between the original ion and the surface.

Anion Exchange

In anion exchange negatively charged ions on the clay mineral are replaced by anions in the intermicellar solution. The anion exchange capacity of the 2:1 layer structure minerals is much less than their cation exchange capacity. In smectites, for example, it is generally less than 5 meq/100g. Kaolinite gives similar values for both types of exchange capacity. The mechanism of anion exchange has been reviewed by MARSHALL (1949) who concludes that it occurs at exposed hydroxyl groups. Either replacement or addition may be involved in different cases. VAN OLPHEN (1977, p. 94) has suggested that the exchange capacity for anions shown by kaolinite in acid solution results from aluminium ions on the crystal edges which acquire a positive potential. This is balanced by exchangeable anions which act as counter ions. Hydrous oxides of iron and aluminium probably contribute to the anion exchange capacity of acid soils. This type of exchange is essentially a non-specific adsorption phenomenon (MOTT, 1970) due to electrostatic attraction between anions and surfaces with a positive pH dependent charge. Specific adsorption is also known most typically involving weakly acidic anions such as phosphate and silicate; similar reactions with sulphates and fluorides have also been reported (HINGSTON et al., 1972). Formation of partly covalent bonds, coordination by cations or anionic decomposition of non-crystalline aluminosilicates are suggested mechanisms of attachment. Allophane and imogolite strongly interact with anions and in Japan high phosphate uptake has been used as a quick method for recognition of allophane in soils (WADA, 1977). Engineering uses of anion exchange include treatment of drilling muds and of clays used as liners in reservoirs.

Exchange Involving Organic Materials

Clay minerals have a sorptive capacity for organic compounds. The mechanism sometimes involves cation exchange as some organic molecules, commonly ones containing nitrogen, are positively charged. For a given charge density strength of electrostatic attraction will vary with the location of the charge in the clay mineral structure. When the charge originates in the octahedral layer the force will be less at the surface than when the charge arises in the tetrahedral layer. Reactions with organic compounds will be affected accordingly (MARTIN-RUBI et al., 1974).

Early work made it evident that uptake of organic compounds sometimes involves processes different from cation exchange and the reaction may not be stoichiometric. Much recent work has shown that clay minerals also form complexes with uncharged polar organic compounds interaction being by a variety of mechanisms which depend on the clay mineral itself and its pre-treatment, the valency and position of the exchange ion, the nature of the organic molecule and the medium in which the reaction takes place.

Clay minerals are able to donate protons - that is to act as Bronsted acids. This has been termed surface acidity though the property arises mainly from water molecules associated with exchange cations. At low relative humidities protons become available from dissociated water molecules particularly when these form the hydration shell of small high-charged strongly polarizing cations (MORTLAND and RAMON, 1968). Clays which have been acid treated provide a ready source of protons whereas treatment of clays with basic reagents inhibits clay-organic interactions which depend on protolysis. Molecules which accept a proton acquire a positive charge and behave as cations. When uptake by the clay mineral involves cation exchange there is competition between the inorganic and organic cations for the negatively charged sites.

A clay mineral is sometimes able to accept an electron pair - act as a Lewis acid when water is absent. These sites have been associated with aluminium ions (SOLOMON, 1968) and are found when coordination is incomplete as when the Al^{3+} is in tetrahedral positions at dehydrated crystal edges. It has also been suggested that an ion within the structure such as ferric iron may act as a site at which a single electron may be accepted (BLOCH et al., 1953). An electron accepting site is an oxidizing site since the species external to the clay loses an electron (is oxidized). Conversely electron-donor sites are reducing sites. Sometimes single electron accepting sites are included in the definition of Lewis acid sites. Reactions involving electron transfer to the clay mineral tend to be inhibited by pre-treatment of the clay with reducing agents such as aqueous hydrazine or stannous chloride or by pre-treatment with phosphates such as Calgon thought to block accessibility of edge sites.

Organic molecules may become attached to exchange ions themselves and bonding may be by hydrogen bonds, ion-dipole interaction or by bridging mechanisms. The variety of modes of interaction between clay minerals and organic molecules requires that consideration be given to factors in addition to the inherent or acquired charge on the organic molecule. Size is important as van der Waals forces become larger as the size of the molecule increases. Steric factors affect the ability of the molecule to key into the silicate structure and thereby affect the stability of the complex. Minerals show preferential adsorption of organic molecules in which the distances between charged sites match those on the mineral surface. Large molecules, particularly if polar and strongly associated, may be too large to occupy all the charge sites available. They may be unable to enter the interlayer space of expandable minerals or may do so only with difficulty. For example large molecules found in bitumens, asphaltenes and resins such as occur in the Athabasca oil sands seem to adsorb primarily on external surfaces of clay minerals. They have difficulty penetrating the interlayer space of montmorillonite but render the mineral less hydrophilic at low relative humidity. At high relative humidity however montmorillonite treated with these compounds was found to take-up interlayer water and penetration by glycerol was not prevented (CZARNECKA and GILLOTT, 1979). Some small, highly polar organic molecules can penetrate the layers of kaolinite - a mineral not normally expandable. WADA (1961) found that potassium acetate was able to expand the kaolinite structure and since then many other compounds which react similarly with kaolinite have been found. Some molecules are only able to enter kaolinite in the presence of entraining agents such as urea, formamide and hydrazine (WEISS et al., 1963; OLEJNIK, et al., 1970).

It is a general principle that the medium itself affects clay mineral-organic reactions. The pH is a factor, in the case of amphoteric compounds for example, which have both basic and acidic functional groups, the molecule has a positive charge below a certain pH and a negative charge above that pH. Molecular dissociation is affected by the dielectric strength of the medium. Resins and asphaltenes are large organic molecules found in oil deposits. CLEMENTZ (1976) found that montmorillonite adsorbed more of these compounds from nitrobenzene than from chloroform. He suggested that this may have resulted from ionization of the resins and asphaltenes in the nitrobenzene due to its higher dielectric strength. This would have led to a decrease in the force of attraction between positive and negative groups in the molecules.

The most useful methods for studying the nature of clay-organic complexes and the mechanisms of clay-organic reactions include adsorption, x-ray diffraction and infrared spectroscopy. Other techniques include electron microscopy, differential thermal analysis, chromatography, calorimetry, etc. In general a combination of techniques particularly the first three has provided the greatest insight into the nature of clay mineral-organic interactions.

Clay-organic complexes have distinctive properties some of which are of considerable economic importance. In the petroleum industry, for example, they are used as drilling muds, they have uses in agriculture, and in the manufacturing and construction industries their rheological properties lead to their use as greases and in paints, etc. Chemical reactions can be catalyzed by clays and some of those in which clay-organic interactions are involved include initiation of polymerization, degradation reactions such as petroleum cracking and formation of coloured complexes. Pioneer studies were carried out by MACEWAN (1960) and WEISS (1963) and reviews have been given by GRIM (1953), VAN OLPHEN (1967), MORTLAND (1970) and THENG (1974).

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Chapter 6

MOISTURE INTERACTION WITH CLAYS AND CLAY MINERALS

The properties of clays are affected by the total water content and by the energy with which the moisture is held: gradients lead to moisture migration. The water content affects consistency, strength, the density which can be achieved by a given compactive effort and other properties. The energy with which the moisture is held influences volume change characteristics, such as are shown on consolidation, drying, moisture uptake, freezing and other properties such as hydraulic conductivity, etc., which are affected by moisture migration and permeability. Flow-rate affects yield from wells and rates of leakage from reservoirs and through earth dams. Settlement or heave of foundations results from moisture movements. Differential movement is particularly undesirable as it tends to cause distortion. Damage may be caused to roads, aircraft runways, railways, shallow underground service lines, retaining walls and building foundations of all kinds. Dimensional changes due to moisture movements are also of concern in the industrial use of clays as in ceramics.

Most engineering operations disturb the natural moisture regime of the soil. Externally applied stress due either to shear or to natural or artificial loading may cause moisture movement as a relatively incidental accompaniment to other effects such as slope failure or consolidation. Moisture migration may, however, be directly responsible for changes in the volumetric or linear dimensions of clays. The magnitude of the dimensional change depends upon the interrelated variables of geological history, fabric, mineralogical composition and nature of exchange ions. Such moisture movements occur because internal gradients generate forces within the clay-water system. Such gradients arise from variations in the temperature, extent of saturation, and chemical composition or concentration of pore solutions. Shrinkage on drying, swelling on moisture uptake and the worst results of frost action are typical effects. Drying may result from surface evaporation, transpiration from plants or heating. Gain in moisture may result from a rise in the water table, from precipitation, or from water leakage from man-made structures such as reservoirs or drains. Local climate is of major importance since it controls the distribution and amount of precipitation, the duration of any dry periods and whether the soil is subject to frost-action. Over half the land area of the northern hemisphere is affected by seasonal freezing and thawing.

In order to minimize the deleterious effects of moisture movement in soils, engineers frequently place footings and foundations at depths below those

affected by seasonal fluctuations of moisture content. This is not always feasible owing to the dictates of economy so in such cases the design of the structure has to be such as to allow for changes in volume or strength of the soil foundation. When soils with large potential volume change characteristics are encountered there are various other ways of dealing with the problem. The potentially troublesome soil may be removed and replaced with more stable material; an attempt may be made to prevent or limit changes in moisture content; or the soil may be treated in some way so as to reduce its susceptibility to volume change.

THE NATURE OF WATER AND IONIC SOLUTIONS

The nature of water and ionic solutions plays a significant role in the processes which occur when moisture interacts with clay minerals and clays. The phase diagram of water is shown in Fig. 6.1. Water has unexpected properties when compared with similar compounds. Thus its melting point,

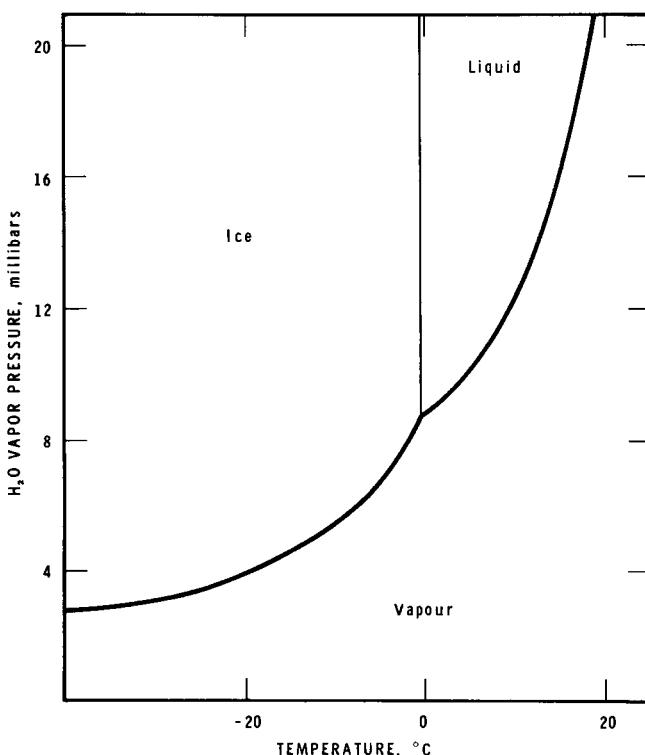


Fig. 6.1 The phase diagram of water.

boiling point, specific heat, viscosity and dielectric constant are unusually high. A number of attempts have been made to account for these peculiarities on a structural basis. The most commonly accepted view is based on proposals by BERNAL and FOWLER (1933) and MORGAN and WARREN (1938). They suggested that the water molecule contains a tetrahedral charge distribution in which there are two corners where a positive charge is located and two corners where there is a negative charge. The molecule has a permanent dipole moment. The charge separation within the molecule leads to electrical interaction between adjoining molecules. They tend to become oriented with a negative corner of one being adjacent to a positive corner of its neighbour. Water is pictured as a "network of linked four-coordinated molecules forming rings of four, five, six, seven or even more molecules arranged in various sets of random order" (BERNAL, 1964). Three molecular configurations were suggested with water I having an ice-tridymite-like structure present principally below 4°C, water II having a more compact quartz-like structure and found at about 4°C and water III having a more close-packed structure stable at significantly higher temperatures. Theoretical studies of three-dimensional lattice models have helped explain the water phase diagram and the existence of open- and more closely-packed structures (BELL and SALT, 1976).

The molecular association and more or less open structural arrangement of water allows void spaces to be continuously formed and destroyed by the jostling motions of the molecules. These spaces will assume a certain average size distribution at a given temperature and pressure. Ions in solution are thought to be accommodated with greater or lesser ease within these cavities depending on the size of the ion relative to the size of the void spaces. Hence ions in solution may appear to occupy less volume than in solids. Ions have been subdivided into three groups, A, B and C depending on whether they are smaller, slightly larger or very much larger than the void space within the network of associated water molecules. Ions in group A include H, Li, Na, Ag and OH and have negative partial molal volumes. Ions in group B include K, Rb, Cs, NH₄, Cl, Br and I. Large organic ions fall into group C. The number of water molecules associated with a given ion has been considered in terms of the coordination number - the number of nearest neighbour water molecules in association with the ion - and the hydration number - the number of water molecules which remain associated with the ion as it diffuses through the solution. These factors together with other physical considerations led SADEK (1983) to conclude that the motion of ions in groups A and B involves a quite different mechanism from that of ions in group C.

The magnitude of the changes in physical properties and molecular structure of water, under given conditions, will also depend on the charge on the dissolved ions. The negative charges on the water molecule tend to be

directed towards the cations whilst the positive charges are attracted by the anions. Small ions, particularly if polyvalent, have a large charge to surface ratio and the strongest association with the polar water molecules is to be expected.

Radial distribution analysis of diffraction data has long been used to derive information concerning the structure of liquids and solutions (JAMES, 1965). Theoretical considerations have shown however that in conventional diffraction studies the weight of the terms due to the water itself (O-O, H-H, O-H) is large whereas the weight of the ion-ion and ion-hydration terms is very small. Unfortunately these are the very terms of most significance to the understanding of ion hydration. SOPER et al (1977) found that this drawback may be largely overcome by recording the neutron diffraction pattern from separate solutions of the same compound but which contain different isotopes such as K³⁵Cl and K³⁷Cl. Because of differences in scattering between the isotopes the relative contribution from the most significant terms is greatly enhanced. This makes it possible to obtain much more information relating to the distribution of water molecules surrounding a particular dissolved ion and in principle the contribution of any one of the ion-ion terms can be enhanced.

ENDERBY (1981) has summarized results from some of these recent studies. He reports that in the case of chloride ion-water molecule geometry only second order effects can be attributed to ionic strength and to the counter ion (the cation). Li-ions appear to be surrounded by 6 rather than 4 water molecules in solutions of concentrations which are 3 molal or less. The presence of a second shell of coordinated water surrounding the cation, and predicted on theoretical grounds, has been demonstrated in some cases. For example in solutions of Ni salts it was found that the cation was associated with about 15 molecules of water the physical properties of which were different from those of water in bulk. Packing considerations due to ionic size, specific chemical effects and the mechanism of ion selective processes are being investigated. The present trend in this work is to compare predictions made by computer simulation of solution models with experimental evidence of structure derived by these techniques. The solution numbers of ions in solution have been investigated by a great variety of other techniques often with varying results (HINTON and AMIS, 1971). Comprehensive reviews of the nature of water and solutions have been published in books by EISENBERG and KAUZMANN (1969), FLETCHER (1970), HORNE (1972) and FRANKS (1973).

The nature of water associated with exchange ions and in the interstitial space of clays has also been investigated by neutron diffraction (HALL et al., 1979; HAWKINS and EGELSTAFF, 1980). Counter ions associated with montmorillonite were found to have well-defined hydration shells. Much of the

interlayer water is not highly structured and only about half of the first molecular layer of water is associated with the silicate structure of the clay mineral surface; interstitial water has a structure similar to that of water in bulk. FRIPAT and STONE (1978) concluded from studies using nuclear magnetic resonance that while the translational freedom of interlayer water is reduced compared to that of water in bulk the interlayer water molecules spin freely about a precessing axis of fixed orientation.

THE RETENTION OF MOISTURE

Part of the meteoric water which percolates into the ground is retained within the pores of rocks and soils. The composition and fabric affects the amount retained which is higher for clays than silts or sands. As is to be expected high surface area clays particularly smectites have a high potential for moisture uptake and retention. Studies of heats of immersion have shown that allophane and imogolite may have an even higher capacity (AOMINE and EGASHIRA, 1970).

Moisture interaction can be understood in general terms by regarding soil as composed of a mass of interconnected capillary tubes of different diameters. In this hypothesis surface tension forces associated with the air-water interface were thought to be mainly responsible for the retention of moisture. The behaviour of coarse-grained soils agrees fairly well with this suggestion. In finer soils pore sizes decrease and capillary forces increase so the water is more strongly held; also there are, in general, greater differences between observed and predicted behaviour. This is because of the major influence of adsorption, particularly when clay minerals are present, and in that case also because of the large effect of moisture uptake by the hydrous double layers.

In an alternative approach the energy with which moisture is held is considered. This makes possible a more accurate quantitative treatment in terms of the "capillary potential" (BUCKINGHAM, 1907) or soil water potential. This is defined as "the force required to pull a unit mass of water away from a unit mass of soil" (BAVER, 1956, p.227). The magnitude of the capillary potential indicates the force with which moisture is held and the potential gradient indicates the direction of moisture migration. The capillary potential incorporates the hydrostatic pressure, the osmotic pressure and the adsorption potential.* Moisture moves from wet to dry clay and will move upwards under the influence of the potential gradient against the force of gravity until equilibrium is established. Therefore gravitational forces also

*Many of the terms relating to the soil-water system are defined by the Soil Science Society of America (Proceedings, Vol. 29, 1965, p.330) and by The International Society of Soil Science (Bull. 23, 1963, pp. 7-11).

have to be considered in evaluating the total potential which acts on pore-water in soils. The understanding of the energy relationships of soil moisture has been further extended by thermodynamic methods. EDLEFSEN and ANDERSON (1943) considered that capillary condensation was the dominant process near merging cusps between particles and that on concave surfaces away from contact points adsorption became of over-riding importance. The chemical potential of soil water is generally expressed as the sum of four terms. These take into account the hydraulic pressure, the osmotic potential, the capillary potential or matric potential (which includes effects due to moisture adsorption), and temperature differences respectively. The relationship may be expressed by the following equation:

$$d\mu = \left(\frac{\delta\mu}{\delta P}\right)_{n_w} n_j dP + \sum_j \frac{\delta\mu}{\delta n_j} dn_j + \frac{\delta\mu}{\delta n_j} dn_w + \frac{\delta\mu}{\delta T} dT$$

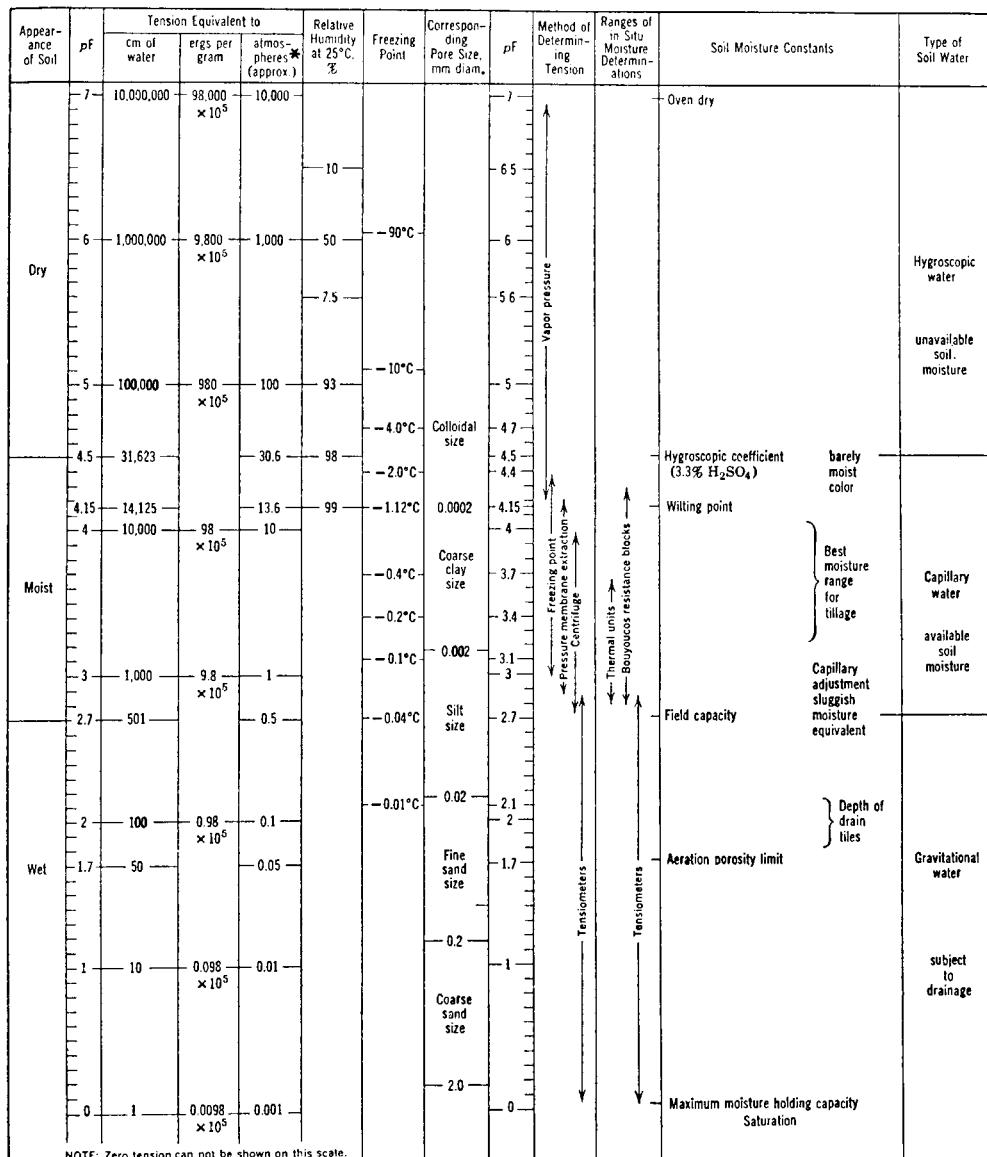
where μ = chemical potential, n_w = mole fraction of water, n_j = mole fraction of solute, P = pressure, and T = temperature.

Various attempts to treat the problem of soil-moisture interaction quantitatively have made use of the Kelvin equation. Proposals to improve the agreement between theory and observation included modifying the radius of curvature to take account of an adsorbed film of assumed constant thickness. On the assumption that at equilibrium the liquid-vapour interface is a surface of constant potential PHILIP (1977) developed a differential equation of the interface. He concluded that the use of the Kelvin equation does not adequately describe capillary condensation and adsorption. From consideration of various models including parallel plates, wedge-shaped pores and circular tubes he found that the Kelvin equation, even when modified, often seriously underestimates the quantity of condensate.

If the potential of free water under atmospheric pressure is taken as zero pore water above the phreatic surface is at a negative potential. At equilibrium the pore-water pressure decreases linearly with height above the water table. The decrease in pressure results from the surface tension, adsorptive, and osmotic forces by which the water is held against gravity. The pore water potential of a soil varies continuously with water content and there are no sharp breaks so that strictly speaking classification of soil water into types such as capillary and gravitational (Fig. 6.2) is arbitrary.

It is often convenient to consider soil water potential in terms of the soil moisture "suction". This is defined with respect to soil free from external stress as the difference between the pore-water pressure and atmospheric pressure. It is directly related to the negative hydraulic head of the liquid phase. Soil moisture suction increases on drying and can reach values of several thousands of atmospheres in a dry soil (Fig. 6.2). It is

frequently expressed on a logarithmic scale termed pF. This is the common logarithm of the suction expressed in centimetres of water. The term pF was introduced by SCHOFIELD (1935). The use of the pF scale has several advantages. Changes in relative humidity between zero and four correspond to small variations in relative vapour pressure. In this range, however, there



* 1 ATMOSPHERE = 101.325 kPa

Fig. 6.2 Relationships between soil properties and pore-moisture tension.
(After KOHNKE, 1946, p.65. Reprinted by permission of the publisher.)

are often large changes in total moisture content. Hence the expanded pF scale makes it possible to show the relationship of tension to moisture content on one graph (BAVER, 1956, p.244; PENNER, 1958). Tension measurements, however, do not take into account possible osmotic-pressure effects. The relationship of pF to relative vapour pressure and suction in p.s.i. are shown in Table 6.1.

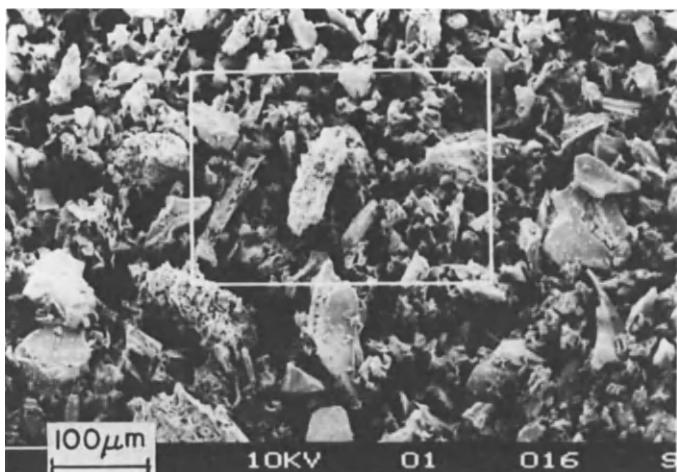
The water in soils is retained in very irregular and tortuous channels and pore spaces. The fabric of the soil and the particle size of the minerals exert a large influence on the nature of the forces which are dominant in any particular case. When agglomerations are present two categories of pore space may be distinguished - larger interparticle pores between agglomerations and individual primary minerals (Fig. 6.3A, C) and intraparticle pores within agglomerations (Fig. 6.3 B,D). When marked this type of distribution may have a significant effect upon engineering behaviour (CLARK and GILLOTT, in press). When particles are of sand size retention of water is influenced largely by capillary forces which depend upon the surface tension and mass density of the water and curvature of the air-water interfaces within the pores. Surface tension is affected by the temperature and amount and nature of dissolved substances. The curvature of the air-water interface depends upon the size and configuration of the pore-spaces and wettability of the minerals. In clays forces of a colloid chemical nature associated with the high specific surface

Table 6.1

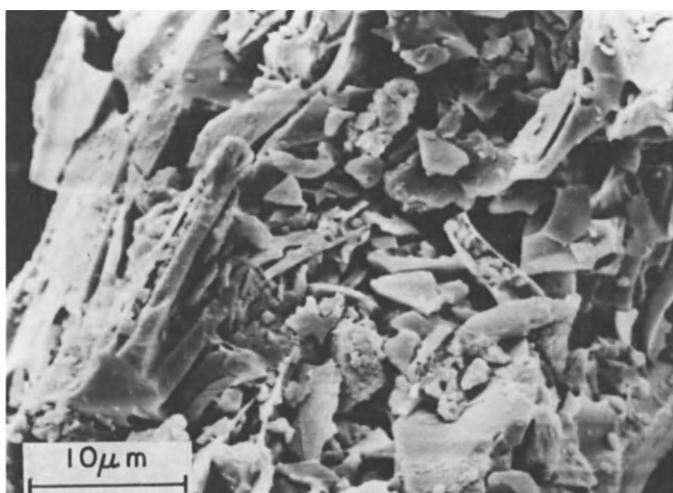
THE RELATIONSHIPS BETWEEN RELATIVE VAPOR PRESSURE, RADIUS OF CURVATURE OF MENISCUS, EQUIVALENT HEIGHT OF COLUMN OF WATER (h) AND pF
(After PENNER, 1958, p.1207.)

| P/p_0^1 (%) | Radius of curvature of meniscus (r) | Equivalent height of water (h) (cm) | h (p.s.i.) | Schofield's pF |
|------------------|---|--|----------------------|-------------------|
| 0.08 | 0.000147 | 10^7 | $1.42 \cdot 10^5$ | 7 |
| 49.0 | 0.00147 | 10^6 | $1.42 \cdot 10^4$ | 6 |
| 93.0 | 0.0147 | 10^5 | $1.42 \cdot 10^3$ | 5 |
| 99.3 | 0.147 | 10^4 | $1.42 \cdot 10^2$ | 4 |
| 99.9 | 14.7 | 10^3 | $1.42 \cdot 10$ | 3 |
| 99.99 | 147.0 | 10^2 | 1.42 | 2 |
| 99.999 | 0.0 | 10 | $1.42 \cdot 10^{-1}$ | 1 |
| 100.0 | | 0 | 0 | |

¹ p = the vapor pressure over the curved surface; p_0 = the vapor pressure of free water.

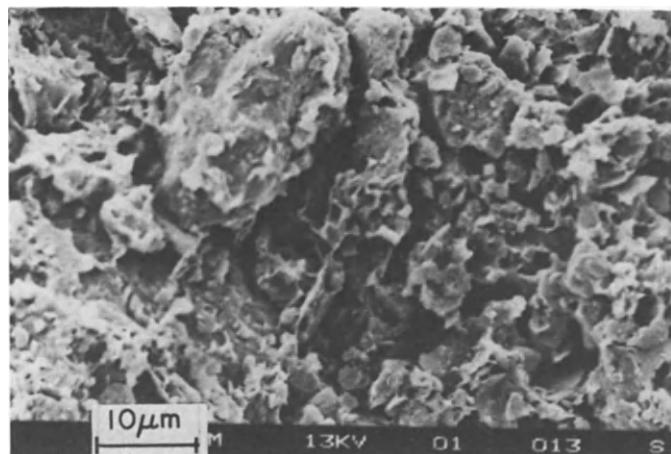


A. Interparticle porosity

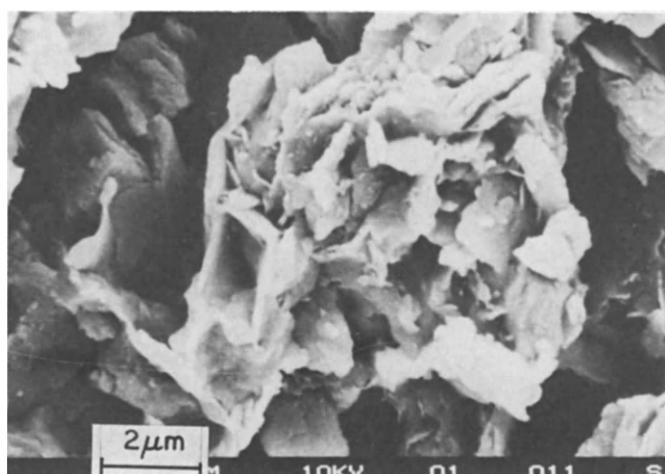


B. Intraparticle porosity in agglomeration

Fig. 6.3 Scanning electron micrographs showing interparticle and intraparticle porosity in silt. Banff, Alberta.



C. Interparticle porosity



D. Intraparticle porosity in clay agglomeration

Fig. 6.3 Scanning electron micrographs showing interparticle and intraparticle porosity, Calgary, Alberta

area of the minerals often become dominant. In the potential concept the mechanism by which the forces originate need not be understood. Nonetheless experience shows that progress is made most surely when this more fundamental knowledge is acquired.

THE MIGRATION OF MOISTURE

Moisture may migrate when the soil is either saturated or unsaturated and in either a vertical or horizontal direction. Moisture movements result from loading, from stress relief, from fabric changes and from changes in the moisture potential or suction. Water infiltrates downwards after rain. When water soaks into dry soil it saturates a thin surface layer of the order of 1 cm in thickness. Below this the moisture is transmitted through a zone in which the soil remains unsaturated. Below this again the water content rises rapidly as the zone of water saturation is reached. Moisture also often moves upwards in dry periods in regions such as western Canada. This may lead to development of saline soils which can have important engineering side effects such as sulphate attack on concrete. In construction work the natural moisture regime of the soil is often disturbed due for instance to the placement of an impervious cover such as a road or aircraft runway. This can result in water movement in a horizontal direction. Trees and other kinds of vegetation set up gradients sufficient to cause moisture migration sometimes causing shrinkage of clay soil (BOZOZUK and BURN, 1960) (Fig. 6.4).

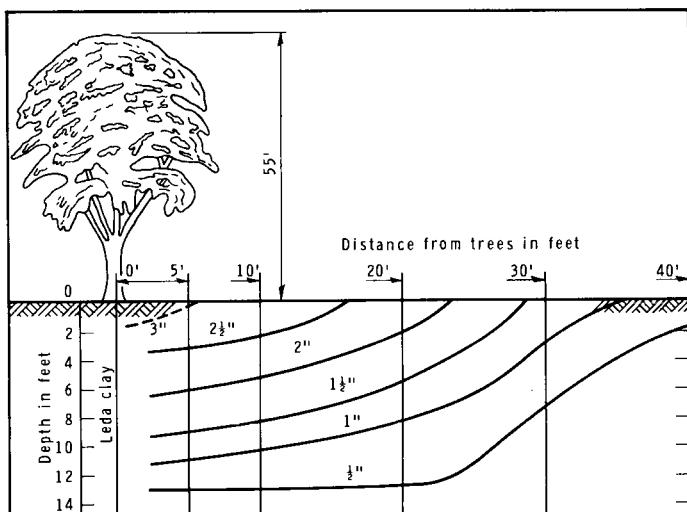


Fig. 6.4 Variation in maximum vertical ground movements near elm tree in Leda clay, Ottawa, Canada. (After BOZOZUK, 1962, p.36).

The water content is not reliable as a means of assessing whether moisture migration will occur between different parts of the soil mass since soils in moisture equilibrium may contain different water contents. Moisture migration takes place in response to the development of a gradient caused by a variety of forces such as arise from stress differences, gravity and from differences in chemical potential; the velocity and rate of flow depend on the capillary flow properties of the soil.

Water moves as a liquid in saturated deposits and in either liquid or vapour phase in unsaturated deposits. Liquid moves under the influence of gravitational, capillary, osmotic, or other forces while vapour migrates because of a difference in temperature or solution concentration. Moisture migrates from warm to colder regions and from regions of higher vapour pressure to regions where it is lower. In a saturated deposit containing large voids gravitational forces are dominant. In a fine-grained material or deposit which is unsaturated surface forces have more importance.

In 1856 DARCY showed that in a saturated deposit a linear relationship exists between the hydraulic gradient and the velocity of water flow through porous material such as sand. This relationship is known as Darcy's law. It may be expressed by the following equation:

$$v = - k dh/ds$$

where k = coefficient of permeability, $- dh/ds$ = hydraulic gradient, h = total head, s = distance, and v = velocity of flow.

For many engineering purposes and particularly in granular deposits Darcy's law is sufficiently accurate. However, the equation only takes account of gravitational forces and assumes laminar flow under constant gradient conditions. Also the linear relationship expressed in the equation has been found not to be valid for all clays (HANSBO, 1960). In clays the capillary potential is much greater than in granular soils but the rate of water migration is very slow due to the low coefficient of permeability. In flow through unsaturated media k , in Darcy's law, is not a constant but varies with the soil moisture suction. Water flows most readily through the large pores but since these are the first to drain there is a relatively rapid decrease in hydraulic conductivity when the deposit becomes unsaturated. As the deposit becomes drier some moisture transfer probably occurs in the vapour phase. For unsaturated soils values of the coefficient in Darcy's law, expressed as a function of soil suction, $k(h)$, may be derived from an equation developed by MARSHALL (1958). Good agreement is reported for non-swelling soils over the whole suction range provided an empirical constant is introduced which is derived by matching a theoretical and experimental value at only one point. Because of problems with expanding soils however RICHARDS (1974) recommends

that $k(h)$ be determined experimentally for most natural unsaturated soils.

An equation was proposed by KOZENY (1927) and improved by CARMAN (1937) which relates the coefficient of permeability to physical properties of the system such as porosity and surface area of the particles. It is known as the Kozeny-Carman equation and it may be expressed as follows:

$$k = \frac{1}{k_0 S^2} \cdot \frac{\gamma}{\mu} \cdot \frac{e^3}{1+e}$$

where k_0 = constant depending on pore shape and ratio of length of actual flow path to soil bed thickness, S = specific surface area, γ = unit weight of permeant, μ = viscosity of permeant, and e = void ratio.

Although this equation is a refinement and improvement on that proposed by Darcy it suffers from similar shortcomings. The experimentally determined rate of flow of water through clays often differs from the calculated rate. This has been attributed to interactions between the clay minerals and the pore solutions, to the platy shape of the clay minerals, to complimentary effects such as greater tortuosity of flow path than assumed, and to major permeability effects from small fabric changes. Hydraulic conductivity has also been found to be significantly greater when measurements are made on large samples. It is thought that this results from the increased probability of the sample containing joints, cracks and large pores through which flow-rate is more rapid. Sand and coarse silt filling cracks and joints and present as interbedded lenticles also have a major effect on rate of moisture movement which in the field correspondingly affects rate of drainage, rate of evaporation and rate of moisture uptake following drying.

The flow-rate is also affected by the nature of the exchange complex and by the mineralogical composition. For example sodium montmorillonite is less permeable than calcium montmorillonite; it has been shown that there is a rapid decrease in hydraulic conductivity when sodium saturation reaches 15 per cent (SHAINBERG and CAISERMAN, 1971). The difference in permeability between sodium and calcium montmorillonite was exploited in the construction of the Treasure Island lagoon, San Fransisco, where the calcium clay was converted to the sodium form by ion exchange accomplished by use of salt (LEE, 1940). Interaction of clays with organic compounds also has a significant effect on hydraulic conductivity. This has been attributed to change in the nature of the clay mineral surface from hydrophilic to organophilic, to changes in the distance from a mineral surface over which water molecules are oriented and to changes in fabric affecting tortuosity, etc. Clays containing minerals with elongate or fibrous shapes such as halloysite and attapulgite tend to be more permeable than clays composed mainly of platy minerals. Small amounts of clay minerals have an important influence on the permeability of granular deposits.

Porous beds such as sands which contain some clay are sometimes much more permeable to salt water than to fresh water. Such beds have been termed water sensitive.

Many attempts have been made to obtain at least a qualitative understanding of the unusual permeability properties of clays. Several authors have concluded that clay minerals are surrounded by thick layers of oriented water molecules (LOW, 1961). It has been proposed that this water has an increased viscosity and decreased mobility so permeability is reduced. Differences in permeability between clays composed of different clay minerals of similar shape are ascribed on this view to differences in the thickness of the oriented water layers caused either by the nature of the exchange ion or by the properties of the mineral. The range over which the different clay minerals cause perturbation of the normal properties of water is, however, controversial although there is little doubt of the reality of such effects in close proximity to the clay mineral surfaces.

Other authors have attributed greater importance to porosity, fabric and state of flocculation of the clay minerals. Permeability has been measured as a function of porosity in combined consolidation-permeability tests; the permeability was found to decrease more rapidly with decrease in porosity than predicted by theory (LAMBE, 1958a). Changes in fabric of the clay may be responsible particularly when account is taken of its effect upon the pore-size distribution within and between separate aggregations of clay minerals (MICHAELS and LIN, 1954; OLSEN, 1962).

Permeability is thought to be affected mostly by the coarser pores, which exist between agglomerations, and by the presence (or absence) of continuous inter-connections. Support for these ideas was obtained from consolidation-permeability studies and from the investigation of clays and silt-clay mixtures compacted on the dry and wet sides of optimum. Data obtained with the mercury porosimeter have shown a bimodal pore-size distribution in some soils with larger pores being in the 1-10 μm size range and smaller pores being in the range of 0.1 μm . In soils compacted dry of optimum it has been suggested that there are aggregations which are strong enough to resist deformation with little distortion. As the water content is increased the agglomerations become deformable and compaction decreases the inter-aggregate pore volume so the dry density increases. By the water-content reaches optimum the air permeability drops to zero suggesting that the inter-aggregate pores are no longer continuously connected. Above optimum water content the aggregations may fuse together on compaction with disappearance of the bimodal pore-size distribution (McKINLAY and SAFIULLAH, 1980). Based on these studies GARCIA-BENGOCHEA et al., (1979) developed new equations for the calculation of permeability from pore-size distribution parameters.

Changes in permeability of clays and clay containing granular deposits may also be accounted for in terms of changes in the state of flocculation of the clay minerals. In the flocculated state they tend to adopt an open type of textural arrangement with a relatively high permeability. When dispersed the clay minerals may be transported and deposited in narrow pore openings where they have a clogging effect. This may account for the water-sensitive behaviour of some rocks and for the greater influence of fine-grained clay minerals such as smectites than relatively coarser grained clay minerals. FRENKEL and RHOADES (1978) concluded however that dispersion and swelling may either increase or decrease the hydraulic conductivity. Important factors which influence the outcome include the soil bulk density, clay content, flow-rates and concentration and nature of electrolytes in the pore fluids, particularly the critical exchangeable sodium percentage. Changes in state of flocculation can be effected accidentally, or deliberately by changing the composition of the pore fluid. Factors affecting flocculation and resulting fabric of clays have been discussed in Ch. 5.

VOLUME CHANGES DUE TO MOISTURE MIGRATION

Changes in the moisture content of clay soils are generally accompanied by corresponding volume changes. On moisture uptake there is generally a volume increase and moisture loss is accompanied by shrinkage. Damage due to swelling and shrinking of soils in the U.S.A., for example, is considered to exceed that caused by earthquakes, tornadoes, hurricanes and floods combined and in terms of 1982 dollars has been estimated at about \$6000 million annually (HOLTZ, 1983). The importance of the subject is also reflected in the large numbers of papers in technical journals as well as those presented at the series of international conferences held on the subject (PROC. INTERNATL. CONF. ON EXPANSIVE SOILS, 1980; 1973). Volume change has been correlated with a variety of properties of the soil including specific surface area, cation exchange capacity, nature of exchange ion, degree of consolidation, content of organic matter and presence of cementitious agents.

Volume increase

A dry surface tends to adsorb water because this results in a lowering of the surface free energy and the material dilates. Dry clay has a considerable capacity for moisture uptake due to a combination of factors. Wet clay also often imbibes moisture if the load is reduced. For example, disturbance of an overconsolidated clay soil can result in heave. Moisture is taken up and the volume increases until an equilibrium void ratio is attained. If no change in

void ratio takes place when a soil is sheared to failure the void ratio is termed the critical void ratio (ROSCOE et al., 1958). The behaviour of saturated soils with positive pore pressure may generally be successfully described in terms of the effective stress principle. In the case of unsaturated soils and particularly expansive soils with negative pore pressure, however, the operative effective stress is much less readily placed on a quantitative basis. Unsaturated soils are encountered naturally in many parts of the world with low rainfall and high rates of evaporation and compacted soils that are unsaturated are used in the construction of highways, airport runways and earthfill dams.

Soils with the greatest potential for expansion often have features which aid recognition in the field and in hand sample. If wet such soils adhere to footwear and vehicles and are sticky when handled. If dry the soil is often cracked and may form hard lumps which when broken-up yield a very fine powder. Soils of that sort sometimes show gilgai structure in the field. This is a mound-depression feature often on a scale of 6m - 21m with depths which may reach 2m (O'NEILL and POORMOAYED, 1980). It is defined by BATES and JACKSON (1980) as "The microrelief of heavy clay soils with high coefficients of expansion and contraction according to changes in moisture. Gilgai is typical of Vertisols". Climatic rating systems (HAMILTON, 1963), the weathering index (p. 53) and the use of pedological classification (p. 15) and maps produced by Departments of Agriculture often give an indication of probable soil behaviour. Other information to do with climate and experience with existing structures is also invaluable in making a balanced judgement of the potential of the soil for volume change.

Heave potential has been estimated also from index test data, particle size distribution, overburden pressure, thickness and nature of clay layers, presence of permeable layers or lenses, distribution and depth of cracks, depth to water table, moisture content, soil permeability, suction characteristics and density. Soils were grouped by VAN DER MERWE (1964) into four classes from very high to very low potential expansivity and plotted on a graph showing plasticity index versus clay fraction (Fig. 6.5). WILLIAMS and DONALDSON (1980) concluded that this, and most other classifications, have shortcomings particularly when applied to soils and climatic conditions which differ from those in the regions where they were developed. The van der Merwe diagram for example implies that only a small change in clay content can change the classification of a soil, with a clay content above about 45 per cent, from low to high potential expansiveness. WILLIAMS and DONALDSON (1980) suggest that an appropriate modification is to use only the plasticity index of the whole soil and to disregard the percentage clay fraction. They thus classify soils into four groups as follows:

| Potential Expansiveness | P. I. of whole sample |
|-------------------------|-----------------------|
| low | < 12 |
| medium | 12 - 24 |
| high | 24 - 32 |
| very high | > 32 |

An alternative scheme was proposed by SNETHEN et al., (1977) in which liquid limit, plasticity index and in-situ suction are employed. In that classification a soil with a high potential for swelling is one in which the liquid limit is greater than 60, the plasticity index is greater than 35 and the initial suction is greater than 4 tons per sq. ft. Corresponding values for a soil with low swell potential are liquid limit less than 50, plasticity index less than 25 and initial suction less than 1.5 tons per sq. ft. Other relationships using data from index tests have been proposed by a number of authors (BANDYOPADHYAY, 1981; SHERIF et al., 1982). A good correlation between expansion index and the magnitude of dielectric dispersion was found by FERNANDO et al., (1975) who suggested that this could be used in the

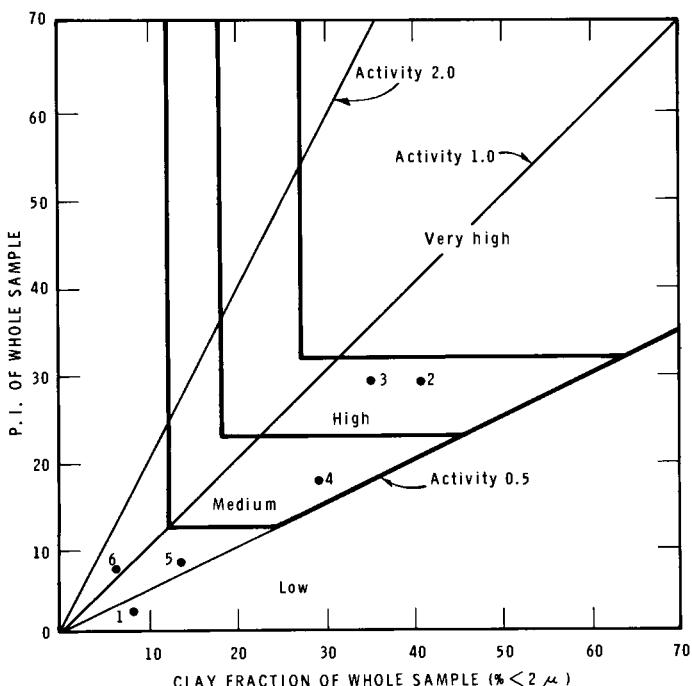


Fig. 6.5 Determination of potential expansiveness of soils. (After VAN DER MERWE, 1964, p.103. By permission of The South African Institution of Civil Engineers.)

classification of the swelling potential of soils.

Attempts to estimate rate and amount of heave have been made on the basis of consolidation theory in terms of the effective stress principle. Account was taken of pore air pressure as well as pore water pressure in partly saturated soils (JENNINGS and BURLAND, 1962; JENNINGS and KERRICH, 1962; BISHOP and BLIGHT, 1963; BLIGHT, 1965a,b; BURLAND, 1965). Dissatisfaction with results based on the effective stress principle, particularly in the case of unsaturated soils, have led to various other suggestions. For example AITCHISON (1973 a, b) proposed use of instability indices which are similar in principle to the compression index in consolidation. FREDLUND and MORGENSEN (1977) used a stress state variable approach based on multiphase continuum mechanics. In their treatment they considered an unsaturated soil to be made up of four phases - gas, liquid, solid and the air-water interface, treated as a separate phase. They thus visualized an element of unsaturated soil as a mixture of, "two phases that come to equilibrium under applied stress gradients (i.e. soil particles and contractile skin) and two phases that flow under applied stress gradients (i.e. air and water)." In general, construction procedures for building on expansive soils have been based on a combination of factors involving classification, experience and experimental observation coupled with semi-empirical methods of calculation and design considerations.

The increase in volume which actually occurs on moisture uptake is commonly estimated by consolidation tests, by use of the double oedometer (Ch. 12) or by measurements of change in soil moisture suction (DESAI and CHRISTIAN, 1977; JOHNSON, 1979). The volume increase is a function of the load on the soil, the degree of saturation, access to moisture, changes in moisture regime due

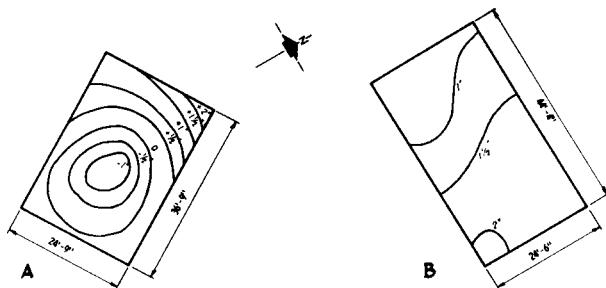


Fig. 6.6 Contours of slab-on-ground movements, Regina, Sask. (After Hamilton, 1965. Reproduced by permission.)

A. Floor slab contours on July 19, 1960, relative to assumed level condition at time of construction: October 28, 1955.

B. Floor slab contours on July 9, 1964, relative to level condition at time of construction: July, 10, 1960.

to construction and the swelling pressure. Changes in dimensions have been expressed quantitatively on the basis of both linear and volumetric measurements and swelling pressures have been determined experimentally by workers using different sorts of apparatus (GROSSMAN et al., 1968; FRANZMEIER and ROSS, 1968; AMERICAN SOCIETY FOR TESTING AND MATERIALS, 1983). Statistical methods indicate correlation between swelling pressure and a combination of density, moisture content and liquid limit (KOMORNÍK and DAVID, 1969). Pressures have been reported which vary from a fraction of a ton per sq. ft. (< 50 kPa) to pressures of the order of 5 to 12 tons per sq. ft. (500 to 1200 kPa) when smectite minerals are present. As such pressures exceed the load normally placed on soil due to construction heave may cause serious foundation problems (Fig. 6.6). The magnitude of the swelling pressure depends on circumstances and on the nature of the soil. Significant variables are the mineralogy, the fabric, the composition and concentration of pore solutions and the degree of saturation, consolidation and cementation.

Of all the clay minerals montmorillonite saturated with sodium as exchange ion has the greatest potential for expansion. Crystals of this mineral dissociate in water into platelets which are of the same order of thickness as the unit cell (10\AA). The sodium exchange ions and water molecules occupy the space between the sheets. When water penetrates between the unit layers of a crystal in this manner the resulting volume expansion is described as intra-crystalline swelling. The term intercrystalline swelling is used when the uptake of water is restricted to the external crystal surfaces and the void spaces between the crystals (Fig. 6.7). Apart from the smectites other minerals with expanding lattices which are capable of taking up water on internal surfaces include vermiculite, swelling chlorites, halloysite and some inter-stratified mixed-layer minerals. The extent of swelling is more restricted than in the case of Na-montmorillonite. When water can gain access to internal surfaces the volume imbibed per unit mass of clay is much greater than when only external surfaces are involved so the dimensional change is larger.

When intra-crystalline swelling takes place it does so because the attractive forces linking together the sheets are lower than the attractive forces responsible for the moisture uptake. The remarkable behaviour of the expansive clay minerals results not from a difference in the nature of the forces involved but from differences in their magnitude. This arises from a combination of factors the most important of which concerns the crystal chemistry of the minerals. In structure, montmorillonite is superficially similar to the non-expanding mineral illite. In illite, however, there is a higher charge per unit area of surface than in montmorillonite. Furthermore the negative charge is located in the tetrahedral layer and is closer to the

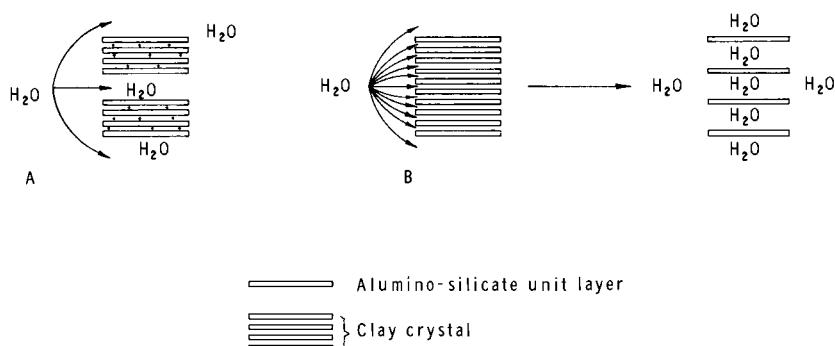


Fig. 6.7. Moisture uptake by clay minerals. A. With non-expanding lattice. B. With expanding lattice.

interlayer cation than in montmorillonite where the charge is concentrated in the octahedral layer. Hence the interlayer bond in illite is stronger and water and other liquids are normally unable to penetrate between the layers.

The first molecules of water taken up on the surface of a clay mineral are strongly held. Attractive forces arise from different mechanisms some of which have been described in Chapter 5. The negative charge on the basal surfaces and the positive charge sometimes present on edge surfaces will both attract water because of the polar nature of that molecule. Hydrogen bonds may be expected to form between the water molecules and the oxygen atoms of the surface. Bonding may also occur between water molecules and surface hydroxyls. It has been suggested also that exchange cations, particularly when small and highly charged hydrate and surround themselves with an envelope of oriented water molecules (MERING, 1946; MACKENZIE, 1950). It is certain that the nature of the interlayer cation does have an effect on water uptake. Ca-montmorillonite commonly takes up only two layers of water whereas Na-montmorillonite imbibes more water the amount being variable. In pyrophyllite and talc there are no ionic substitutions in the structure so the sheets are neutral. No interlayer cations are present and the layers are held together by Van der Waals forces. These minerals do not show interlayer swelling and this supports the contention that ion hydration plays a large part in the initial stages of water uptake by clay minerals. Cogent though this argument is it also has to be noted that the layer separations in talc and pyrophyllite are less than in the expanding 2:1 layer structure clay minerals. There the interlayer attraction arising from Van der Waals forces will be stronger and more resistance will be offered to interlayer hydration than in the case of such minerals as the smectites. Colloid chemical

reasoning based on adsorption data lead VAN OLPHEN (1954) to conclude that it was not possible to differentiate between hydrogen bonding to the surface, ion hydration, or both as the factor mainly responsible for the energy of water uptake by clay surfaces. GIESE (1978) calculated the energy necessary to expand a layer structure and concluded that minerals of this type can be subdivided into three major groups which have common bonding properties.

Uptake of water at greater distances from the clay mineral surface involves a different mechanism. Beyond the first few monolayers water is thought to be imbibed in response to a concentration gradient. This arises because there are more ions per unit volume of solution in the vicinity of a clay-mineral surface than in the bulk of the solution. Water uptake therefore dilutes the double layer solution the concentration of which is made more similar to that of the solution outside the double layer. If pore solutions are concentrated, however, swelling due to this mechanism is likely to be limited. This stage of moisture uptake has been analyzed in terms of osmotic theory and from the viewpoint of the Donnan membrane principle (LANGMUIR, 1938; SCHOFIELD, 1946; VERWEY and OVERBEEK, 1948). It has also been suggested as an alternative to this view that the orientation of water molecules which may exist close to the clay-mineral surfaces may be perpetuated in succeeding layers (HENDRICKS and JEFFERSON, 1938; LOW AND ANDERSON, 1958) and so may contribute to the mechanism of moisture uptake. Ion hydration probably has a disrupting effect on the regularity of the water structure so that beyond the first few monolayers it seems most likely that water uptake results from an osmotic-type mechanism.

Hence moisture uptake by a clay mineral can be thought of as occurring in two stages though the dividing line is not sharp. In the sorption of the first few monolayers surface chemical and ion-hydration effects are of greatestest importance. The uptake of water at distances greater than about 10\AA from the surface probably involves osmotic or Donnan equilibrium-type processes (Fig. 6.8). The relative contribution of these two mechanisms to the total moisture uptake remains unclear. In all cases van der Waals attraction will also contribute to the total amount of water associated with the clay minerals. CEBULA et al., (1979) listed voids, edge-to-face stacking, regions of gross folding, ordered domains, regions of disordered stacking and the spread in orientation of the platelets as factors of importance in the clay-water system. They concluded that at low water contents about 10% of platelets are randomly oriented while the remainder are partially oriented with a spread of about 40° about the mean orientation in the montmorillonite-water system. RAVINA and LOW (1977) reported a relationship between the b-dimension of montmorillonite and the water-content at maximum swelling. They found that the water-content at maximum swelling decreased as

the b-dimension increased and that this occurred whether the change in b-dimension resulted from isomorphous substitution or from the nature of the exchange cation. The effect was considered due to epitaxy. A similar relationship between swelling and b-dimension was reported by ODOM and LOW (1978).

PROST (1975) used water-vapour adsorption isotherms, changes in basal spacing with relative humidity and infrared spectroscopy in studies of clay-water interaction. He reported that Na-beidellite shows an adsorption isotherm with two steps whereas Ca-beidellite, Na-montmorillonite and Na-hectorite adsorb water continuously with increase in relative humidity. The spacing of Na-hectorite however was found to increase by steps. The first step was attributed to the formation of wedges resulting from hydration of exchange cations by one or two water molecules; the second step was attributed to wedges formed by further hydration of exchange cations by six water molecules. He interpreted the continuous uptake of water between steps as due to the infilling of voids between wedges and to the accumulation of water on external surfaces. Infrared spectroscopy has shown that adsorbed water molecules or exchangeable cations perturb the structural OH-groups of clay minerals. PROST (1975) used infrared methods to observe the percentage of

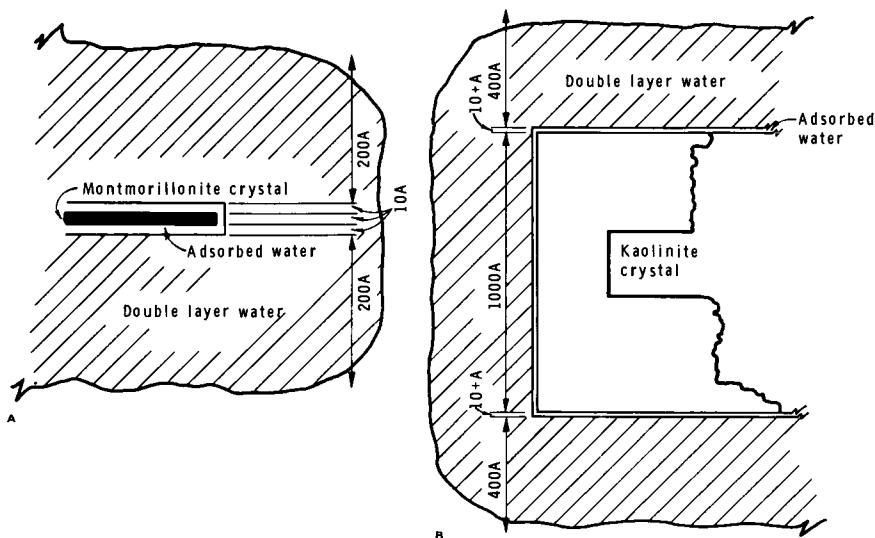


Fig. 6.8 Relationships of clay crystals to surface and double layer water. (After LAMBE, 1958b, p.17).

- A. Typical montmorillonite particle 1,000 Å by 10 Å.
- B. Typical kaolinite particle 10,000 Å by 1,000 Å.

perturbed OH-groups on various clay minerals and so deduced the quantity of adsorbed water in interlayer spaces and above external hexagonal cavities. Conversely he distinguished the quantity of adsorbed water not in contact with the clay surface as external water.

Values obtained by experimental measurement of swelling pressure have been compared with those calculated from double layer theory according to methods described by LANGMUIR (1938), SCHOFIELD (1946) and VERWEY and OVERBEEK (1948). In the pressure range from 0.2 to 50 atm fairly good agreement has been obtained in experiments using Na-montmorillonite but Ca-montmorillonite exerted smaller pressures than predicted by theory (WARKENTIN et al., 1957). It is thought that stacks of platelets termed tactoids form the sizes of which have been estimated from x-ray and other data by BLACKMORE and MILLER (1961). The stability of tactoids has been discussed on the basis of an electrostatic model by KLEIJN and OSTER (1982). Once conditions favour tactoid formation the individual platelets may be relatively strongly held so interlayer expansion is restricted. Swelling by the osmotic mechanism takes place only on external surfaces of the oriented packets of platelets where diffuse double layers are developed. Consequently the overall increase in volume is reduced.

Further work concerning the effect of solution concentration and compaction on the mechanisms of swelling has been carried out by PARKER et al., (1980). They found that Ca-montmorillonite in 0.01N CaCl_2 solution had an estimated intracrystalline expansion which was about 4x greater than the estimated osmotic expansion; in 0.001N CaCl_2 solution the intracrystalline expansion was only about 1.5x greater thus supporting an osmotic component to swelling. Higher expansions in $\text{Ca}(\text{H}_2\text{PO}_4)_2$ than in CaCl_2 solutions, of the same concentration, were taken as evidence that edge-to-face bonds limit expansion in the CaCl_2 solution. Density differences, produced by dry static compaction under different loads, were associated with significant differences in measured water adsorption. This was attributed to pressure ahead of advancing wetting fronts generated by compression of gases trapped in pores. Indeed this factor was thought responsible for about 50 to 75% of the total swelling in 0.01N CaCl_2 . An inverse relationship of gas pressure to pore size, predicted by the Laplace equation, was used to support the suggestion. Presumably further support could be obtained if the volume change was measured as water was admitted to degassed samples under vacuum. Other factors which may influence volume change characteristics include TERZAGHI'S (1927) concept of crystal bending on drying followed by relaxation on rewetting. Pore spaces and interstices may trap water in amounts which will vary with changes in the arrangement of the fabric elements.

The influence of fabric on volume change characteristics is interrelated with the influence of pore solutions the nature and concentration of which

largely determines whether a parallel oriented arrangement, an arrangement with edge-to-face bonds, or a random arrangement is stable. Clay samples containing a moisture content less than the optimum for maximum compacted density, and believed to have a flocculated fabric, were found by SEED and CHAN (1959, p.92) to exert greater swelling pressures than samples compacted wet of optimum and believed to have a more strongly oriented fabric. This result is unexpected since one would anticipate the potential volume of water uptake and the swelling pressure to be greater for a larger surface area between the interacting platelets. Hence in uncemented clays a parallel oriented arrangement of platelets if stable would be expected to be potentially more expansive than a clay with a flocculated fabric. Changes in pore solution, however, may affect the stability of the fabric and could be expected to cause the clay to have a considerable potential for volume change.

Studies of the relationship between porosity and permeability (p.180) and the disappearance of a bimodal pore size distribution have been used as evidence of the closing of an interaggregate pore system in soils compacted on the wet side of optimum moisture content. This suggestion and the possible presence of aggregations need to be considered in trying to account for the greater swelling pressure exerted by samples compacted dry of optimum. It seems possible that capillary forces play a larger role in the drier system and so help to account for the reported difference in swelling pressure.

Cementitious agents which bond minerals together tend to limit swelling both by increasing the strength of the material which places an internal restraint upon expansion and by reducing the surface area available to take up moisture. SRIDHARAN and ALLAM (1982) have provided evidence in support of this concept. They suggest that cemented aggregations are particularly common in soils subjected to repeated wetting and drying, the effect of desiccation being similar to heavy over consolidation. Two principal mechanisms which control volume change behaviour are proposed. In mechanism I volume change is controlled mainly by the shearing resistance at contact points between aggregations. In mechanism II long range forces associated with the hydrous double layers are of prime importance. They suggest that when sufficiently strongly bonded aggregations are present the response of the soil to volume change is mainly controlled by mechanism I. This behaviour is thought typical of soils containing non-swelling clays but is also sometimes found even when swelling clay minerals form a significant component in the soil. Soils which are composed of swelling clay minerals which are disaggregated or only lightly aggregated respond mainly by mechanism II.

It is hardly surprising that exact agreement is not always obtained between experimental and calculated values since the theory of VERWEY and OVERBEEK

(1948) was derived for dilute colloidal suspensions. Furthermore most calculations are based upon a parallel plate model of clay structure and edge-to-face bonds are neglected. When clays gain or lose water structural change and stress relaxation probably occurs and may well account for lack of agreement or poor reproducibility in experiments involving cycles of compression and decompression. These effects can not be allowed for quantitatively in any current theoretical treatment. These limitations of the theory together with the concept of structural change as a factor in the moisture expansion of clays has led to the general conclusion that when misorientation between clay minerals and clay-mineral packets and "dead volume" are taken into account swelling behaviour of clays is not incompatible with double layer theory.

Volume decrease

The volume of a soil may decrease because of consolidation under load due to expulsion of water, because of changes in fabric which in certain soils even lead to volume decrease on water uptake, and because of moisture loss due to drying or transpiration from plants. Consolidation has been discussed previously (p.69-74); it normally leads to a gain in shear strength if there is no build-up of excess pore-water pressure. Therefore knowledge of flow-rate is useful because, among other things, the appropriate time intervals may be deduced after which the addition of suitable pre-loading increments may be made for optimum strength gain.

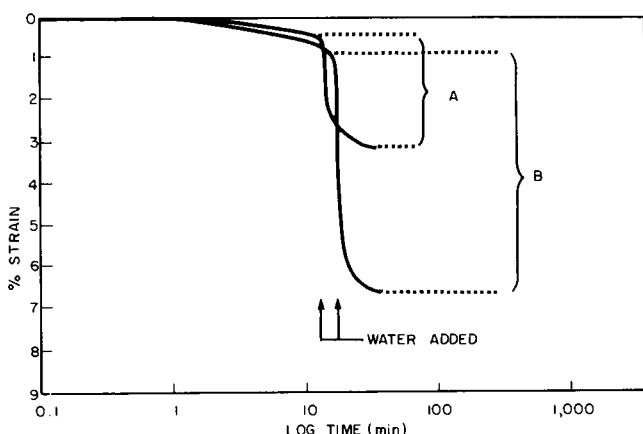


Fig. 6.9. Decrease in bulk volume of two samples of loess, A, B on moisture uptake (Adapted from CLARK and GILLOTT, 1985).

Volume decrease on water uptake seems contradictory because soils commonly swell when they take in water. The decrease in the bulk volume (Fig. 6.9) occurs because the soil minerals assume a more close-packed arrangement (Fig. 6.10A, B). This behaviour is termed soil collapse, subsidence or hydroconsolidation and may occur even when there is no additional loading. Soils which behave in this way are relatively common and include loess, some residual and alluvial deposits and man-made fill materials. Collapsing soils characteristically have an open fabric and high void ratio and are made-up of particles of sand, silt, shale or, possibly, of flocculated clay platelets. The grains are weakly bonded at points of contact by clay, by surface tension forces in water partly filling capillary spaces, or by chemical deposits (Fig. 6.11). The clay may be authigenic having formed by weathering of primary minerals or may be allogenic. The clay may have been introduced in suspension and deposited to buttress cusps by periodic evaporation of suspensions percolating through the pore system or the silt or sand particles may have had a clay-coating on deposition (Fig. 6.12). Residual deposits sometimes develop an open fabric due either to leaching of soluble materials or to removal by eluviation of fine-grained and colloidal materials.

The interparticle bonds help to maintain the metastable loose packing of the open fabric. If, under an existing or increased load, the interparticle bonds are weakened the grains may assume a more closely packed arrangement with decrease in the bulk volume of the deposit. This may result from moisture uptake since on saturation menisci disappear as capillary spaces are filled and so there is a decrease in the overall contribution of surface tension forces to bonding. Water may also remove chemical cements in solution and bonds due to clay may be weakened by water uptake or because the clay is removed in suspension. Moisture uptake by clay lumps with softening and distortion has been considered a factor in the hydroconsolidation of partly saturated fill material by DUSSEAUT et al., (1985). Saturation may result from a rise in the ground-water table due to increased precipitation caused by climatic change, irrigation, leakage from pipe-lines and other utilities, discharge of industrial waste-water, and from flooding. Change in the moisture regime may also result from such construction practices as placement of concrete cover or change in the vegetation.

Fill materials have differences in fabric when compacted at different water contents. These materials sometimes have a potential for collapse when the moisture content is on the dry side of optimum for maximum compacted dry density (Fig. 8.1). ALTSCHAEFFL (1982) concluded that there is a rapid increase in the magnitude of collapse when the water content falls below 1½ to 2½ per cent of optimum. LLORET and ALONSO (1980) developed a general model

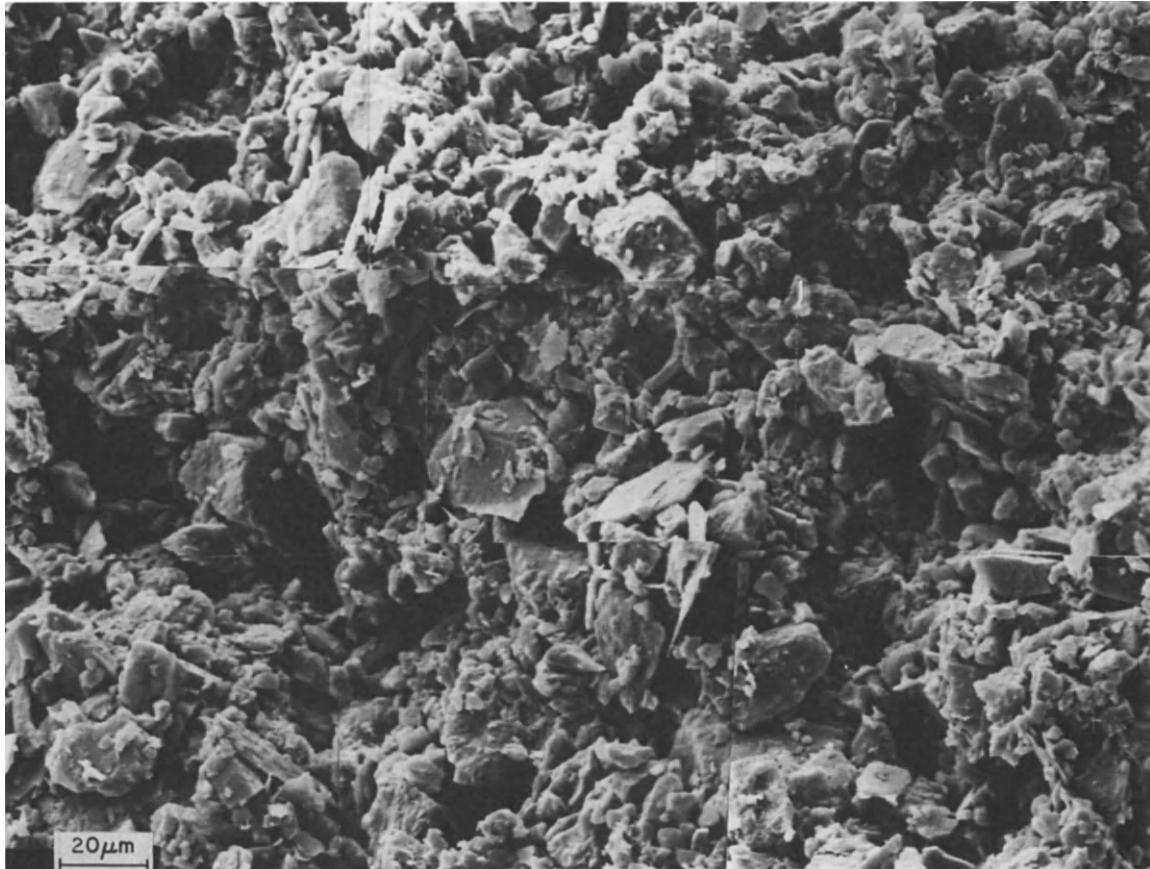


Fig. 6.10A Mosaic of scanning electron micrographs of loess, "undisturbed". Kamloops, B.C., Canada

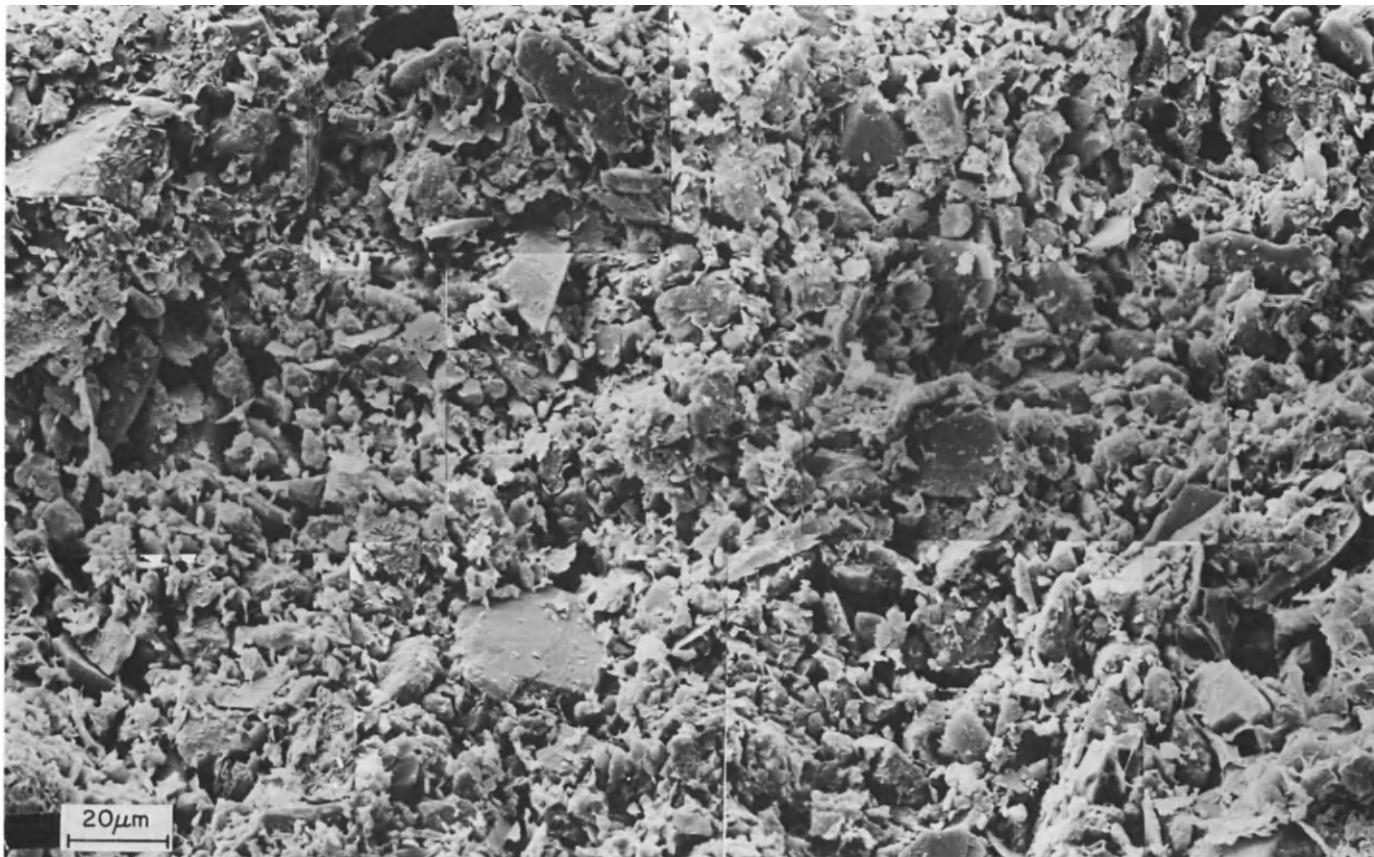
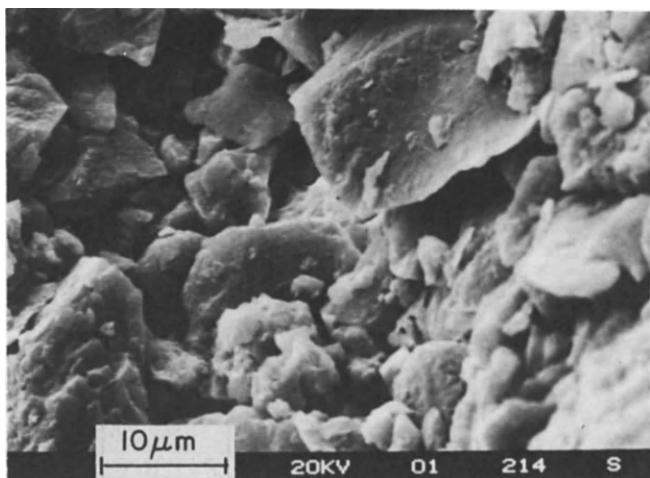
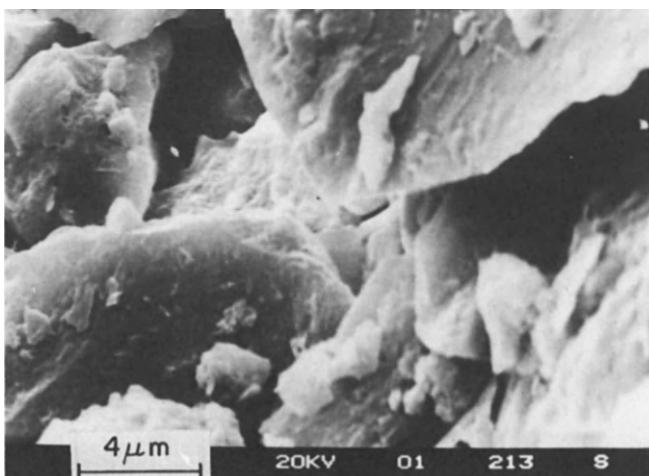


Fig. 6.10B. Mosaic of scanning electron micrographs of loess, "collapsed". Kamloops, B.C., Canada

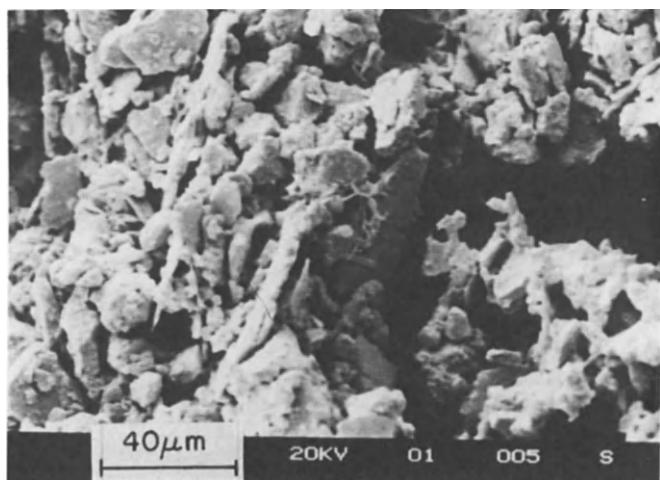


A. Cusp buttressed with clay or chemical precipitate. Loess, U.S.S.R.

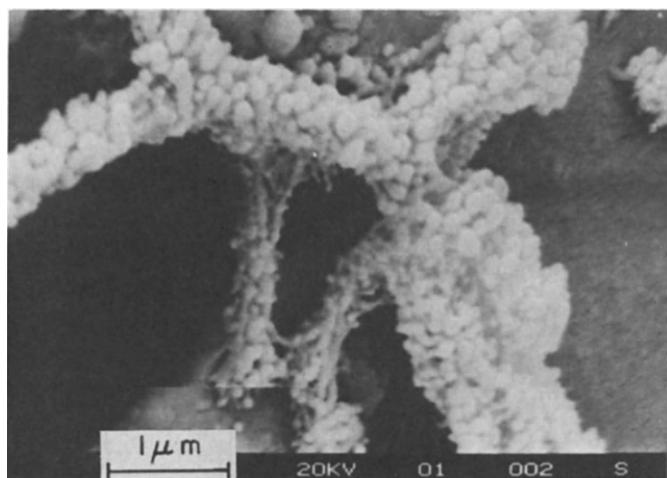


B. Cusp buttressed with clay or chemical precipitate. Loess, U.S.S.R.

Fig. 6.11 Scanning electron micrographs of contact relations between minerals in loess.

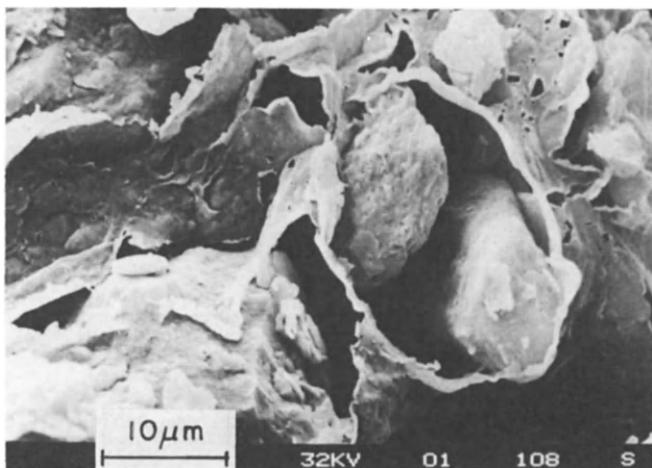


C. Chemical precipitate on clay. Loess, Kamloops, Canada.

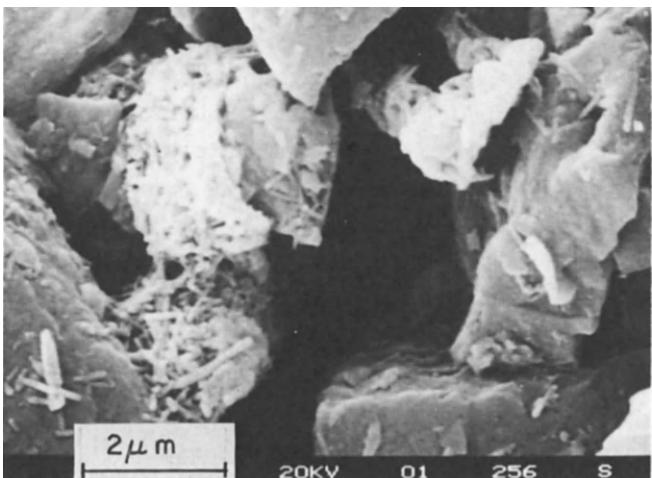


D. Chemical precipitate on clay. Loess, Kamloops, Canada.

Fig. 6.11 Scanning electron micrographs of contact relations between minerals in loess.



E. Clay coating silt. Loess, Kamloops, Canada



F. Precipitate or agglomeration in silt. Loess, Kamloops, Canada.

Fig. 6.11 Scanning electron micrographs of contact relations between minerals in loess.

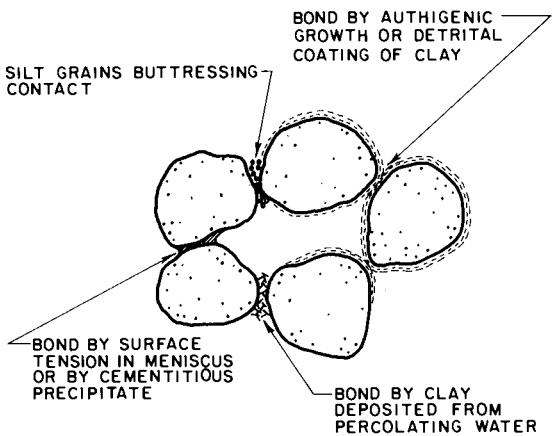


Fig. 6.12. Schematic of collapsing soil (Adapted from Dudley, 1970; Barden et al., 1973).

for the complex joint swelling-collapse behaviour of unsaturated soil. Changes in the air-water menisci and the redistribution of interparticle stress were considered responsible for the inability of the effective stress principle to predict volume change behaviour. Monitoring of both air and water pressure as well as measurement of volume change under load are required. Behaviour may be interpreted from plots of void ratio versus two of three possible stress variables in three possible combinations. The load at which a compacted soil changes from swelling to collapse behaviour depends on the compactive energy, water content and soil type, particularly the nature of the clay fraction.

Soils liable to collapse behaviour have been recognized by use of index tests combined with the determination of moisture content and soil density. JENNINGS and KNIGHT (1975) described the use of a double consolidation test to estimate the potential magnitude of collapse and other tests have been used in design. The subject has been discussed in detail by DUDLEY (1970), BARDELL et al., (1973), KNODEL (1981), CLEMENCE and FINBARR (1981) and MINKOV (1984).

As the moisture content of a soil or wet clay is decreased there is a proportional reduction in volume until the shrinkage limit is reached. On further drying air enters void spaces in place of water and the volume of the material decreases only very slightly. Shrinkage properties may be represented diagrammatically (Fig. 6.13). The volume occupied by a soil at a given moisture content is generally smaller on re-wetting than it was before an original drying cycle; such hysteresis effects are generally smaller for compacted samples. Many present day shrinkage concepts derive from work

carried out by HAINES (1923). Surface tension forces exist at an air-water interface and these forces increase as capillary pore diameter decreases. Since pore diameter decreases with decreasing particle size the force becomes considerable in clays. It is probable that drying shrinkage is largely due to surface tension forces.

Drying of the soil may be accompanied by formation of shrinkage cracks which significantly affect both the depth and the rate of drying. The soil suction (pF) gives a good indication of the tendency of a clay soil to shrink or swell but the magnitude of the volume change is often difficult to predict. This depends upon the type of soil, the moisture regime, the climate and the type of vegetation. The soil itself is influenced by the depth and pattern of cracking and by the presence or absence of permeable seams or lenses. The type of clay in a soil has a particularly important effect on the shrinkage characteristics and the amount of movement. The amount of shrinkage is also affected by the packing arrangement of the particles. In some soils such as the Leda clay in eastern Canada part of the decrease in volume which takes place on drying is permanent and the original volume is not recovered on moisture uptake. This may have serious engineering consequences. Such irreversible changes in volume probably reflect permanent changes in fabric.

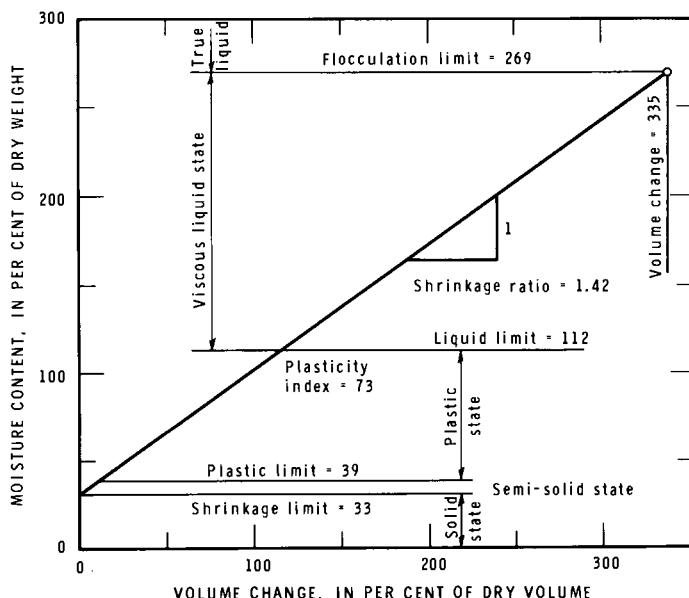


Fig. 6.13. Shrinkage diagram to show relation between loss of moisture and loss of volume of muck soil on drying. (After HOGENTOGLER, 1937, p.107.)

Water is removed from the soil not only by evaporation and drainage but also by transpiration from plants (Fig. 6.4). Those which have the greatest effect are the deep rooted varieties which include certain types of trees particularly poplar, elm, oak and possibly willow (BIDDLE, 1983). Plants do not extract water when the moisture content falls below the wilting point which corresponds to about 4.2 pF (Fig. 6.2). At this point the moisture content is generally above the shrinkage limit in soils of high clay content but below this value in soils of low clay content. Volume changes may be progressive when the plant cover is changed or may vary with the season in a cyclical fashion. If trees are removed from soil which has established an approximate moisture equilibrium heave is probable particularly when there is some degree of desiccation in the soil. Watering of plants by gardeners also alters the natural soil moisture regime.

In house construction in particular it is uncommon to carry out detailed soil investigations and, in general, when semi-quantitative methods only are used potential volume change characteristics are estimated from index properties and moisture content. The plasticity index, liquid limit and shrinkage limit are commonly employed. In general soils with a high clay fraction (> 95%) and high plasticity index (> 35%) have a very high shrinkage potential and soils with a low clay fraction (< 30%) and low plasticity index (< 18%) have a low shrinkage potential. In more detailed work various authors have derived useful information by relating plots of moisture content versus suction to index properties.

Consideration of rates of change of moisture content with suction led DRISCOLL (1983) to conclude that linear relationships exist between liquid limit (LL) and moisture content (w) given by $w=0.5 \text{ LL}$ at 2 pF and by $w=0.4 \text{ LL}$ at 3 pF. If the first of these relationships is satisfied it may be concluded that desiccation has commenced; if the second relationship is satisfied the moisture content has been reduced to a point where sufficient stress may be mobilized in the soil on moisture uptake or moisture loss to damage lightly loaded structures since 3 pF corresponds to a pressure of about 100 kPa. In detailed laboratory investigations the consolidometer is used to determine the potential for shrinkage, expansion and uplift pressure (AMERICAN SOCIETY FOR TESTING AND MATERIALS, 1983). In recent field studies the thermocouple psychrometer has been used successfully to measure soil suction (WILLIAMS and PIDGEON, 1983). Other methods for field measurement of soil properties have been described however without emphasis on volume change characteristics (Conference on in-situ Measurement of Soil Properties, 1975). The potential use of electro-osmosis in the in-situ estimation of the coefficient of consolidation and volume change properties has also received consideration

(MITCHELL and BANERJEE, 1980; BANERJEE and MITCHELL, 1980).

Construction problems associated with volume changes of soils due to moisture gain or loss may be reduced in various ways (GROMKO, 1974; van der MERWE, 1980). The unstable soil may be replaced with a non-expansive fill but this may be technically impractical or too costly. A variety of methods of soil stabilization are available (see Ch. 8). These include physical stabilization by such methods as compaction and selective wetting, or chemical stabilization by addition of lime, cement or inorganic or organic chemicals. Moisture barriers are sometimes employed and drilled piers, piles or caissons may be anchored in competent rock or stable soil below the zone subject to moisture movement. This approach may be expensive and recent studies have shown that in arid regions expansive movements may extend to depths of 15 to 20 m which are much greater than commonly experienced (WILLIAMS and DONALDSON, 1980). The structure may be designed to accommodate movements by adopting semi-flexible or split construction techniques. When severe differential movements are predicted the effectiveness of these methods may be increased by use of movement gaps or joints. Articulated connections of beams to columns and columns to foundations may be incorporated. Construction on a stiffened slab or raft foundation is another alternative which is becoming of increased importance (LYTTON and WOODBURN, 1973; BURLAND and WROTH, 1975; POST TENSIONING INSTITUTE, 1978; WALSH, 1978; PIDGEON, 1979, 1980 a, b).

FROST ACTION

When the air temperature falls below 0°C the pore water in soils may freeze. Near the poles pore water remains frozen throughout the year; such permanently frozen ground has been termed permafrost. Such terrain is sometimes termed perennially frozen ground. In high latitude regions of the earth it attains a thickness in excess of 1000 m. Approximately one-fifth of the world's land area is affected by permafrost (J. E. BROWN and JOHNSTON, 1964). As lower latitudes are approached the permafrost becomes discontinuous. Frozen ground is overlain by the "active layer" which freezes in winter and thaws in summer. This also occurs where there is no perennially frozen subsoil in temperate climates and at high altitudes close to the equator. The thickness of the active layer varies from a few centimetres to a few metres. The effects of repeated cycles of freezing and thawing constitute frost action.

The depth to which frost penetrates the ground depends upon the nature of the soil, the nature and composition of the pore water, the temperature of the air and the time for which the temperature remains below the freezing point.

It is affected also by other factors such as depth of snow cover and climate. An estimate of probable depth of frost penetration may be made by use of the freezing index, F. This is measured in units of degree days which are calculated from the air temperature and the time for which below freezing temperatures are recorded. The mean temperature between day and night is used. Thus if the average temperature is -6°C (22°F) for 1 day then -6 degree-days Celsius (-10 degree-days Fahrenheit) for that day are registered. The freezing index is the total number of degree days below freezing for a winter. Depth of frost penetration has been considered proportional to the square root of the freezing index. Use of the relationship has been described by MCCORMICK (1971) and others. Maps have been produced which show the distribution of the mean freezing index in different geographic areas.

Freezing may generate expansive forces causing heave. The conversion of water into ice is accompanied by a 9% volume increase and the generation of large pressures. The heave resulting from this cause may, however, be much



Fig. 6.14. Disruption of concrete pavement caused by heave due to growth of ice lens, Ottawa, Canada. (Photograph: Division of Building Research, National Research Council, Canada. Reproduced by permission.)

less than that caused by the growth of ice lenses (Fig. 6.14). These are "ice formations in soil occurring essentially parallel to each other, generally normal to the direction of heat loss, and commonly in repeated layers" (HIGHWAY RESEARCH BOARD, 1955) (Fig. 6.15). Their growth may continue indefinitely due to the inflow of extra water resulting in a considerable increase in volume before conditions favourable to their development are terminated. Amount of heave is affected by temperature regime, nature of the soil, availability of water and overburden pressure.

In permafrost areas ice wedges and pore ice are present in addition to thick ice lenses. In lake and marine clays, fine-grained glacial tills and mudflow deposits MacKAY (1974) and others have described a three dimensional ice-vein network pattern which subdivides frozen soil into irregular blocks. Moisture has evidently migrated to form the essentially mineral-free ice and the dewatered soil blocks are often overconsolidated when thawed. The reticulate pattern is thought to result from ice filling cracks which formed on shrinkage of the clay due to moisture loss. Although the clay blocks are themselves well consolidated the discontinuities may lower overall soil strength and may raise overall permeability. These observed structures have



Fig. 6.15. Segregation of ice in varved clay. (Photograph: G.H. Johnston, Division of Building Research, National Research Council, Canada. Reproduced by permission.)

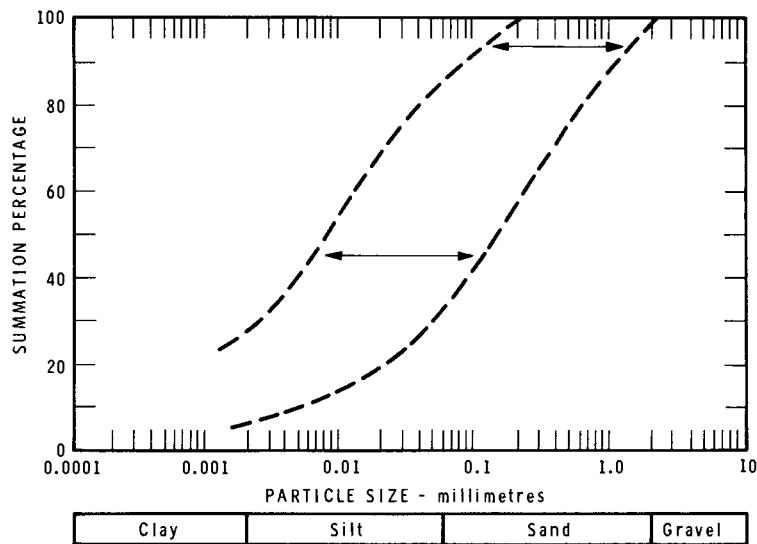


Fig. 6.16. Particle-size limits within which soils are likely to be frost susceptible. (After CRONEY, 1952, p.282).

relevance not only to regions where permafrost exists today but also to soils in many formerly glaciated areas. In such regions structures which formed when low temperatures prevailed may affect present soil behaviour and may make it unexpectedly complicated.

At an early date it was observed that ice lenses did not develop in all soils but formed most readily in silts and lean clays; growth was related to grain-size (TABER 1929; BESKOW, 1935). CASAGRANDE (1931) concluded that as a general rule non-uniform soils which by weight contain more than 3% of grains smaller than 0.02 mm in diameter and very uniform¹ soils which contain more than 10% smaller than 0.02 mm, are liable to show considerable ice-lens formation if an adequate water supply is available. Similar conclusions have been reached by other workers (Fig. 6.16) (CRONEY, 1952). Grain-size criteria though not absolute in themselves are the basis of most systems of classification for recognition of frost-susceptible soils. Soils are classified by the U.S. Army Corps of Engineers in order of increasing frost-susceptibility as F1, F2, F3 and F4 (JOHNSON et al., 1975). F1 soils are gravelly with 3 to 10 per cent finer than 0.02 mm by weight; F2 soils are gravelly soils or sands

¹ See pp. 379 for engineering use of particle size terms.

with 10 to 20 or 3 to 15 per cent finer than 0.02 mm respectively. F1 material may be expected to show higher bearing capacity than F2 material during thaw. Soils in the F3 category are subdivided into three groups a, b and c: in group a, are gravelly soils with more than 20 per cent finer than 0.02 mm; in group b are sands, except fine silty sands, with more than 15 per cent finer than 0.02 mm; and in group c, are clays with the plasticity index greater than 12 per cent, except varved clays. The F4 category is subdivided into four groups a to d. In group a, are silts, in group b, are very fine silty sands with more than 15 per cent finer than 0.02 mm, in group c, are lean clays with plasticity index less than 12 per cent and in group d, are varved clays. The F3 and F4 soils show the greatest weakening during thaw. Frost susceptibility has been based on criteria other than grain size such as pore size distribution (REED et al., 1979), maximum heave pressure generated, ice segregation ratio and rates of heaving in laboratory tests. PENNER (1981) used a step freezing test in which initial rate of heaving is employed.

The formation of ice lenses requires a supply of water so a high water table or perched water table favours their formation assuming soil type and freezing conditions are also favourable. If too much clay is present it reduces permeability and so limits the rate at which water can be supplied to the nascent ice lens so growth is inhibited. Different clay minerals produce different effects on susceptibility to frost heaving (ENDELL, 1935, 1941; LAMBE and MARTIN, 1953).

The nature and concentration of the ions in the pore solutions also has an effect. When polyvalent ions are present more migration of water takes place than when monovalent ions are present. This most probably results from differences in permeability due to changes in fabric caused by the flocculation state of the clay minerals. The growth of the ice crystals themselves is also affected. When polyvalent cations are present the ice crystals grow mainly along the optic axes. When cations are monovalent growth is mainly along the basal plane and orientation is random (TYUTYUNOV, 1964).

Drying of soils is accompanied by a progressive reduction in the freezing point of the water which remains. SCHOFIELD (1935) showed that a relationship exists between the suction, or tensional force at a given moisture content by which water is drawn into unsaturated soil, and the temperature at which freezing commences in the absence of supercooling. Thus suction and freezing point may be related and the higher the suction the lower the freezing point. Thus as the temperature of a given soil is decreased more water is converted into ice and the remaining water is under increasing suction. WILLIAMS (1982) has illustrated this point differently. He showed that curves of both permeability and unfrozen water content when plotted against temperature below

0°C are similar in form so that there is certainly some correlation. The problem however is complicated. For example it has been shown that the suction towards the freezing interface decreases with increase of overburden pressure and above a certain pressure (sometimes termed the shutoff pressure) moisture is expelled from the freezing zone. The pressure at which this occurs is affected by the soil type and its particle size distribution, the stress history, temperature regime and other factors (PENNER and WALTON, 1979).

Water in close proximity to a mineral is affected by surface forces the intensity of which increases as the surface is approached. Clay minerals have a high specific surface area and in clay soils surface effects are of considerable importance. The mobility of the water molecules within the range of the surface forces is decreased and calorimetric studies have shown that such water will not freeze until temperatures are below 0°C. The depression of the freezing point depends in part upon the intensity of the force field and decreases with distance from a surface so freezing takes place over a range of temperatures. In addition to the effect of surface adsorption and the hydrous double layer on clay minerals freezing point depression results also from capillary phenomena and solution effects. Much of the water in fine-grained soils remains unfrozen until temperatures which are considerably below 0°C (BOUYOUCOS and MCCOOL, 1916).

The reason why ice grows as a lens generating heaving pressures instead of propagating downwards through the pores has provoked extensive investigations. It has been suggested that the energy required is derived from the freezing of soil water at supercooled temperatures (TABER, 1929). Once ice formation in soil has been initiated its downward propagation through fine pores will not take place until some critical lowering of the temperature below freezing point has occurred. However, migration of soil moisture to the ice is possible due to the establishment of a suction gradient (Fig. 6.17).

Ice lens growth involves the complex problem of coupled transport of both water and heat. The Clausius Clapeyron equation has been used as the basis of several attempts to analyze the situation. In older literature it was customary to consider heave in terms of a frost line whereas it appears now that a freezing zone or "frozen fringe" separates the 0°C isotherm from the somewhat lower temperature isotherm at which ice lens growth takes place. Water migration may take place through this frozen fringe via films of unfrozen water close to mineral surfaces. Liquid water and film water in contact with mineral surfaces have a higher free energy than ice so the potential (or suction) gradient favours migration of water towards the ice lens. MILLER et al., (1975) have proposed that ice movement involving a

process of regelation is also a significant factor. Transport of heat and moisture take place via the ice itself whenever mineral particles are separated from ice by an unfrozen film. It is argued that heat of fusion is consumed by phase changes at each "windward" ice-film interface and liberated at "leeward" interfaces. Transport of heat therefore occurs in a direction opposite to that of ice movement. Hence mass movements may occur in a zone of frozen soil via both pore ice and unfrozen films. The problem has been discussed by many authors and in various symposia (FONDATION FRANCAISE D'ETUDES NORDIQUES, 1979; ENGINEERING GEOLOGY, 1979; 1981; PENNER and WALTON, 1979; KONRAD AND MORGESTERN, 1984).

Frost action may cause damage to foundations due to thawing as well as freezing. The spring thaw penetrates frozen ground from the surface downwards so the near surface soil in which melting has occurred is underlain by impermeable soil which still contains ice. This impedes drainage so the soil in which the ice has melted often becomes over saturated, and may suffer an almost complete loss in strength so that foundation failure is a strong possibility. The spring break-up of surface pavement on trafficked roads

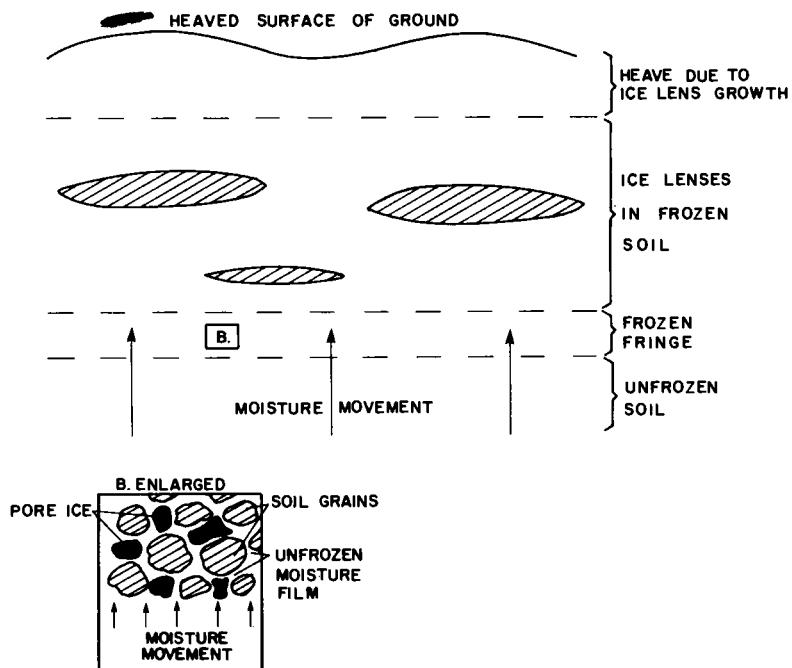


Fig. 6.17. Schematic illustration of moisture movement and ice lens growth causing frost heave.

often results from this cause (Fig. 6.18). Thaw-weakening may be more serious in a clay soil due to its low permeability than in a relatively more pervious frost-susceptible soil. Methods of decreasing the risk of damage to pavement include improved drainage, the placement of a sufficient depth of non frost-susceptible granular material above the soil to prevent freezing in the subgrade or the use of a design which makes allowance for the reduced strength of the subgrade during thaw; in the latter case a smaller thickness of granular material may be used. Various tests have been devised for evaluating the freeze-thaw durability of compacted soils, soil cement, soil lime and other partially stabilized highway materials (e.g. THOMPSON and DEMPSEY, 1976).



Fig. 6.18. Break-up of road surface due to spring thaw, Ottawa, Canada. (Photograph: Division of Building Research, National Research Council, Canada. Reproduced by permission.)

Artificial ground freezing to improve soil properties has been used in engineering for over 100 years. It has only achieved widespread application however during the last 10 or 20 years. The technique has been used in excavations, the sinking of shafts, construction of cofferdams, tunneling and in temporary stabilization of slides. Examples of its use and problems in the application of the method have been reviewed in ENGINEERING GEOLOGY (1979, 1980).

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Chapter 7

STRENGTH AND RHEOLOGY OF CLAYS

The strength of a material is measured by its capacity "to sustain the application of force without yielding or breaking" (FUNK and WAGNALLS, 1982, p. 1324). Under externally applied loads, materials develop internal reactive forces which depend on the nature of the load. A load may cause tension or compression, shearing, bending, or torsion in the material. Engineers employ relations to evaluate the magnitude of the tensile, compressive, and shear forces which a material can resist on load application. When the strength of a material is exceeded failure occurs by brittle fracture or by plastic yielding. In rheology the deformation of materials by flow is investigated. Strength and rheology determine the mechanical behaviour of clays. This is important to those engineers and geologists concerned with predicting such variables as the stability of slopes, bearing capacity and settlement. Strength and rheological properties of moist and dry clays are also of concern in the industrial use of clays as they affect processes and techniques such as are used in the forming of clay bodies in ceramics.

The strength and rheological properties of clays depend upon the extent of aggregation and cementation of the minerals, the nature of the minerals, their arrangement and packing density and on the mechanical, physical and chemical interaction of the minerals with one another and with entrapped pore solutions and air. The physical nature of water in close proximity to mineral surfaces and the amount of water and composition of solutions actually present are also important.

STRESS AND STRAIN

Stress is defined as force per unit area. When a randomly directed stress is applied to a plane solid surface it can be resolved into two components one at right angles, and the other parallel, to the surface. The component which is at right angles to the surface is defined as the normal stress, σ , and the component which is parallel to the surface is defined as the shear stress, τ (Fig. 7.1). A plane acted on only by a normal stress is termed a principal plane; such a plane is acted on by no shearing stress. In general there are three principal planes which intersect at 90° and three principal stresses known as the major principal stress σ_1 , the intermediate principal stress σ_2 , and the minor principal stress σ_3 , which act normally to the corresponding principal planes. The difference between the major and minor principal

stresses is termed the stress difference. When a force is applied to a plane which is inclined to the principal planes it is acted on by both a normal stress and a shear stress. The magnitude of these forces may be calculated from knowledge of the three principal stresses and the laws of statics.

Strain is the change induced by stress in the volumetric or linear dimension of a material body; distortion is change in shape and dilation is change in volume. If similar portions of a homogeneous body remain similar after deformation the strain is defined as affine or homogeneous. In affine strain a plane transforms into another plane, straight lines remain straight and parallel lines remain parallel. A sphere may be transformed into an ellipsoid, known as the strain ellipsoid, which has three unequal orthogonal axes termed the principal directions of strain. The strain ellipsoid has been much used in structural geology. There are several types of homogeneous strain which include simple or pure extension or compression, uniform dilation, pure rotation, general strain, pure shear, and simple shear. In pure shear (Fig. 7.2) a body is elongated in one direction and shortened at right angles to this so that there is no change in volume and the deformation is accompanied by no rotation of the principal planes. A strain of this type which is accompanied by rotation of the principal planes about the intermediate axis is termed simple shear (Fig. 7.2) (NADAI, 1950, pp. 109-113; TURNER and WEISS, 1963, pp. 269-272).

The deformation properties of materials are commonly represented graphically on a diagram in which stress is plotted as ordinate versus strain as abscissa. This graph generally shows an initial linear relationship between stress and strain as an applied force at first induces an elastic

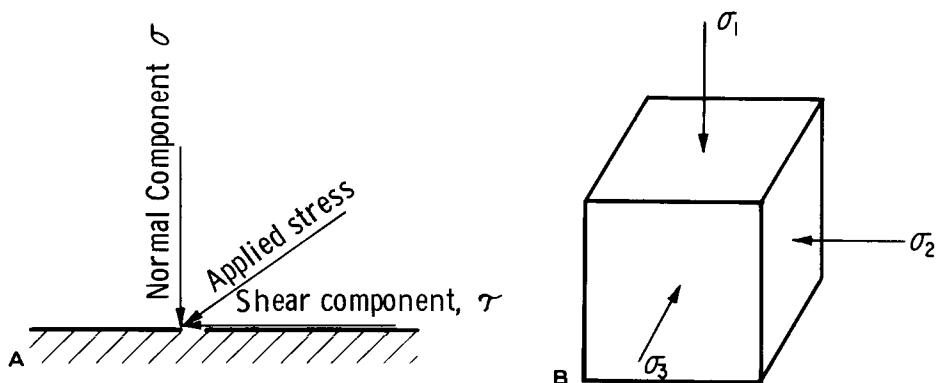


Fig. 7.1 Types of stress.

- A. Resolution of stress into shear stress and normal stress.
- B. Principal stresses. σ_1 =major principal stress; σ_2 =intermediate principal stress; σ_3 =minor principal stress.

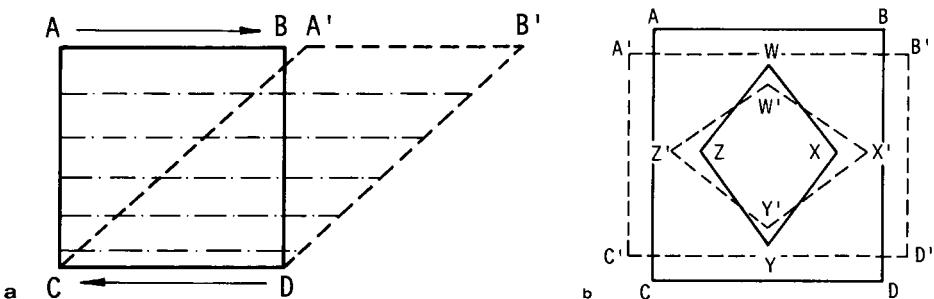


Fig. 7.2 Types of shear.

a. Simple shear. Cube ABCD is deformed into the oblique parallelepiped A'B'CD. Any straight line parallel to CD moves parallel to that direction through a distance proportional to its height above CD.

b. Pure shear. Parallelepiped ABCD deforms into the parallelepiped A'B'C'D' of equal volume. The rhombus WXYZ deforms into the congruent rhombus W'X'Y'Z' in which acute and obtuse angles have been interchanged.

deformation in many materials. At higher stresses the relationship between stress and strain ceases to be linear. The stress required to cause permanent strain may be termed the yield strength and the stress required to cause rupture may be termed the breaking strength. The point on the stress-strain curve beyond which linearity ceases is known as the elastic limit, the proportional limit or the yield point. This has been variously defined as the maximum stress at which Hooke's law is obeyed, the minimum stress at which the material is permanently deformed after removal of the stress and the minimum stress at which continuous flow occurs. BLOOR (1957, p.447) concluded that in clays there is little difference in yield points defined by the first two definitions. The value of the yield point obtained, however, varies with the experimental conditions, the rate of stressing, the water content of the sample and in some cases with the thixotropy. Although rigid divisions between the states of matter with regard to rheological properties may not be strictly valid, for practical purposes many authorities consider a yield stress to be the most characteristic property by which a solid may be distinguished from a liquid. The absence of a yield stress is also often regarded as characteristic of the liquid state (SCOTT-BLAIR, 1933, p.118) though according to REINER (1960, p.118) this is not necessarily the case.

There is no unique stress-strain curve for all clays and the shape of the stress-strain relationship for a particular clay will be influenced by the type of loading and the testing conditions (load controlled, strain rate controlled, drained or undrained, boundary restraints). A typical stress-strain curve for clay subject to static loading in compression is shown in

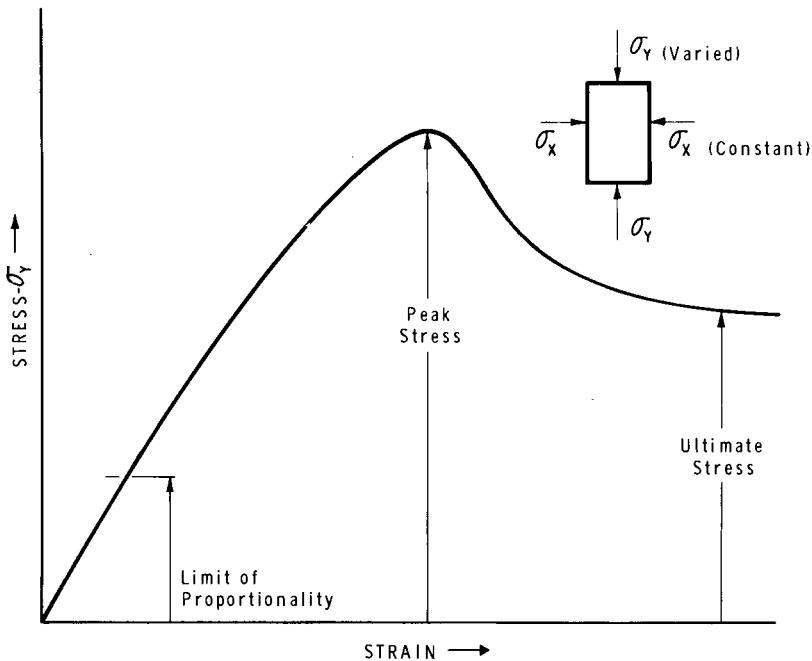


Fig. 7.3 Stress-strain relationship for soil. (After HER MAJESTY'S STATIONERY OFFICE, 1952. British Crown copyright, reproduced by permission of Her Britannic Majesty's Stationery Office.)

Fig. 7.3. When the stress rises to a maximum and then falls to a lower value the maximum has been termed the peak stress and the lower value the ultimate stress. The peak stress is commonly used as a measure of soil strength (HER MAJESTY'S STATIONERY OFFICE, 1952, p. 353). The form of this curve, however, may change significantly when the same clay is subject to static loading in tension (AJAZ and PARRY, 1975) or to dynamic loadings (RICHART Jr., in YOSHIMI, et al, 1977). Clays show only a small amount of elasticity so the linear portion of the stress-strain graph is limited to very low pressures. For many soils the ultimate stress may be a better measure of soil strength than the peak stress. SKEMPTON (1964) suggested that this is particularly true for fissured or jointed overconsolidated clays. Continuous loading of some soils leads to slow deformation accompanied by strength loss with time (strain softening). It appears however that the ultimate stress (which defines the residual strength) is retained by many soils even after large displacements. Soils containing significant amounts of clay, particularly montmorillonite, have been found to have low residual strengths whereas those composed mainly of primary minerals have higher residual strengths (KENNEY,

1967). Residual strength has been determined by reversible direct shear tests and by use of ring shear devices (Chapter 12).

Engineers found it convenient to classify materials as brittle or ductile. A brittle material fails by fracture beyond the elastic limit but a ductile material can accommodate further non-reversible strain before rupture. It is more correct to regard brittleness or ductility as a reflection of the physical state, as materials which are brittle under one set of conditions become ductile and may be deformed plastically under other conditions. Temperature, pressure, time (stress duration), grain-size, and presence or absence of fluids are all important.

ELASTICITY, PLASTICITY AND VISCOSITY

So far as is known there are no ideally elastic, plastic, or viscous materials. These properties are therefore considered to be shown to perfection by hypothetical materials named after the scientists who first studied them. A perfectly elastic substance is termed a Hooke solid, a perfectly viscous material a Newtonian liquid, and the concept of perfect plasticity is embodied in the St. Venant body.

Elasticity

In an ideally elastic material strain is directly proportional to stress and the deformation is completely reversible when the force is removed. The elastic "constants" in common use are Young's modulus, the modulus of rigidity or shear modulus, Poisson's ratio, and the compressibility or its reciprocal the bulk modulus. There are mathematical relationships between these "constants" such that if any two of them are known the others may be derived. The elastic constants for many rocks and minerals have been tabulated (BIRCH, 1966, p.97). The relationships become more complicated for anisotropic materials. If the value of one of the elastic parameters ceases to be constant it implies that deformation has exceeded the yield point. According to Hooke's law the ratio of unit stress over unit strain gives the modulus of elasticity or Young's modulus of a material. This is sometimes referred to as the modulus of deformation in soil mechanics.

Poisson's ratio is given by the ratio of lateral strain to longitudinal strain. If the decrease in volume in the direction of compression is equal to the increase in volume in the other directions a material is described as incompressible. Fully saturated clay soils often behave as incompressible materials when subjected to rapid loading. According to BLOOR (1957, p.462) the amount of elasticity shown by clays increases continuously as the water content is decreased. Elastic recovery of original size or shape may be

immediate or may take place slowly over an interval of time. The linear relationship between stress and strain only applies to clays at low stresses and the stress versus strain curve shows increasing departure from linearity with increasing stress. An increase of the lateral confining pressure is accompanied by an increase of both the modulus of deformation and the failure stress.

Plasticity

An ideally plastic material stressed beyond the yield value, deforms continuously under constant stress and becomes permanently changed in shape or size. Over a certain range of moisture contents clays generally show plastic properties whereas when dry, clays show little or no plasticity. The mineralogical composition affects the plasticity of a clay. In general attapulgite and the smectites are associated with the most plastic clays, illites are intermediate and the kaolinites confer the least plastic properties. The problem is complicated, however, as plasticity is also affected by the nature of the exchange ion, the crystallite size and size distribution of the minerals, the amount of water and nature and concentration of ions in the pore solutions and the geological history of the sample, i.e., amount of consolidation, dehydration due to drying on subaerial exposure, and cementation.

Plasticity has been studied by a great variety of experimental techniques. In modern work on clays compression, tension, torsion, shear and indentation tests have been carried out by means of a variety of apparatuses. These include concentric rotating cylinder viscometers, shear boxes, confined and unconfined compression machines, torsional devices and conical and flat-ended plungers for indentation tests. In many of these techniques measurements are made of the yield value and the rate of flow when shearing stress is applied. In soil mechanics the range in moisture contents is determined over which plastic properties are observed; this is expressed numerically as the plasticity index.

SKEMPTON (1953a, b) gave quantitative expression to the influence of the clay grade upon plasticity of soils by defining a parameter termed the "activity". This is the ratio of the plasticity index to the clay fraction of the soil expressed as the per cent dry weight of the less than 2 μm fraction. Soils were classified into groups on the basis of their activity as shown in Table 7.1. The activity of the soil gives a measure of the plasticity index of the clay fraction. There is a general correlation between activity and clay-mineral composition but it is inexact owing to the influence of other factors such as composition and concentration of pore solutions and influence of organic soil constituents. Plasticity has been discussed by numerous authors (EYRING, 1936; WHITAKER, 1939; MACEY, 1948; REE and EYRING, 1955;

TABLE 7.1
CLASSIFICATION OF CLAYS IN TERMS OF ACTIVITY
(After Skempton, 1953a, p.58.)

| Description of clay | Activity |
|---------------------|-----------|
| Inactive | < 0.75 |
| Normal | 0.75-1.25 |
| Active | > 1.25 |

GRIM, 1962; ASTBURY, 1963; ROSENTHAL, 1963; FANG et al., 1974; CHEN, 1975).

Viscosity

An ideal liquid is unable to resist shear; it flows at a rate which is directly proportional to the force. Newton developed an equation which describes the flow of most liquids. They are said to have Newtonian flow characteristics. Stress and rate of strain are related by a coefficient termed the coefficient of viscosity. Its inverse is termed the fluidity. If the velocity of flow becomes too great, the viscosity is not given by Newton's equation, as laminar or streamline flow is replaced by turbulent flow. Viscosity is a measure of resistance to flow and arises from the internal forces between the ions or molecules in the liquid. The unit of measurement is the poise which is equal to 1 dyne/sec/cm². (In SI units 1 poise = 0.1 Pa.s.). Fractions of a poise such as millipoise and centipoise are commonly used. Dilute suspensions of small spherical particles, in which particle interaction can be neglected, exhibit Newtonian flow characteristics. Einstein derived an equation connecting viscosity with the volume of the particles. Clay suspensions have properties which generally depart from those predicted by the Einstein equation. This has been attributed to the platy or elongated shape of the clay minerals, to electrical interaction between the particles, and to interaction between the particles and ions in the suspension medium. Systems which cannot be defined in terms of Newton's equation are described as non-Newtonian. In such a system, sheared at any particular rate, an apparent viscosity may be defined as the ratio of shearing stress to rate of shear.

Viscosity has been measured by a variety of apparatuses such as the capillary tube or falling sphere viscometer, which is commonly employed for systems which obey Newton's equation. Viscosity is generally measured in a rotational viscometer. There are various types of such instruments. Results are plotted graphically generally in terms of rate of shear versus shearing stress. Such a diagram is known as a consistency or flow curve. The form of the curve varies with the response of the system to shear. Thus the flow

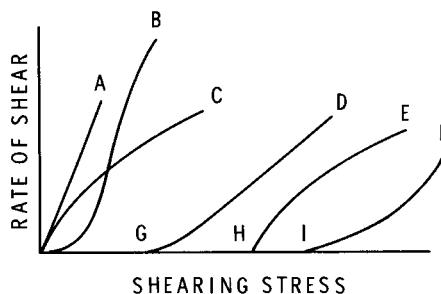


Fig. 7.4. Flow curves showing differences in response to shear. A=Newtonian fluid; B=pseudoplastic fluid, viscosity decreases with increasing rate of shear until very high shear rates; C=viscosity increases with increasing rate of shear; D=Bingham plastic; E=beyond yield point H viscosity increases with shear stress; F=beyond yield point I viscosity decreases with shear stress; G,H,I=yield points.

curve of a liquid which shows Newtonian flow is a straight line through the origin inclined to the x- and y-axes (Fig. 7.4A). Non-Newtonian systems do not give this type of flow diagram.

Systems with variable viscosity and yield point

Certain systems show a change in viscosity and, or, yield stress with either rate or duration of shear. The apparent viscosity may increase with increasing rate of shear; such a system is termed dilatant as a volume increase is generally observed. The flow-curve is concave towards the shear-stress axis (Fig. 7.4C). Alternatively the apparent viscosity may decrease with increasing rate of shear (Fig. 7.4B). A flow curve convex towards the shear stress axis which passes through the origin is that of a "pseudoplastic fluid" (FREDRICKSON, 1964, p.22) or "generalized Newtonian liquid" (REINER, 1960, p.217). If such a curve does not start at the origin the material has a yield stress (Fig. 7.4 E,F). Substances which give a flow curve of the type shown in Fig. 7.4D are known as Bingham plastics. Many dispersed systems including clays may show flow behaviour of this type.

A system which loses part of its consistency with time when sheared at a constant rate but which regains its original consistency when allowed to rest is termed thixotropic. Thixotropy is a time-dependent property of a flocculated system; however, not all flocculated systems are thixotropic. Sometimes shear is accompanied by a consistency increase with time. This is called rheopexy or antithixotropy. The commonly observed change in the consistency of a clay-water system which is allowed to stand undisturbed for a time following shear is termed ageing.

The yield stress of a sheared clay is often found to have a value which is

several hundred per cent less than the corresponding value of the undisturbed sample. If a sheared (remoulded) clay is maintained undisturbed and at the same moisture content for some weeks the yield stress generally increases. Creep, stress relaxation and thixotropy have been suggested as factors responsible for this behaviour (PUSCH, 1982). In some clays the strength attained is close to that determined for the original undisturbed sample but in other clays it reaches only a small fraction of the original value. The Champlain sea sediments in eastern Canada and certain Scandinavian leached, postglacial marine clays are of the latter variety. Materials show many complex types of rheological behaviour depending on the physical conditions. A recently suggested classification based on response to shear is shown in Fig. 7.5.

RHEOLOGICAL BEHAVIOUR AND MODELS

Physical models are commonly employed by rheologists to represent the behaviour of materials. Such models have merit as both an aid to memory and in formulating mathematical equations. Three simple elements are often used, which are combined when necessary, to make models of varying complexity. A helical spring, fixed at one end, is the model element used to represent elasticity. Such a spring, (Fig. 7.6A) is the mechanical analogue of a perfectly elastic solid or Hooke body. A viscous fluid (Newtonian liquid) is represented by a "dashpot". This consists of a piston fitted loosely into a cylinder containing a viscous fluid (Fig. 7.6B). When a force is applied to the piston it moves at a rate which is proportional to the force. Unlike the spring the piston has no tendency to return to its initial position on removal of the force. A weight resting on a flat-topped surface (Fig. 7.6C) has been used to represent yield stress. The application of a force causes movement only when it is great enough to overcome the frictional resistance between the weight and flat surface.

These elements are combined to represent different types of rheological behaviour which approximates more closely to actual materials. A weight and spring joined together in series are used as a mechanical model of a material which responds by elastic deformation to a small applied force; a large force, capable of moving the weight, causes permanent deformation in addition to the elastic response (Fig. 7.7A). A visco-elastic body is represented by a spring and dashpot joined together in series (Fig. 7.7B). Application of a force causes elastic deformation of the spring. If this is kept in the stretched state the elastic strain is slowly relieved by movement of the piston in the dashpot. This is the mechanical analogue of stress relaxation. If the force is removed prior to complete stress relaxation the spring contracts and the

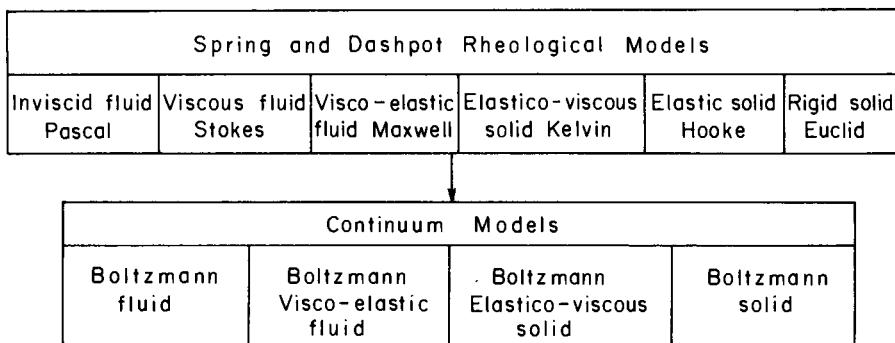


Fig. 7.5. Basic rheological models. (Adapted from FREDRICKSON, 1964. By permission of Prentice-Hall, Inc., Englewood Cliffs, N.J.)

system is said to recoil. According to HVORSLEV (1960, p.182) the deformation characteristics of most cohesive soils are visco-elastic in nature. A spring and dashpot arranged in parallel may be used as a model of a Kelvin body (Fig. 7.7C). Such a material deforms elastically but at a rate which is controlled by the viscosity of the fluid in the dashpot. According to REINER (1960, p. 136) the honeycomb structure proposed by CASAGRANDE (1932) for undisturbed marine clay (Fig. 4.15) should show rheological behaviour of this type. In such a system small volume changes may be accommodated by changes of void fraction which cause changes in the pressure of the fluid within the voids. Changes in fluid pressure will be relieved at a rate which depends on the permeability of the clay soil. The analogy in response to change of pressure between the model and the proposed soil structure is apparent. The Kelvin model has also been employed to illustrate the concept used in soil mechanics of pore pressure caused by the transmission of stress to fluid contained in voids (KLAUSNER, 1960, p.1096). A weight and dashpot joined in parallel (Fig. 7.7D) have been used as a model of a Bingham body. A material with such plastico-viscous rheological properties flows once the yield point has been exceeded. The Bingham model gives a good approximation to the rheological characteristics of mudflows and similar slurries in which the fines exert a controlling influence on behaviour. The shear stress and viscosity may be calculated from the grain size distribution and water content by a method developed by TAYLOR et al., (1986) from earlier work by others.

There are three fairly recent approaches to modelling which require mention. In the first, use is made of a hyperbolic representation of the stress-strain relationship, based on the concept of incrementally nonlinear elastic behaviour (DUNCAN, 1980). In the second, an approach to modelling based on the theory of elasto-plasticity is employed, in which strain increments are

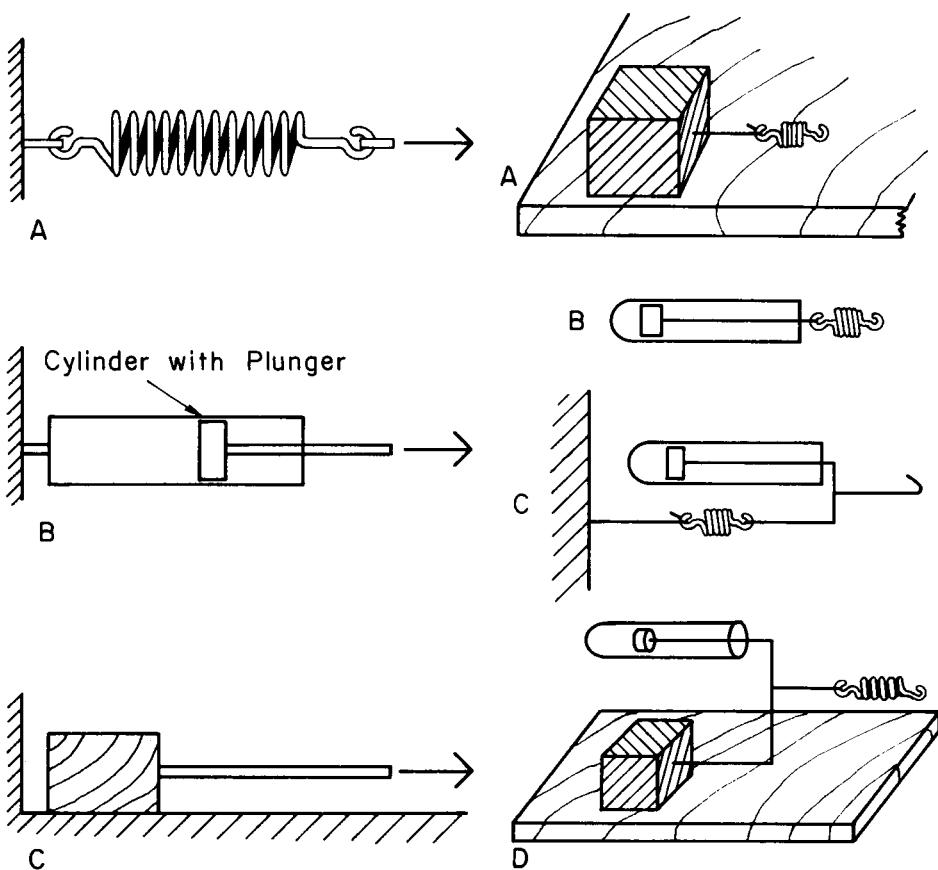


Fig. 7.6. Rheological models.
 A. Model of elastic material or Hooke body.
 B. Model of viscous material or Newtonian body.
 C. Model of Saint-Venant body.

Fig. 7.7. Rheological models made by combination of primary elements.
 A. Plastic model.
 B. Visco-elastic model.
 C. Elastico-viscous model.
 D. Model of Bingham body.

functions of the absolute stresses (WROTH and HOULSBY, 1980; DAFALIAS et al., 1980). In the third, an endochronic (*endo*=internal+*chronos* =time) approach to modelling is developed in which the viscosity coefficients depend on the strain rate (BAZANT et al., 1980). Many different combinations of springs and dashpots have been used as models of clays (TAYLOR, 1942; BAUDRAN, 1956; TAN, 1957; MURAYAMA and SHIBATA, 1959; ASTBURY, 1963; KOMAMURA and HUANG, 1974; TER-STEPANIAN, 1975; SCOTT and CRAIG, 1980; MESRI et al., 1981) (Fig. 7.8). The rheological soil models shown in Fig. 7.8 can be generalized by including an arbitrary number of springs and dashpots to form Kelvin and Maxwell chains. These models are represented by one-dimensional stress-strain laws in the form

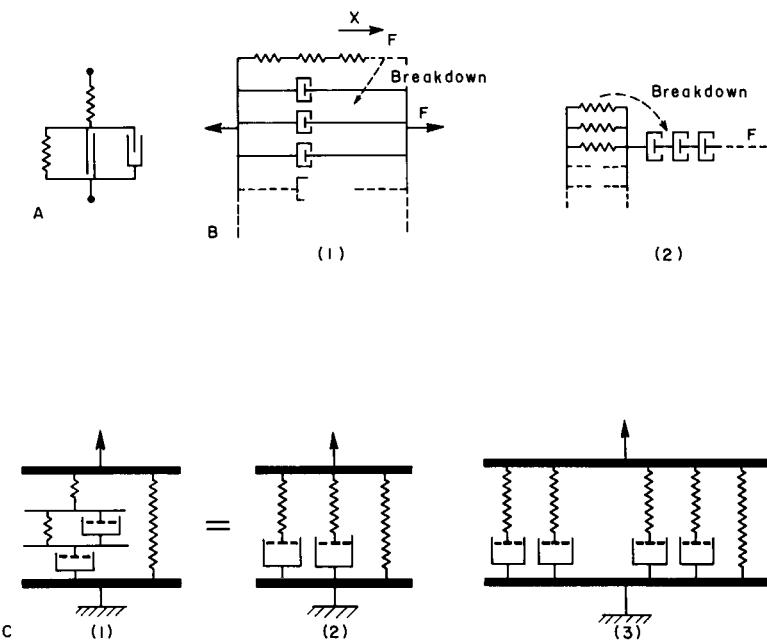


Fig. 7.8. Mechanical analogues of rheology of clay.

- A. Mechanical model of clay skeleton. (After MURAYAMA and SHIBATA, 1959, p.178.)
- B. Spring-dashpot models. 1=Imposed strain-displacement; 2=imposed stress-force. (After ASTBURY, 1963, p.11.)
- C. 1=rheological model for clays; 2=model analogous to 1; 3=generalized model, in which structural disintegrations are described by gradual decoupling of the Maxwell elements. (After TAN, 1957).

of differential equations (FLÜGGE, 1975).

A more consistent constitutive representation of the rheological properties of clays is provided by linear viscoelastic continuum theory (SUKLJE, 1969; 1978). This approach is based upon two fundamental assumptions, the concept of "fading memory" and Boltzmann's superposition principle (CHRISTENSEN, 1971). The assumption of fading memory implies that the material response to a certain loading history depends upon both the immediate and the distant load increments. The influence of the distant loadings decreases with time. The Boltzmann superposition principle states that at any time the material response can be derived by summation of the responses to the load increments applied prior to the point of observation. The linear viscoelastic continuum model of clays is formulated in terms of three-dimensional integral constitutive equations. Both dilatational and distortional rheological effects are included through two experimentally determined creep or relaxation functions.

SHEAR STRENGTH AND THE MOHR-COULOMB HYPOTHESIS

Soil strength is generally considered in terms of shear strength by soil engineers. The shear-strength value determined experimentally is not a unique constant which is characteristic of the material but varies with the method of test. Experience has shown, however, that the concept is of considerable practical utility. The approach is based on theories derived from consideration of stress distribution as, in much engineering analysis, stress is a measurable quantity. Among such theories of strength the Mohr-Coulomb hypothesis has been of particular importance.

It was proposed by MOHR (1900) that there are two general conditions under which permanent deformation or fracture of a body may take place. He considered that one possibility of failure occurs when the shearing stress in the slip planes attains a limiting value. The actual limiting value of shear will itself also generally depend upon the stress normal to the slip planes so that on the plane of failure shear stress may be expressed as a function of the normal stress. The other proposed condition under which failure may occur is when the maximum tensile normal stress reaches a value characteristic of the material. It has been observed that samples which have been stressed to failure commonly show two sets of slip planes which intersect along the intermediate principal stress direction and are symmetrically oriented with respect to the major and minor principal stress. The normal and the shearing stress on the probable plane of failure may be derived from mathematical equations or from a graphical construction known as the Mohr diagram. The orientation of the slip planes may also be deduced (MOHR, 1914).

An equation was proposed by Coulomb for expressing the condition of rupture of a brittle material in compression (NADAI, 1950, p.219). An equation of the same type has been much used in calculations to do with shear strength and is commonly known as Coulomb's Law. This equation, which represents a special case of Mohr's strength theory, is as follows:

$$\tau = c + \sigma \tan \phi$$

where τ =shear strength, c =apparent cohesion, σ =pressure normal to the shear plane, ϕ =angle of shearing resistance or internal friction, and $\tan \phi$ =coefficient of internal friction.

It defines a straight line known as Mohr's envelope which may be plotted on a graph showing shear stress as ordinate versus normal stress as abscissa (Fig. 12.4). By combining Mohr's hypothesis and Coulomb's law it is possible to determine the conditions under which failure is likely. The Mohr-Coulomb condition of failure can be generalized; in three dimensions the failure surface is a pyramid which in cross-section is an irregular hexagon. Its nature and relationships to other failure criteria such as the extended Von

Mises and extended Tresca have been reviewed by BISHOP (1966) and to the Hvorslev failure criterion by HASHIGUCHI and UENO (1977). The Tresca failure criterion describes the behaviour of an ideal elastic-plastic material. However it can be generalized to include strain hardening and strain softening of clays. In this case the response of the actual material is replaced by that of a hypothetical ideally plastic material but with the same ultimate characteristics as those of the original material. As an alternative, Tresca's criterion is frequently replaced by Von Mises condition in which the octahedral total shear stress is substituted for the maximum shear stress. Discussions of the advantages and limitations of these procedures have been given by SALEEB and CHEN (1982) and DAS (1983).

The Coulomb equation is still used in its original form for some purposes but several modifications have been proposed. Among these one of the most significant makes allowance for the pressure of pore solutions which develops due to shearing. The minerals in a soil may be thought of as forming a framework or skeleton which carries the shear stress. The normal stress on any plane, however, results not only from the stress carried by the solid particles but also from the pressure of the pore fluids. Therefore the total stress normal to the shear plane is replaced in Coulomb's equation by the "effective stress", σ' . This is given by $\sigma-u$, the difference between the total stress, σ , and the pore-water pressure, u . The principle of effective stress developed from the work of TERZAGHI (1923, 1932) and has been amplified and discussed in work by HVORSLEV (1937), RENDULIC (1937), TAYLOR (1944), BISHOP and ELDIN (1950), SKEMPTON (1960), SRIDHARAN and VENKATAPPA RAO (1979) and others.

The Coulomb equation may be further modified and expressed in the following form:

$$\tau = c_r + \sigma' \tan \phi_r$$

where c_r =true cohesion which depends only on water content at failure, ϕ_r =true angle of internal friction, and σ' =effective normal stress on the plane of failure. Hvorslev suggested a method whereby the "true cohesion" and "true internal friction" can be derived. The true angle of internal friction can also be determined from Mohr's construction using values obtained in undrained triaxial compression tests in which pore-pressure measurements are made (SKEMPTON and BISHOP, 1954). If a sample is not fully saturated further modification to the expression for effective stress has been suggested (BISHOP et al., 1960; JENNINGS and BURLAND, 1962; BURLAND, 1965). The term for the pressure of the pore fluid in the equation for effective stress may be replaced by a term representing the "suction" of the moisture in the soil. This represents negative pressure so appears as a positive quantity in the

TABLE 7.2
CLASSIFICATION OF CLAY SENSITIVITY¹
(After Leonards, 1962, p.78)

| Sensitivity | Classification |
|-------------|----------------------|
| < 2 | Insensitive |
| 2-4 | Moderately sensitive |
| 4-8 | Sensitive |
| 8-16 | Very sensitive |
| 16-32 | Slightly quick |
| 32-64 | Medium quick |
| > 64 | Quick |

¹ Reproduced by permission of McGraw-Hill Book Company, Inc., New York, N.Y.

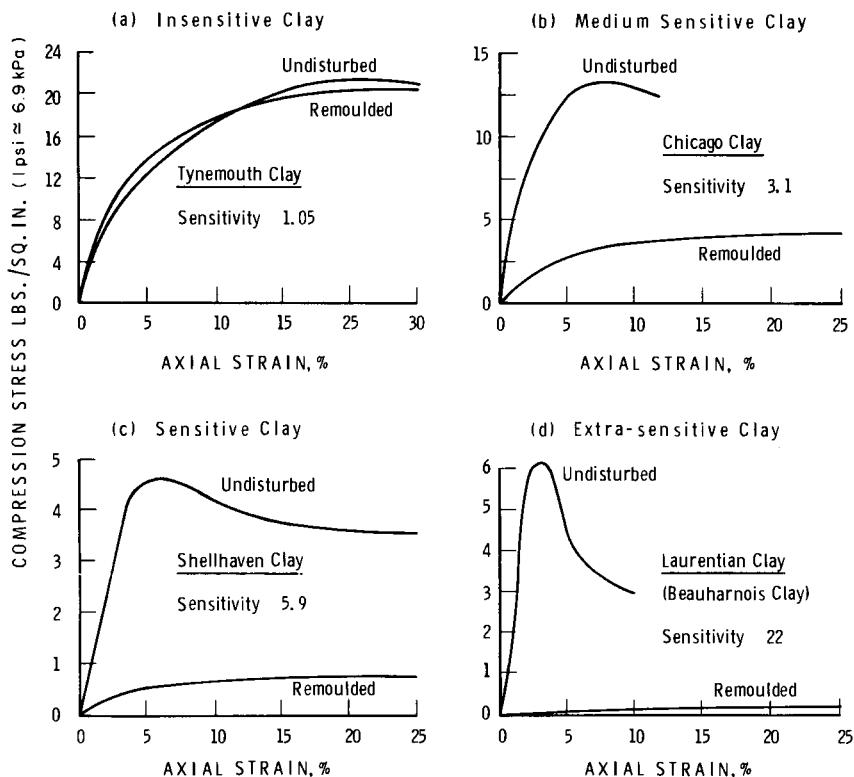


Fig. 7.9. Graphs showing stress-strain curves of clays of various sensitivities. (After SKEMPTON, 1953b, p.56. Reproduced by permission of the Council of the Yorkshire Geological Society.)

modified equation which is:

$$\sigma' = \sigma + p''$$

where p'' =moisture "suction". Considerable importance has been attached by some authors to the magnitude of soil-moisture suction in determining the strength of unsaturated cohesive soils. Various other modifications have been suggested such as that proposed by BAKER and KRIZEK (1970) for the analysis of anisotropic soils.

The shear strength of an undisturbed clay is generally found to be greater than that of a remoulded clay which is tested under the same conditions and at the same water content. The effect of remoulding on clays of various sensitivity is shown by means of stress-strain curves illustrated in Fig. 7.9. The ratio of the undisturbed strength to the remoulded strength is defined as the sensitivity of the clay (TERZAGHI, 1944, p.613). Clays have been subdivided into classes (SKEMPTON and NORTHEY, 1952; LEONARDS, 1962) on the basis of their sensitivity as shown in Table 7.2. The strength values used to determine this ratio have been found by the unconfined compression test, the vane shear test and the Swedish fall cone test. It has also been suggested that the amount of remoulding required to cause structural breakdown, expressed as the "rapidity number", should be used in classification (SÖDERBLOM, 1974).

Some sensitivity is shown by nearly all normally consolidated and lightly overconsolidated clays. In quick clays however, the sensitivity may become very large because the remoulded strength (which appears in the denominator in the ratio) becomes so small that the material flows like a viscous liquid. Indeed the viscometric behaviour of the remoulded soil has been used to investigate sensitivity differences (BENTLEY, 1979) and attempts are being made to relate viscosity to pore fluid chemistry (TORRANCE, 1984). The possibility of significant changes in physical properties leads to a number of engineering problems of which flow slides are the most serious. These are sometimes disastrous because the liqufaction of the soil is sudden and the change in properties unpredictable.

DISCUSSION

Clays show striking differences in their response to shear as the moisture content is changed. When the proportion of water is high they behave like fluid suspensions even if interactions between the markedly anisotropic particles and the ions and molecules of the suspension medium make their properties unusual. As the quantity of water is decreased the consistency becomes greater. At water contents above the plastic range, and to a lesser degree within that range, many clays show variable viscosity and yield point

with rate or duration of shear. These phenomena have been attributed to changes in a structural skeleton formed by a girder-like arrangement of bonded particles with enmeshed liquid (BOSWELL, 1961, p.38). A broken bond which is due to a net electrical attraction may re-form rather easily if the conditions are favourable but once a cemented union has been fractured it is unlikely to re-establish itself readily. Thus bonds may behave in a brittle or viscous fashion (DENISOV and RELTOV, 1957; GOLDSTEIN and TER-STEPANIAN, 1957). Changes in the viscosity and in the extent and perfection of orientation of layers of water molecules adsorbed on the clay-mineral surfaces may also be a factor (GRIM, 1962, pp.238-240).

A reduction in viscosity of the suspension due to shear may result from a tendency of platy or elongated particles such as clay minerals to acquire a parallel orientation during laminar flow. Structural breakdown caused by shear may also be accompanied by release of fluid previously trapped within pores. On the other hand, shear is likely to decrease the sizes of the structural units and so may lead to an increase with time in the frequency of collisions between the particles. In some systems this may have a dominant effect on viscosity and may account for antithixotropy.

In a dilatant system the apparent viscosity increases with increasing rate of shear. It is a property sometimes shown by close-packed systems. When disturbed the solid phase occupies a larger volume and there is temporarily insufficient fluid available to fill the increased void space so the resistance to shear increases. This is the classical explanation of dilatancy as observed in the much quoted example of moist sand on a beach. Dilatancy is also sometimes shown by clay sediments which accumulated in the deflocculated condition. The clay minerals repel one another and tend to adopt a close-packed configuration. When sheared, the parallel arrangement of the particles is destroyed causing an increase in the consistency of the system believed due to tangling-up and mutual interference between the particles.

Thixotropy is common in clay soils allowed to age following disturbance; it is a factor responsible for stiffening and strength regain. Thixotropy is of importance under both static and dynamic conditions of shear; the latter conditions are induced by earthquakes or traffic. It has been thought that thixotropy results mainly from a change in yield stress (VAN OLPHEN, 1977, p.138). This can be explained if it is accepted that shear breaks interparticle bonds causing a disruption of the stable fabric. In this interpretation the strength recovery on ageing implies that conditions in the system favour re-establishment of bonds broken during shear and a fabric similar to that in the undisturbed material is reconstructed. Reversible changes in the thickness of layers of oriented water molecules associated with the clay minerals has also been postulated. OSIPOV et al. (1984) used a

rotary viscometer with vibrostand to subject coarse and fine clay soils to static and dynamic shear. Microstructure was observed on a scanning electron microscope and quantitative measures of pore area, pore distribution and microaggregate size and distribution were obtained with an image analyser. They concluded that without vibration a shear zone forms over a limited soil volume within which a negative pore pressure develops, porosity and moisture content increase, structural bonds are weakened and structural elements are partially reoriented parallel to the direction of shear. The combined effect of shear and vibration resulted in the disappearance of the shear zone and the development of a more homogeneous microstructure with increased mobility of the structural elements over the entire sample volume.

Plastic behaviour of soils may result from changes in interparticle bonding and fabric, though changes or differences in the extent of ordered molecular layers of water associated with the clay minerals have also been considered (GRIM, 1962, pp. 219-227). Dry clays and clays mixed with a non-polar liquid fail to show plasticity (ROSENQVIST, 1959, p.47). The view that water plays an essential role in the mechanism of plasticity development has been held by many authors (MACEY, 1942; WILLIAMSON, 1951; NORTON, 1952). There is little doubt that the water within a few molecular layers of a clay-mineral surface does have different properties from water in bulk. The evidence has been presented by HOUWINK (1953), ANDERSON and LOW (1958), ROSENQVIST (1959) and LOW (1960). The manner in which the properties of this near-surface water differ from those of normal water has also been much debated by competent authorities. In a clay-water system there is likely to be a range in the forces of interparticle attraction due to differences in bond-type so that the energy barrier to motion between particles will vary. Application of a force insufficient to cause rupture may cause yielding of the weaker bonds. Hence plasticity may be partly explained as involving a kind of gradual "letting go" of weaker bonds (BOSWELL, 1961, p.61).

Soils under constant load often show slow, essentially continuous movement referred to as creep. This may result from gravitational forces which are responsible for the downhill movement of soils on natural or artificial slopes or from increased load due to construction. In soils the effects are most significant when the soil is plastic and contains a high water content. While either loss or gain of strength may occur for a time, continued application of constant stress, above a certain level, leads to failure. Strength loss results from rupture of cemented junctions between particles, from decreases in effective stress due to increases in pore pressure, from development of bands of greater preferred orientation of clay platelets and from formation or extension of fissures. As with other materials the strain versus time curve has been subdivided into three sections; the creep is termed primary,

secondary and tertiary. In the first stage deformation is partly elastic, in the second stage "steady state" creep occurs approximated by a straight line and in the third stage accelerating irrecoverable deformation takes place prior to failure. Upon stress release the gradual recovery of elastic strain is referred to as creep recovery.

Deformation of a clay soil induces changes in the spatial arrangement and orientation of the fabric elements which include the clay crystallites and other mineral constituents and pores. X-ray methods showed that compressed samples of kaolinite-water mixtures developed a preferred orientation of the clay platelets normal to the pressure (BUESSEM and NAGY, 1954). The fabric of an extruded clay cylinder made up of alternate layers of stained and unstained clay was investigated by WILLIAMSON (1960). He found that the clay layers which were originally normal to the axis of the cylinder lay on U-shaped surfaces following extrusion. The clay was also crossed by slipbands which formed two series of cones which were coaxial with the cylinder. The clay orientation within the slipbands was different from that of the matrix. The orientation within the slipbands indicated lengthwise stretching of the cylinder along with radial compression. Rotational rolling of a clay cylinder gave helicitic structures.

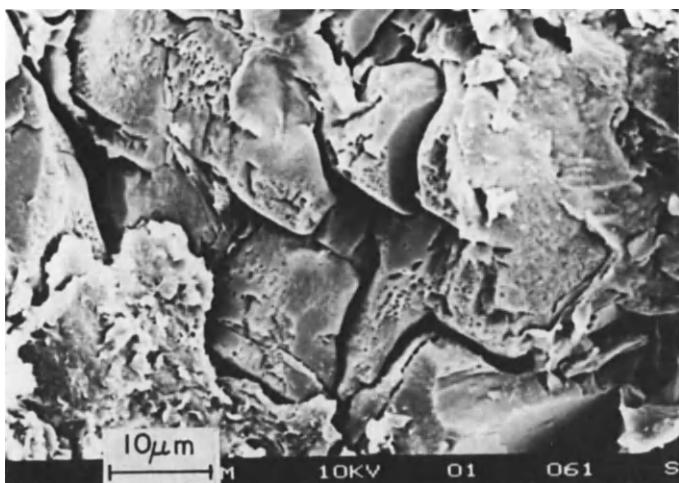
Shear tends to orient platy or elongate particles parallel to the plane of movement due to drag or flow. The relative resistance to such re-orientation varies with the fabric of the clay, the strength of the interparticle bonds, and with the orientation of the shear plane. Rate of shear may also be a factor. GRAHAM et al., (1983) found that a tenfold decrease in strain rate caused a decrease of 10-20 per cent in such important engineering properties as undrained strength and preconsolidation pressure in a wide variety of soft clays. Ageing was found to produce a stiffer arrangement of soil particles. If the clay minerals have a random or flocculated arrangement considerable energy will be required to reorient the particles regardless of the orientation of the shear plane. If the clay minerals already have a parallel arrangement less effort will be needed to effect shearing provided the orientation of the shear plane lies close to the direction of parallelism of the clay minerals. Hence the fabric of clay soils and the orientation of potential shear planes with respect to a plane of preferred orientation of the clay minerals require consideration in estimating the shearing resistance.

These factors have been studied by LUPINI et al., (1981) in detailed investigations of the nature of the drained residual strength of cohesive soils. The proportions of platy to rotund particles and the coefficient of interparticle friction of the platy particles were found to control the type of residual shearing mechanism. Three modes of residual shear were recognized and termed turbulent, sliding and transitional. In the turbulent mode the

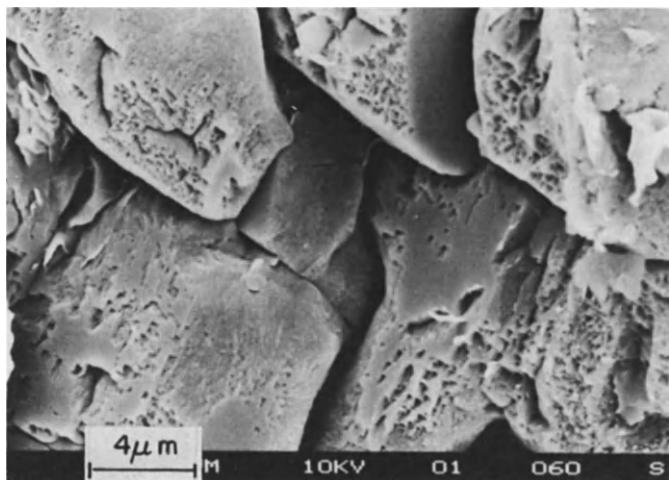
proportion of rotund particles is high, or the platy particles lack preferred orientation. A shear zone has a different porosity and brittleness results from dilatant behaviour. In the sliding mode, shear is dominated by low friction platy particles; initial brittle behaviour results from development of strong preferred orientation of particles on a plane which offers low shear resistance. The transitional mode occurs when there is no dominant particle shape so both turbulent and sliding modes occur together in different parts of a shear zone. Thin bands of clay particularly those rich in smectite minerals are often associated with landslides. Clay minerals have a high capacity for water uptake and when they are oriented the shearing resistance is low and such a band offers a favourable surface on which sliding may take place. Drainage is used nowadays as one method of landslide control.

The mechanical and strength properties of soils were related to fabric at an early date (TERZAGHI, 1925; CASAGRANDE, 1932). Geotechnical scientists generally believe that the minerals forming the structural skeleton of a soil are in contact, with water occupying the pores and void spaces within the framework. Stress is transmitted by grain-to-grain contacts. Evidence in support of this has been obtained from scanning electron micrographs of particle surfaces scratched during shear and from acoustic emissions (MATSUI et al., 1980). These workers used this evidence to develop a clearer understanding of the physical significance of true angle of friction and conventional strength parameters in the effective stress concept. ALLAM and SRIDHARAN (1984) concluded that increases in viscosity of pore fluids close to mineral surfaces, though real, probably make only a very small contribution to shear resistance. Shear resistance in clay soils has long been considered by engineers to be derived from forces of cohesion and friction. This viewpoint is reflected in the physical significance attached to the mathematical parameters in Coulomb's Law in which c is equated with cohesion and $\sigma \tan \phi$ with friction. There is widespread agreement that shear resistance results from the combined influence of physical and physico-chemical components. The relative significance of the contribution to strength made by these components depends upon the nature of the soil and other factors.

Friction is an important physical factor which results from surface roughness and interlocking of sand, and silt (Fig. 7.10). Clay-sized mineral particles may contribute to friction since surface steps may occur. Physical tangling-up due to interference between minerals when sheared may also contribute to frictional resistance. In a close-packed system shear causes dilatancy so that one particle must be so-to-speak lifted over an adjacent particle against surface roughness. Such movements take place normal to the shear plane. Electrical forces both of attraction and repulsion may also be involved. The greater the compressive force normal to the shear plane the



A. Void Space and Particle Interlock



B. Detail of Void Space and Particle Interlock

Fig. 7.10 Scanning Electron Micrographs Showing Void Space and Particle Interlocking in Silt.
Calgary, Alberta.

more intimate is likely to be the contact between the surfaces so that frictional resistance is likely to be enhanced. Sediments which lack cohesion but show significant shear resistance due to grain surface rugosity and an interpenetrative fabric have been termed "locked sands" by DUSSEAUT and MORGESTERN (1979). Such deposits have a high density, display brittle behaviour, peak frictional strengths in excess of those shown by a dense sand and large dilation rates at failure.

Separate particles joined by cohesive forces are able to withstand finite tensile stress. Flocculated colloidal particles such as clay minerals stick together because the net electrical attractive force exceeds the net repulsion. Mineral agglomerations often result from the deposition of cementitious compounds which adhere to the surfaces of the minerals and bond them together. The magnitude of the cohesion in bulk is a function of the nature and number of bonded interparticle contacts per unit volume. This is affected by the stress history, by the particle arrangement or fabric, and by the mineralogy. KRIZEK (1977) prepared samples of kaolin with controlled fabric. He concluded that interparticle bonds have a greater effect on mechanical behaviour than particle arrangement although fabric did affect some properties such as rate of creep strain. Samples consolidated from a flocculated slurry appeared to have more bonds resisting creep deformation than samples of the same void ratio consolidated from a dispersed slurry.

Soviet scientists have related differences in shear strength and deformation behaviour of soils to lithogenesis, ageing phenomena and to changes in contact relations between fabric elements (OSIPOV, 1984; SERGEYEV et al., 1978). They show that very recent deposits and sediments at an early stage of diagenesis have a cellular microstructure. At that stage particle contacts are thought to be via thin films of water and bonds are termed coagulative. Viscous deformation, low strengths, high compressibility and thixotropic features are characteristic of such clays; uniaxial compressive strengths range from 0.02 to 0.1 MPa, angle of internal friction is from 0° to 12° and values of cohesion vary from <0.01 to 0.03 MPa. Increased compaction produces "transitional" contacts in which the water is gradually expelled and fabric elements come into direct physical contact. Deformation behaviour changes from viscous via plastic to elastic plastic; uniaxial compressive strength increases from 0.03 to 1.2 MPa, friction angle increases from 12° to 26° and cohesion increases from 0.03 to 0.2 MPa. In later stages cemented junctions develop between fabric elements and finally bonds are formed by recrystallization at contact points. These changes are accompanied by further increases of strength and by the development of a "matrix", "turbulent" or "laminar" microstructure (Ch. 4, p.120). Thus an interesting attempt is made to link microstructure directly with engineering properties.

In quick clays a large proportion of the undisturbed strength is permanently lost following shear. A small proportion of the original strength may be regained when a remoulded quick clay is allowed to age and this may be accounted for by the development of some form of interparticle bonding. This, however, evidently differs from that in the undisturbed clay either with respect to the nature of bond or number of bonds per unit volume. It appears unlikely, however, that anything more than a small fraction of the original strength would ever be recovered as the rate at which strength develops is much too slow. Hence additional factors to those present in a thixotropic system are involved. Major importance is generally attached to the fabric. This is commonly open and is sometimes strikingly similar to the edge-to-edge and edge-to-face arrangements predicted earlier on theoretical grounds. Some authors have considered the dominant fabric elements to be primary mineral particles but others have stressed the importance of agglomerations. Evidence for the type of fabric has been obtained by optical microscopy, x-ray diffraction, scanning electron microscopy, high voltage electron microscopy and mercury porosimetry (GILLOTT, 1970, 1979, 1980, 1982; MOON, 1978; DELAGE and LEFEBVRE, 1984).

At genesis the stable arrangement of the constituent particles is believed to be relatively open and loose packed. Changes during the geological history of the material render the open fabric out of equilibrium. It persists, however, due to cementation, electro-chemical bonding, loading and interlocking caused by the mutual interference of particles which prevents their free rotation in space. When the soil is disturbed or remoulded the particles assume a more close packed configuration which is closer to equilibrium with the existing conditions. As the water content is constant the deposit becomes oversaturated and may flow like a viscous liquid (Fig. 7.11).

Highly sensitive soils are most typically found in places which were glaciated during the Pleistocene; generally they accumulated under marine conditions shortly after the withdrawal of the continental ice sheets. Apart from flow slides (p.34) they are associated with other serious engineering problems such as irreversible shrinkage on drying, low bearing capacity and high settlement. Prediction of slope stability, compressibility under load and other aspects of engineering behaviour is often unreliable.

Sensitive soils have a number of features in common in addition to their relatively open fabric. Index properties are often similar - commonly they are inactive (< 0.5), have a liquidity index > 1 and a liquid limit $< 40\%$. They contain a large proportion of rock flour (primary minerals in the $< 2\mu\text{m}$ size range); clay minerals are typically illite and chlorite (though swelling clays are sometimes present). Carbonates are relatively common and non-crystalline minerals are now thought to form a significant fraction of the soil (GILLOTT,

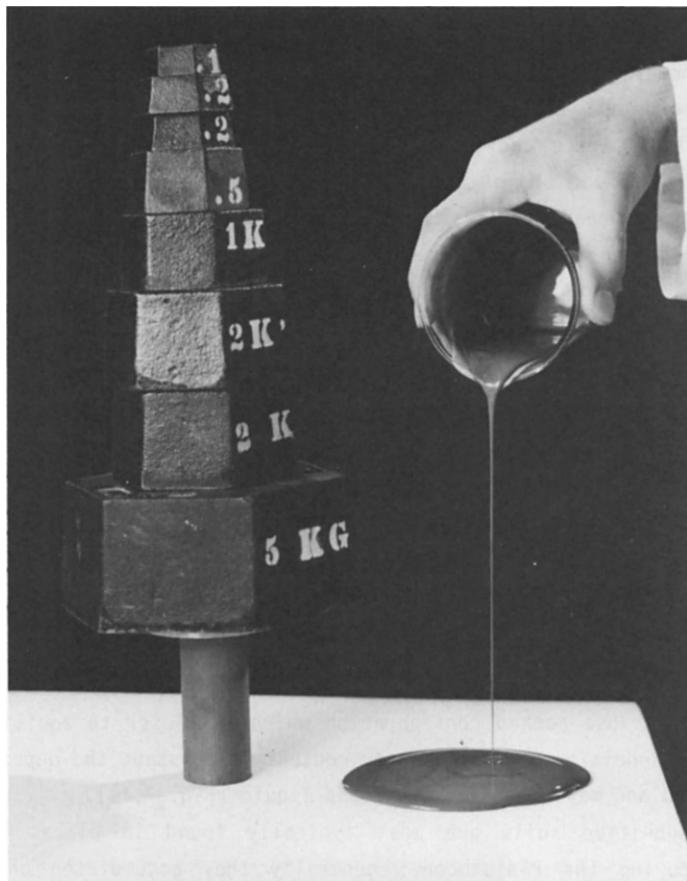


Fig. 7.11. Undisturbed and remoulded strength of Leda clay (Champlain Sea sediment) at constant water content. (After CRAWFORD, 1963, p.134. Reprinted from Geotechnique by permission of the Institute of Civil Engineers.)

1971; McKYES et al., 1974; YONG et al., 1979; BENTLEY et al., 1980; LOCAT et al., 1984).

Quick clay behaviour has been explained by a number of hypotheses. An early proposal was advanced by ROSENQVIST (1953, 1962) in connection with Norwegian sediments. He suggested that a decrease in salt content of the pore water due to leaching or diffusion caused the flocculated fabric of the marine deposited sediment to become metastable. This would follow if the changes in electrolyte concentration caused the net interparticle balance of charge to shift from one of attraction to one of repulsion. Hence in such a system

conditions following shear do not favour re-establishment of the original fabric and the interparticle bonds which form on ageing may also be different from those in the undisturbed material. Tempting though this proposal is, it is probable that there are other factors involved as marine deposited clays are known in eastern Canada of similar and low salt content which show considerable differences in sensitivity (PENNER, 1963). Even harder to explain on Rosenqvist's hypothesis is the quick behaviour shown by certain clays found on the continental shelf and in ocean basins in which the salinity of the pore fluids (33-35‰) is similar to that in the water above the sea-bed (RICHARDS and ZUIDBERG, 1985; RICHARDS, 1976).

Other physico-chemical changes which may lead to changes in physical properties including the development of high sensitivity include ion exchange, introduction or formation of dispersing agents (SÖDERBLOM, 1966) and changes in the redox potential associated with iron sulfide-sulphate equilibria and accompanying changes in mineralogy and pore fluid chemistry (DONOVAN and LAJOIE, 1979). Purely physical factors may also be involved. A sediment may retain an open fabric formed on deposition due to low rates of loading, buttressing of particle contacts, mutual interference between particles and precipitation of cementitious compounds. Later changes such as dissolution of cementitious compounds may cause the open fabric to be out of equilibrium and under high water content conditions abrupt liquification may occur. Carbonates and particularly amorphous compounds have been considered important in this context. Yet another alternative proposal is that a lack of long-range attractive forces between particles, including single crystals of spherical halloysite, is important. The problem of highly sensitive behaviour in soils has been reviewed in a number of articles and volumes (BENTLEY and SMALLEY, 1978; SMALLEY, 1979; SMALLEY et al., 1980; LOCAT et al., 1985).

Clays are heterogeneous materials composed of elastic and brittle solid components separated by surfaces of discontinuity from the liquid and air which occupies the void spaces. The solid components may be individual minerals or aggregations united with a greater or lesser degree of permanence. The strength and deformation characteristics of clays have been studied from different viewpoints by engineers, rheologists, physical chemists and geologists. The subject is, however, a complex one and at the present time the factors involved are imperfectly understood. A significant number of new constitutive theories have been developed recently and are being actively discussed (WITTKO, 1979). The variety of clay models currently in use clearly indicates that an overall approach which accounts for all the observed facts in a satisfactory and unified way has not been developed. It is hoped that more knowledge acquired by further research work will reconcile some of the divergent viewpoints in the future.

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CHAPTER 8

SOIL STABILIZATION

The term soil stabilization is applied to any process which improves the properties of a soil and which enables it to perform and sustain its intended engineering use (WINTERKORN, 1955, p.1) Soil stabilization as a science started to evolve about 40 years ago (KEZDI, 1979). The chief objectives of stabilization are to improve soil strength, to decrease permeability and water absorption, and to improve bearing capacity and durability under cyclical conditions such as varying moisture content or repeated applications of stress at amplitudes less than the soils ultimate strength - fatigue life. The growth of soil stabilization has economic roots. Its economic importance arises from the possibility of improving soils at the site of construction for use as foundations or materials of construction. If an unstable soil has to be removed and replaced with other foundation material such as gravel or crushed rock the cost is high owing to the weight and bulk of the materials involved. Similarly if soil or stabilized soil can be used as a construction material transportation costs are greatly reduced as fewer building materials have to be transported to the site.

Soil stabilization has been used in the building of roads and aircraft runways, earth dams and embankments, in erosion control (DIAMOND, 1975; KAWAMURA and DIAMOND, 1975) and in the reduction of frost heaving. Soil and clay have been used as materials of construction from very early periods of man's civilized development. The possibility of employing stabilized soil for the building of houses at low cost in underdeveloped regions of the world has been considered by the United Nations Organization and by others (MIDDLETON, 1953; CYTRYN, 1957; FITZMAURICE, 1958). Both mechanical and chemical means have been used to improve the strength and durability of soils. The most appropriate method depends upon economics, engineering requirements and soil characteristics which have to be determined.

No attempt is made here to describe the structural performance of stabilized soil which is outside the scope of this text relating to engineering geology. Information can be obtained on these aspects from the technical literature.

MECHANICAL STABILIZATION

It has long been known that the strength and durability of soils can be improved by mechanical means. This method of stabilization involves soil compaction and densification by application of mechanical energy; various sorts of rollers, rammers, vibration techniques and sometimes blasting are used. In

general strength increases linearly with increase in bulk density or with decrease in voids ratio and permeability. Highest bulk density may only be achieved when there are just sufficient fines to fill the void spaces between coarser particles. There are methods such as that based on mechanical analysis by which a suitable proportion of particle sizes to give optimum grading may be deduced though it should be recognized that the mechanical compaction process itself may break-up grains and change the particle size distribution (FULLER, 1907; AMERICAN SOCIETY FOR TESTING AND MATERIALS, 1980b, pp. 358-260). At a given particle-size distribution there is also an optimum moisture content. If dry density of a soil is plotted against water content it is found that a given amount of compaction gives a maximum in the dry density at this optimum water content (Fig. 8.1). This is because the addition of a little water displaces air and facilitates movement of fine-grained particles past one another due to the formation of adsorbed moisture films. This effect is less important in soils composed of coarse particles because of their lower specific surface. Addition of more than a certain amount of water causes increase in pore pressure with loss of shear strength and takes up space in which solids could have been accommodated and no further air is displaced. It has been suggested that cohesive soils should be compacted only when the moisture content is not more than 2% above the plastic limit (DEPT. OF THE ENVIRONMENT, 1969). Commonly the optimum water content is determined in the laboratory using some modification of the Proctor compaction test (PROCTOR, 1933). Conversely at a constant moisture content, increased compaction increases the dry density until most of the air voids are filled. Maximum strength, as measured in the unconfined compression test, has been found to occur slightly below the optimum moisture content. In cohesive soils, however, it is not considered good practice to compact below optimum moisture content owing to the likelihood of subsequent volume increase resulting from moisture uptake (HER MAJESTY'S STATIONERY OFFICE, 1952, pp. 169-170; HIGHWAY RESEARCH BOARD, 1954). Such samples have been found to exert greater swelling pressures than samples compacted wet of optimum (SEED and CHAN, 1959, p. 92). When shrinkage due to drying is a strong possibility, however, it is probably preferable to compact on the dry side of optimum. This follows from the observation by LAMBE (1958, p. 1654-25) that samples compacted dry of optimum show appreciably less drying shrinkage than samples compacted wet of optimum. This was attributed to a difference in fabric. In samples compacted wet of optimum a strong parallel orientation between particles was believed to develop so that drying shrinkage was at its maximum.

Soil to be stabilized is usually spread and compacted in successive layers each 150 to 300 mm thick. Rollers are often used but the variety of heavy equipment selected depends on soil type, economics, etc. Repeated impact loading (MENARD and BROISE, 1975; WEST and SLOCOMBE, 1973), various other dynamic techniques such

as vibroflotation and vibrocompaction (THOMSON, 1974; GOMERSALL, 1978; LANCASTER-JONES and MCKEAND, 1978), hydrocompaction and addition of chemicals sometimes in trace amounts (INGLES, 1974; HOOVER and HANDY, 1978) have been employed. Consolidation may be achieved by preloading the soil with material from a borrow pit. In clay soils, particularly when sensitive, care must be taken to allow sufficient time for slow dissipation of excess pore water pressure to avoid shear failure, and load may be increased only in successive stages (LAW and BOZOZUK, 1979). Channels of higher permeability, such as sand drains, may be used to speed up compaction.

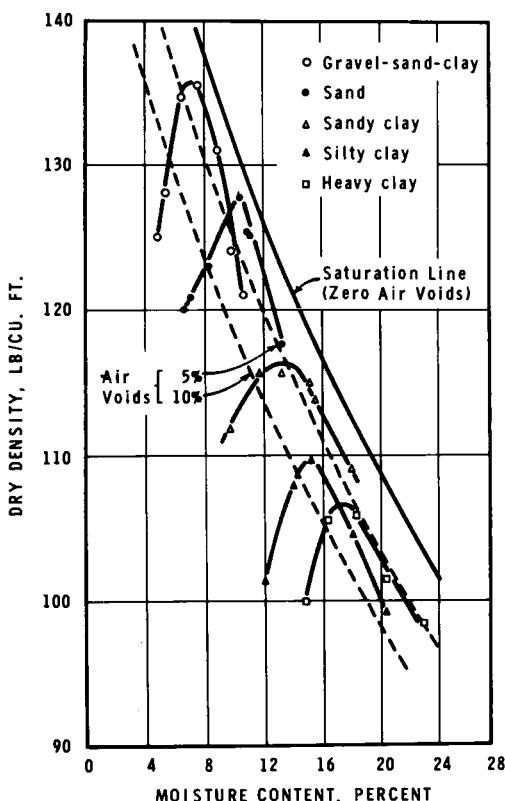


Fig. 8.1. Relationships between dry density and moisture content for five different soils when compacted in 9-inch loose layers by five coverages of a 1/2-ton frog-rammer. (After HER MAJESTY'S STATIONERY OFFICE, 1952. British Crown copyright, reproduced by permission of Her Majesty's Stationery Office.)

In dry regions the moisture content of soils is often much below the saturation level. Construction of a paved road limits evaporation so the moisture content of the soilbase may rise; expansive soils in particular may exert high differential

swelling pressure causing the road surface to become uneven. One solution is to pre-wet the soil so that any volume increase takes place before construction of the road. Soil may be pre-wetted by introducing water through boreholes (BLIGHT and De WET, 1965) or by irrigation. A method used in South Africa (VAN DER MERWE et al., 1980) is to replace topsoil and vegetation by a layer of sand about 150 mm (6 inches) thick. Removal of vegetation helps prevent drying (DE BRUYN, 1973) and the sand traps rainwater and water supplied by irrigation which soaks into the soil. Moisture barriers of polyethylene sheet or bitumen on the sand and shoulders of the road also help prevent evaporation. A trench on either side of the road helps collect run-off from rainfall on the pavement replenishing natural water-loss and maintaining the water level. It is important that this level should be below that of the moisture barrier or it exerts pressure due to development of a hydraulic head and a pumping action results with damage to the road.

The principles of mechanical stabilization were worked out prior to the modern use of additives; however, adequate mixing and compaction are still essential to successful soil stabilization.

STABILIZATION WITH ADDITIVES

The strength, bearing capacity and durability of soils can be increased by addition of inorganic and organic chemical compounds. These function chiefly as cementitious and binding agents or as waterproofers though changes in the consistency of clay soils induced by many compounds are also important.

Inorganic compounds employed include Portland cement, lime, slag, sodium silicate, phosphorous compounds and sometimes combinations of these. Various inorganic salts such as sodium chloride and calcium chloride have long been used in stabilization their chief function being to reduce plasticity and facilitate densification (HOGENTOGLER, 1937, pp. 312-316; SLATE and JOHNSON, 1958; SHEELER, 1961; SLATE, 1961; SALT INSTITUTE; YAMANOUCHI, 1975; BOWLES, 1979; HABERCOM, 1979).

Organic compounds include resinous and bituminous materials which act as waterproofers and sometimes behave similarly to a glue and add to cohesive strength. Chemicals known as surface active agents sometimes impart water repellent properties to soils. Waterproofing agents reduce the capacity of the soil for water uptake and help the soil to retain its dry strength even under wet conditions; bonding agents enhance soil strength by cementing together the soil particles. The main types of soil stabilization with both organic and inorganic additives have been reviewed by JOHNSON et al. (1960).

Soil is mixed with additives either in place by travelling plant mixers or by a stationary mixing plant. A travelling plant mixes and compacts as it is driven over the soil to be treated. Some varieties of stationary plant can be mounted on a trailer and set-up close to the construction site. Soil and additive are mixed

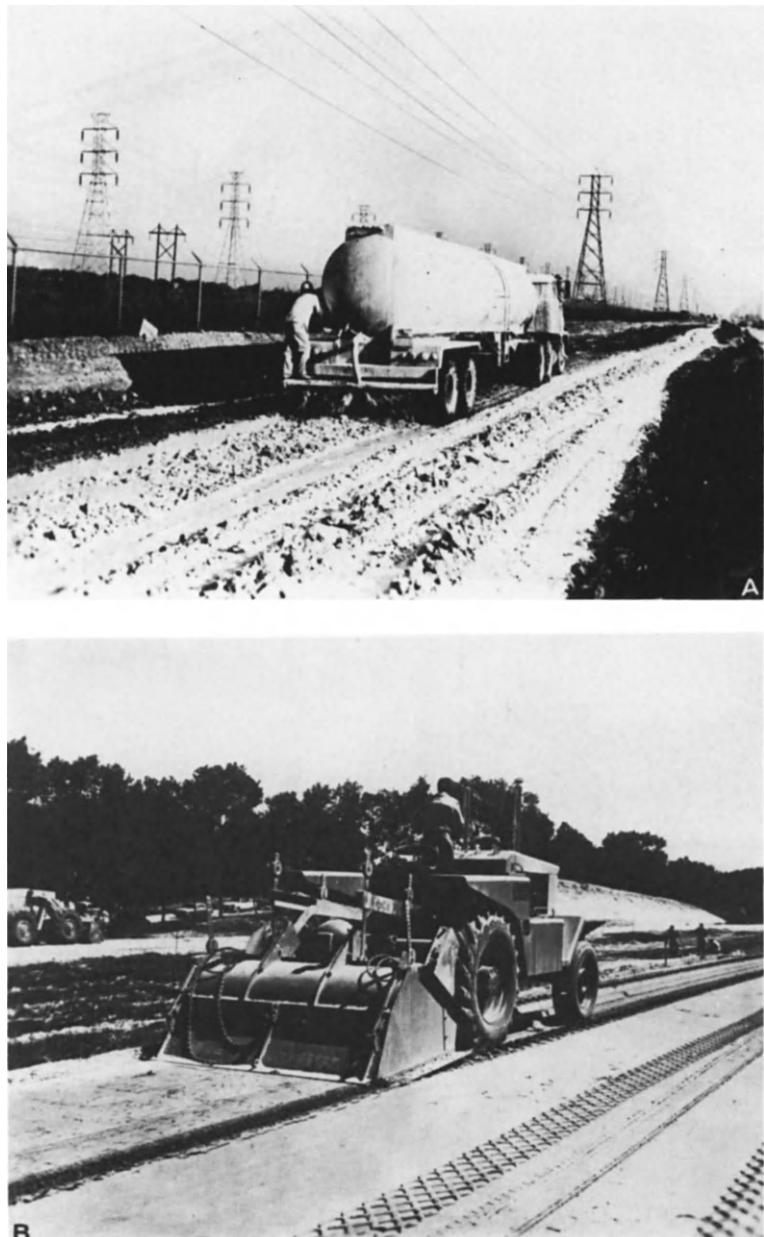
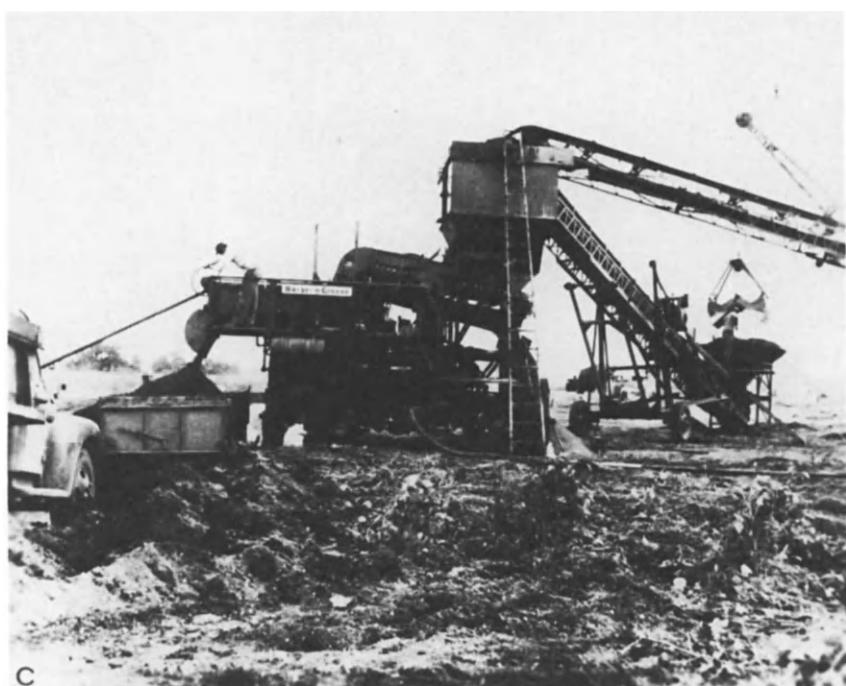


Fig. 8.2 A, B (p.255), C, D (p. 256) (Legend see p. 257).



C



D

Fig. 8.2 C, D

in the plant and transported to where required, spread and compacted. Quantities of the order of 500 tons of soil per hour per machine are often treated. In construction a definite procedure is followed. In roadbuilding for example it involves shaping and grading followed where necessary by pulverizing, scarifying and pre-wetting the soil. The additive is spread and mixed with the soil together with water when required. The mixture is compacted and allowed to cure before the wearing surface is applied. The exact procedure depends on the conditions and nature of the additive (Fig. 8.2).

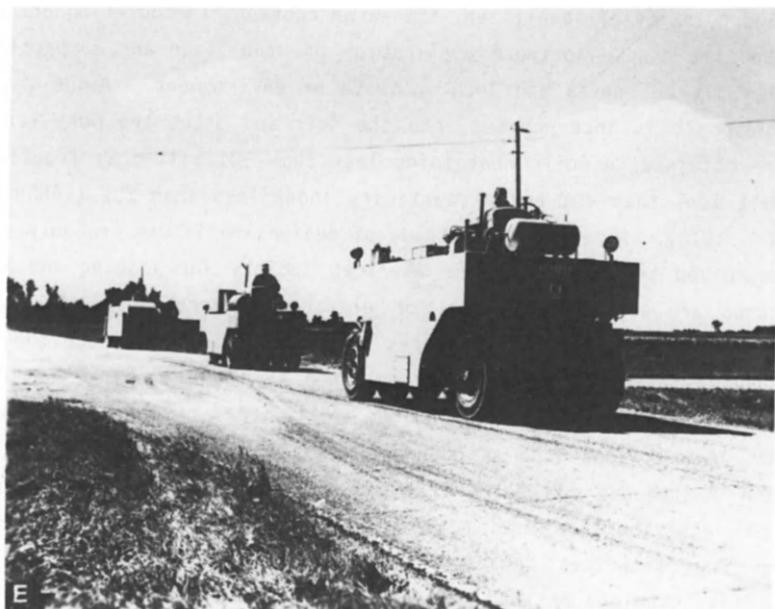


Fig. 8.2. A. Lime slurry being spread in metered amounts on graded and scarified clay roadway. (Photograph supplied by Rex Chainbelt, Canada, Ltd.)

B. In-place multiple pass stabilizer in action. (Photograph supplied by Buffalo-Springfield Division, Koehring Co., Ohio.)

C. Stationary mixing plant. (Photograph supplied by Calcium Chloride Institute, Washington, D.C.)

D. Sheepfoot roller in action. (Photograph supplied by National Lime Association, Washington, D.C.)

E. Heavy tired rollers; two pneumatic tire rollers of different sizes and two-axle tandem roller. (Photograph supplied by Buffalo-Springfield Division, Koehring Co., Ohio.)

Stabilization with bituminous materials, resinous materials, and chemicals

Bitumen is a general term for naturally occurring hydrocarbon-rich mixtures of organic compounds which are soluble in carbon disulphide (TRAXLER, 1961, p.4; ASPHALT INSTITUTE, 1975). Tars, pitches, and asphalts occur within this class of materials. Their use in construction of stabilized road base began in the 1920's

and early 30's in the U.S.A. Presently the trend in that country is to recycle asphalt pavement structures particularly low volume rural roads. In a recent survey by the Asphalt Recycling and Reclaiming Association it is reported that about 29-1/2 million tons of coal recycling incorporating the untreated granular base with emulsions will be done in the U.S.A. in the next five years (V. MARKER, THE ASPHALT INSTITUTE, personal communication, 1981). The method has been most successfully employed in the stabilization of non-cohesive or mildly cohesive soils particularly in warm dry climates where the soil has a low moisture content. Properties of the stabilized soil are influenced by the type of soil, the type and quantity of stabilizer, the water content, the duration and degree of mixing, the time elapsed between application of stabilizer and compaction (which should generally be short) and local climate or environment. About 2 to 10% by weight of asphalt is incorporated into the soil and often the most satisfactory results are obtained in soils containing less than 50% silt-clay fraction with a liquid limit less than 40% and a plasticity index less than 20% (LANCASTER-JONES and MCKEAND, 1978). A variety of methods of design are in use probably one of the most standardized being that of the American Society for Testing and Materials. The compounds are applied at normal or elevated temperatures. For successful mixing with soils at normal temperatures it is necessary to reduce the viscosity of bituminous materials. This is accomplished by two methods. The bitumen is applied to the soil as a "cut-back" or an emulsion. A cut-back is a solution of the bitumen in a solvent such as naphtha, kerosene or fuel oil. In an emulsion the bitumen is reduced to particles of colloidal sizes which are dispersed in water. When emulsions are used to stabilize fine silts or clays the water and dispersed phase sometimes separate and the colloidal suspension is said to "break". This technique has had success, however, and it is discussed in detail by MCKESSON (1940). Cut-backs have been more widely employed in soil stabilization. Cut-back asphalts have been classified in many ways. A common system now used depends on the rate of evaporation of the solvent. Those in which the solvent volatilizes readily are termed rapid curing (R.C.), those in which the solvent is less volatile are termed medium curing (M.C.) and those with the least volatile solvent are termed slow curing (S.C.). Asphalt specifications for pavement construction are published by organizations such as the American Association of State Highway Officials and ASTM and are based on viscosity (Tables 8-1 to 8-3) and penetration testing (Table 8-4).

Bituminous materials change the properties of a soil by adhering to the surfaces of the minerals bonding them together. They are good waterproofers and they confer their hydrophobic qualities on the soil to a degree which depends upon the adhesion of the bitumen to the soil minerals and the efficiency of mixing. In porous soils the more or less continuous coating of the bitumen cements the mineral particles together and imparts cohesion. In granular soils it is thought

TABLE 8.1 Requirements for Asphalt Cement, Viscosity Graded at 140°F(60°C)

NOTE-Grading based on original asphalt.

| Test | Viscosity Grade | | | | |
|--|------------------|----------|----------|----------|----------|
| | AC-2.5 | AC-5 | AC-10 | AC-20 | AC-40 |
| Viscosity, 140°F(60°C), P | 250+50 | 500+100 | 1000+200 | 2000+400 | 4000+800 |
| Viscosity, 275°F(135°C)min,cSt | 80 | 110 | 150 | 210 | 300 |
| Penetration, 77°F(25°C),100g, 5 s, min | 200 | 120 | 70 | 40 | 20 |
| Flash point, Cleveland open cup, min, °F (°C) | 325(163) | 350(177) | 425(219) | 450(232) | 450(232) |
| Solubility in trichloroethylene, min. % | 99.0 | 99.0 | 99.0 | 99.0 | 99.0 |
| Tests on residue from thin-film oven test: | | | | | |
| Viscosity, 140°F(60°C),max,P | 1250 | 2500 | 5000 | 10,000 | 20,000 |
| Ductility, 77°F(25°C),5 cm/min, cm | 100 ^a | 100 | 50 | 20 | 10 |

^aIf ductility is less than 100, material will be accepted if ductility at 60°F(15.5°C) is 100 minimum at a rate of 5 cm/min.

TABLE 8.2 Requirements for Asphalt Cement Viscosity Graded at 140°F(60°C)

NOTE-Grading based on original asphalt.

| Test | Viscosity Grade | | | | |
|--|------------------|----------|----------|----------|----------|
| | AC-2.5 | AC-5 | AC-10 | AC-20 | AC-40 |
| Viscosity, 140°F(60°C), P | 250+50 | 500+100 | 1000+200 | 2000+400 | 4000+800 |
| Viscosity, 275°F(135°C),min,cSt | 125 | 175 | 250 | 300 | 400 |
| Penetration, 77°F(25°C), 100g, 5 s, min | 220 | 140 | 80 | 60 | 40 |
| Flash point, Cleveland open cup, min, °F (°C) | 325(163) | 350(177) | 425(219) | 450(232) | 450(232) |
| Solubility in trichloroethylene, min. % | 99.0 | 99.0 | 99.0 | 99.0 | 99.0 |
| Tests on residue from thin-film oven test: | | | | | |
| Viscosity, 140°F(60°C),max, P | 1250 | 2500 | 5000 | 10,000 | 20,000 |
| Ductility 77°F(25°C), 5 cm/min, min, cm | 100 ^a | 100 | 75 | 50 | 25 |

^aIf ductility is less than 100, material will be accepted if ductility at 60°F(15.5°C) is 100 minimum at a rate of 5 cm/min.

TABLE 8.3 Requirements for Asphalt Cement, Viscosity Graded at 140°F(60°C)

NOTE-Grading based on residue from rolling thin-film oven test.

| Tests on Residue from Rolling Thin-Film Oven Test: ^a | Viscosity Grade | | | | |
|--|------------------|------------------|-----------|-----------|------------|
| | AR-1000 | AR-2000 | AR-4000 | AR-8000 | AR-16000 |
| Viscosity, 140°F(60°C), P | 1000+250 | 2000+500 | 4000+1000 | 8000+2000 | 16000+4000 |
| Viscosity, 275°F(135°C), min, cst | 140 | 200 | 275 | 400 | 550 |
| Penetration, 77°F(25°C).100g.5s. min | 65 | 40 | 25 | 20 | 20 |
| % of original penetration, 77°F (25°C), min | --- | 40 | 45 | 50 | 52 |
| Ductility, 77°F(25°C), 5cm/min. min. cm. | 100 ^b | 100 ^b | 75 | 75 | 75 |
| Tests on original asphalt: | | | | | |
| Flash Point, Cleveland Open Cup, min. °F(°C) | 400(205) | 425(219) | 440(227) | 450(232) | 460(238) |
| Solubility in trichloroethylene, min. % | 99.0 | 99.0 | 99.0 | 99.0 | 99.0 |

^aThin-film oven test may be used but the rolling thin-film oven test shall be the referee method.^bIf ductility is less than 100, material will be accepted if ductility at 60°F (15.5°C) is 100 minimum at a rate of 5 cm/min.

TABLE 8.4 Requirements for Asphalt Cement for Use in Pavement Construction-Penetration-Graded

| | Penetration Grade | | | | | | | | | |
|---|-------------------|-----|-------|-----|--------|-----|---------|-----|------------------|-----|
| | 40-50 | | 60-70 | | 85-100 | | 120-150 | | 200-300 | |
| | Min | Max | Min | Max | Min | Max | Min | Max | Min | Max |
| Penetration at 77°F (25°C)100 g,5s | 40 | 50 | 60 | 70 | | 100 | | 150 | 200 | 300 |
| Flash point, °F (Cleveland open cup) | 450 | --- | 450 | --- | | --- | | --- | 350 | --- |
| Ductility at 77°F(25°C) 5 cm/min, cm | 100 | --- | 100 | --- | 100 | --- | 100 | --- | 100 ^a | --- |
| Retained penetration after thin-film oven test, % | 55+ | --- | 52+ | --- | 47+ | --- | 42+ | --- | 37+ | --- |
| Ductility at 77°F(25°C) 5 cm/min.cm after thin-film oven test | --- | --- | 50 | --- | 75 | --- | 100 | --- | 100 ^a | --- |
| Solubility in trichloroethylene, % | 99.0 | --- | 99.0 | --- | 99.0 | --- | 99.0 | --- | 99.0 | --- |

^aIf ductility at 77°F(25°C) is less than 100 cm. material will be accepted if ductility at 60°F(15.5°C) is 100 cm minimum at the pull rate of 5 cm/min.

Tables 8.1 to 8.4 "Reprinted, with permission, from the Annual Book of ASTM Standards. Part #15. Copyright, American Society for Testing and Materials, 1916 Race Street, Philadelphia, Pa. 19103." (American Society for Testing and Materials, 1980c, pp. 343-344; pp. 869-871).

that the bitumen coats the individual mineral particles. In clay soils this is thought to be unlikely owing to the high surface area and it is believed that mineral aggregations are coated or so-to-speak encapsulated. Bitumen improves the stability of clay soils chiefly by acting as a waterproofer. It is considered that voids are plugged and access of water to the clay minerals made more difficult (KATTI et al., 1960). Thus soils stabilized in this way have increased cohesive strength and show decreased dimensional change associated with swelling and shrinking due to moisture movements caused by frost action, wetting and drying, etc. Various admixtures such as amines and phosphates have been employed in bituminous soil stabilization generally with the object of improving the bond between the bitumen and mineral. Changes in surface properties of clay minerals can be accomplished by exchange reactions (MASSACHUSETTS INSTITUTE, 1954; WINTERKORN and REICH, 1962; KEZDI, 1979).

Many experimental studies have been reported in which the properties of soils have been modified by chemical treatments. Surface active agents have been employed to reduce the susceptibility of soils to volume changes caused by changes in moisture content. Surface active agents function by converting the hydrophilic clay-mineral surface into a hydrophobic or water-repellent surface. When organic cationic surface active agents are employed the mechanism involves an ion-exchange process in which the inorganic cations present on the clay-mineral surface are replaced by the organic molecules. Such molecules are commonly polyfunctional and contain a positively charged portion which is attracted by the negatively charged clay-mineral surface where it becomes attached. The remainder of the molecule has water-repellent properties which are imparted to the clay mineral. Such chemicals have not been widely used in practice but are of considerable potential importance (AMERICAN CHEMICAL SOCIETY, 1955; HOOVER et al., 1960; HIGHWAY RESEARCH BOARD, 1962b).

An important factor in determining the durability of soil stabilization by organic materials is the influence of soil organisms. These often exert a deleterious effect by decomposing the organic stabilizing agent. Such organisms are most numerous and their importance is greatest in tropical soils (TRAXLER, 1961, p.191). Little consideration has been given to the influence of clay-mineral composition in much of the work on soil stabilization by bituminous materials. A basic understanding of the mechanism of stabilization requires its consideration.

Stabilization with cement

The strength of most soils is improved by addition of cement. The mixture is termed "soil-cement". It has been employed for well over a quarter of a century. It is employed chiefly as a base course for roads and airport runways though it has also been widely used for parking lots, service stations, temporary roads,

house foundations, as a lining for ditches and canals and in the manufacture of building blocks. Whenever possible the soil and cement are mixed at the construction site but sometimes materials are premixed (LILLY, 1975; GERBORN, 1975). In general gravels require about 10% by weight of cement, sands require about 7 to 12%, silts about 12 to 15% and clays about 12 to 20% by weight of cement. Laboratory tests are made to establish the optimum quantity of cement and the moisture content at which the soil can be compacted to maximum density (CATTON, 1937, 1940; AMERICAN SOCIETY FOR TESTING AND MATERIALS, 1980c, 1980d, pp. 145-150). When soils are sandy, mixing of cement and soil can be carried out at or slightly above optimum moisture content but with clayey soils mixing is most readily achieved with a moisture content slightly below optimum. In addition to its importance in achieving adequate compacted density, it is also essential that sufficient moisture be present for the cement hydration reaction to go to completion. The water content of the soil is adjusted and the soil-cement thoroughly mixed and compacted; this should be completed within about 6 hours of mixing for maximum strength development. During initial curing a protective waterproof coating commonly of a bituminous material is applied to the soil-cement. The mixture hardens as a result of the hydration of the cement. This takes place rapidly during the first week of curing but continues at a reduced rate for a long period. Some soils do not respond as well as others to cement stabilization and Atterberg limits provide a guide (CROFT, 1968). Cement stabilization tends to become uneconomic for soils with plastic limits greater than 20 or liquid limits in excess of about 45 to 50. However heavy clays can be cement stabilized by previously adding a small amount of lime which reduces the plasticity and makes the soil more workable; the soil with lime is allowed to age for one to three days and is then stabilized with cement.

Strength is often evaluated by means of the unconfined compression test but triaxial loading has also been employed (BALMER, 1958; ROBBINS and PACKARD, 1979). Durability is commonly estimated by test procedures such as the wetting and drying and freeze-thaw tests (BRITISH STANDARDS INSTITUTION, 1957, pp. 76, 79; AMERICAN SOCIETY FOR TESTING AND MATERIALS, 1980e, pp. 151-156; 1980f, pp. 157-162; SHEN and AKKY, 1974). The strength developed by soil-cement (Fig. 8.3) is affected both by the cement and by the soil. The rate of hardening can be influenced by changes in the nature and composition of the cement employed and by the use of additives. DAVIDSON and BRUNS (1960, p.34) showed that much higher strengths up to ages of 28 days were developed by use of a very fine cement which contained more tricalcium silicate ($3\text{CaO} \cdot \text{SiO}_2$) and less dicalcium silicate ($2\text{CaO} \cdot \text{SiO}_2$) than ordinarily used cement. Owing to the fine particle size the cement had a high specific surface area and the rate of hydration was accelerated and a better distribution of the gel product was achieved. Furthermore tricalcium silicate hydrates more rapidly than dicalcium silicate and contributes most to

early strength of Portland cement (Fig. 8.4) (BLANKS AND KENNEDY, 1955, p.32; LEA, 1956, p.165). Rate of hardening and strength may also be increased by addition of certain alkali compounds (LAMBE and MOH, 1958, p.47; LAMBE et al., 1960, p.101; HANDY, 1961, p.97; KEZDI, 1979).

The strength and stabilization characteristics of soils are influenced by their petrography (HANDY et al., 1961). Particle-size distribution, mineralogy, grain shape and distribution of clay minerals with respect to silt-and sand-sized particles are all important. Particle-size distribution of the soil affects bulk density, packing and porosity. Air void content and void-size distribution influence durability factors such as freeze-thaw resistance (POWERS, 1949; KLIEGER, 1952) though the resistance to weathering and subsequent erosion increases as cement content in the mixture increases (SHEN and AKKY, 1974). When clay-grade minerals are present in excess of about 30% it is more difficult to achieve economic stabilization by use of cement due to greater difficulties in pulverizing and mixing. Also in general the quantity of cement required increases with the proportion of clay-grade material.

The physical properties of a soil determine the ease with which it may be mixed with cement. It is, however, not possible on the basis of physical properties to predict the qualities of strength and durability which a soil-cement mixture will develop on curing and ageing. This depends upon chemical properties of the soil. Such properties often vary with depth and result in changes in cement requirements. It is therefore important to know at what level construction is to be carried out. The nature of the soil profile is considered in the system of soil classification employed by pedologists and soil-survey maps and identifications are often of considerable help in predicting the requirements and suitability of a soil for stabilization and in making approximate estimates of cost (LEADABRAND et al., 1957, p.16; SHERWOOD, 1962a, p.12; CROFT, 1968; KOP and VOGELER, 1974). The types of clay minerals in a cohesive soil influence the ease with which it can be stabilized with cement. Kaolinite and well organized illite may, to a first approximation, be regarded as inert and hydration and hardening of cement is little affected. By contrast swelling clays, particularly smectite, have a profound influence on cementitious action. Despite the general usefulness of such information the precise cement requirements for stabilization of different soils have to be determined by laboratory tests of such soil-properties as Atterberg limits as previously mentioned.

Sulphates in a concentration of 1% or less (SHERWOOD, 1957, p. 190) and organic matter (SHERWOOD, 1962a,c; BELL, 1976) may have a detrimental effect upon the stabilization of soils with cement. Concrete deterioration is known to result from attack by sulphate ions. In this case ettringite (calcium sulpho-aluminate, $3\text{CaO} \cdot \text{Al}_2\text{I}_3 \cdot 3\text{CaSO}_4 \cdot 31\text{H}_2\text{O}$) forms due to combination of tricalcium aluminate ($3\text{CaO} \cdot \text{Al}_2\text{O}_3$), lime, water and sulphate ion. Ettringite has a large solid volume

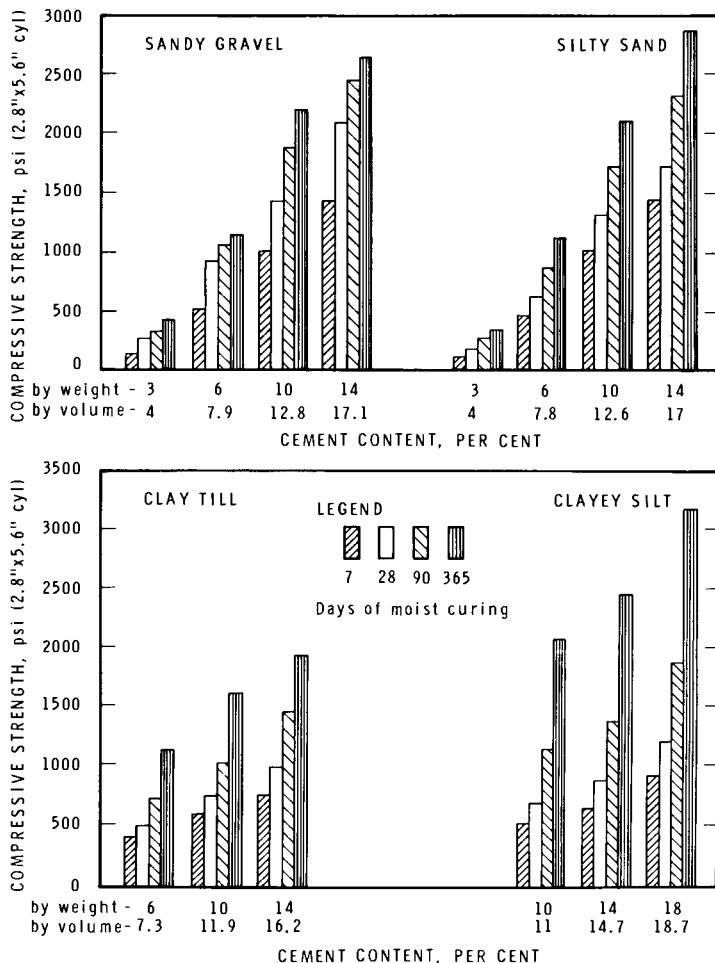


Fig. 8.3 Strength gain of different soils on mixing with cement. (After FELT and ABRAMS, 1957, p. 165)

and growth of this compound exerts an expansive force which may disrupt the material. A similar reaction may take place in soil-cement. Attack upon the clay minerals may also be involved in the formation of ettringite in clay soils (SHERWOOD, 1962b, p.106).

Organic matter in soils can interfere with the normal hydration reaction of the cement (CLARE and SHERWOOD, 1954, 1956; SHERWOOD, 1962a,c). Hydroxyl and carboxyl groups in the organic compounds are believed chiefly responsible. In hydrating cement there is a high pH and dissociation of the hydroxyl groups may occur with replacement of the hydrogen ions by calcium ions from the cement solution. This

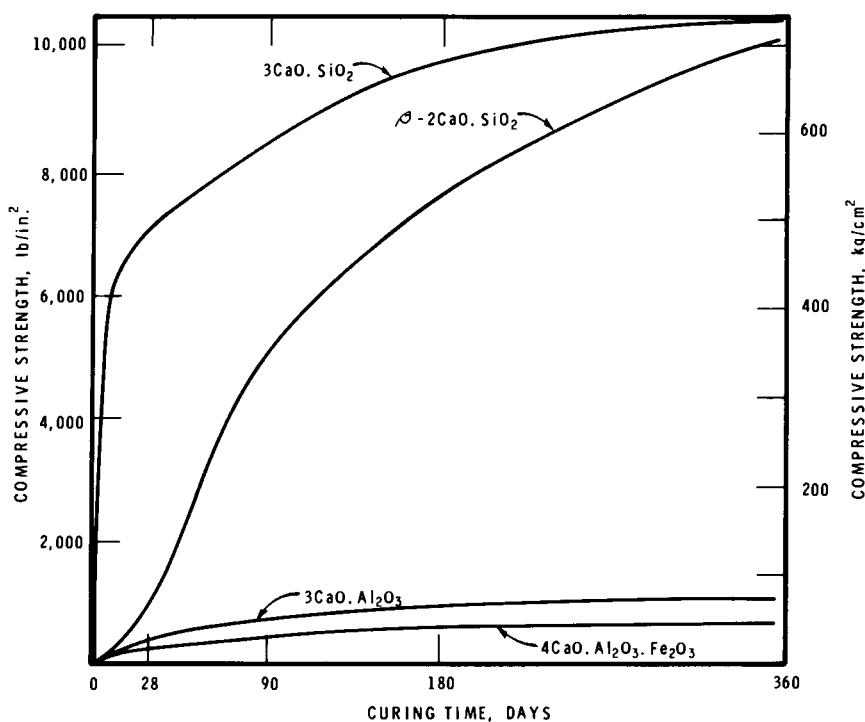


Fig. 8.4. Increase of compressive strength with curing time of pure cement compounds. (Copyright 1966 by the AMERICAN CHEMICAL SOCIETY (1934, p.840) and reprinted by permission of the copyright owner.)

may lead to a lowering of the calcium-ion concentration below that required for hardening of the cement. Addition of calcium chloride or hydrated lime to such organic soils sometimes has a beneficial effect by satisfying the demand of the organic compounds for calcium (CLARE and SHERWOOD, 1954, pp. 627-628; 1956, p.323). Sodium sulphate may also promote strength development in organic soils stabilized by cement (LAMBE et al., 1960, p.90).

Normal hydration of Portland cement generates lime which favours clay flocculation rendering the soil less cohesive and less subject to dimensional change with changes in moisture content. The mechanism by which strength is gained in soil-cement mixtures is believed to depend on the development of chains or agglomerations of hydrated cement and soil grains which enclose voids and soil pockets in a three-dimensional skeleton. It is apparent that strength gain will occur whether clay minerals are present or not. It has been suggested, however, that the mechanism of cementitious action is in part a surface phenomenon and the high specific surface area of the clay minerals may therefore give them an

important role in soil cement stabilization (HANDY, 1958, p.63). Nonetheless it is impossible to coat all the clay mineral particles with cement and in practice cohesive soils are broken into small lumps which are coated with cement and then pressed together by compaction. The shear strength of the compacted soil-cement starts to increase as hydration of the cement leads to setting and hardening. Strength gain depends on the number of points of contact where junctions are cemented, on the amount of cement used and on the state of compaction.

Strong evidence that when clay minerals are present they actively participate in the chemical reactions leading to gain in strength has been provided by EADES and GRIM (1960) and HERZOG and MITCHELL (1963). They propose that in addition to the flocculation and exchange reaction involving uptake of calcium ions (if other exchange ions are previously present on the clay minerals) the clay minerals are attacked at the high pH which prevails in the environment of hydrating cement. Studies of pure clay minerals compacted with cement and pure tricalcium silicate show that after curing montmorillonite suffers considerable alteration and kaolinite alters to a lesser degree. Hydration of the calcium silicates in unhydrated cement leads to formation of tobermorite-like calcium-silicate hydrates and calcium hydroxide. The structure of the newly formed calcium hydroxide is certainly in a state of strain (GILLOTT and SEREDA, 1966) and the compound may be in an unusually reactive state. It is thought to attack the clay minerals and amorphous materials in the soil combining with liberated silica and alumina to form cementitious compounds. The structural similarity between certain cement-hydration products and clay minerals suggests the likelihood of epitaxy-the extension of an already existing crystal structure by oriented overgrowth. It is to be expected that such a process would favour strength development. Similar factors may affect the reactivity of fly ashes in soil stabilization. Free lime or lime liberated in presence of water has been found to have an important bearing on their self-cementitious action. In recent work in Germany (KOHLER, 1981) reactions between clay minerals and cement and lime have been characterized by measurement of electrical conductivity and zeta potential, by chemical analysis and by x-ray diffraction. Results indicate that the cement and lime promote highly complex reactions between the soil constituents and the liquid phase. Comparison of known mineralogical and geochemical transformations during diagenesis and lithification with those occurring in the presence of cement and lime helps to throw light on the engineering behaviour of the stabilized soil.

A bibliography on cement-treated soil mixtures has been published by the HIGHWAY RESEARCH BOARD (1962a). A handbook on the practice of soil-cement construction is available from the Portland Cement Association, Chicago, Illinois and a detailed discussion of the principles of cement stabilization in road construction is given by METCALF (1977).

Stabilization with lime

Lime has been employed in agriculture and in the construction industry from early times and soil-lime mixtures were used in the construction of some Roman roads and in places along the Great Wall of China. About 3/4 million tons per year are now used in soil stabilization in the U.S.A. of which about 80% is hydrate and about 20% quicklime. The principal use is in highway construction and maintenance but it is also used in construction of airfields, building foundations, railway beds and even under hydraulic conditions where the soil is partly or wholly submerged as in irrigation canals, reservoirs, levees and dams (GUTSCHICK, 1978). Lime stabilizes soil both by decreasing soil plasticity and by increasing bearing strength. Amounts of the order of 3 to 4 per cent generally achieve the first objective and larger amounts may be needed for optimum increase of strength.

Lime flocculates the clay minerals due to base exchange and its application causes cohesive soils to become more workable and less plastic; it can also appreciably reduce swelling and shrinking due to gain or loss of moisture. A steady increase in strength takes place at a rate which accelerates with increase of temperature. Lime stabilization has been most extensively used in the United States and in tropical regions of the world where its relatively low cost makes it economically attractive. It has also been used in Europe notably in Germany, France and Belgium and to some extent in Great Britain, South Africa and Japan. Principles and experimental data to do with the state of the art and potential problems have been discussed in a Transportation Research Circular (1976) and by METCALF (1977) and TESORIERE et al (1979).

It is widely used to stabilize soils in road construction for sub-base, sub-grade and base-course improvement. It reacts most readily with clay soils in which the plasticity index exceeds 10 at least. Lime is generally unsuitable for stabilization of coarse soils such as gravels and sands and problems are also encountered with silts but recently this difficulty has been to some extent overcome by incorporation of flyash together with lime and injecting the combination as a slurry (WOODBINE CORPORATION). In general the most favourable grain size distribution of soil for lime stabilization is in the range of fine sands and silts containing some clay (KEZDI, 1979). Lime is generally applied to soils as a powder, as a slurry or in pebble form and mixed with the soil by mechanical means. Precautions to protect workers have to be taken due to the caustic nature of lime and for this reason application as a slurry is often preferable. In addition to its use in highway construction lime has been employed in highway maintenance. A technique termed "drill-lime stabilization" was developed in 1961 in Oklahoma, U.S.A., and successfully used to correct distress resulting from moisture uptake by plastic clay in the road sub-grade

(ANONYMOUS, 1963). In more recent applications it has become common to inject a lime slurry under pressure, the technique being sometimes referred to as lime slurry pressure injection. Pressures of the order of 50-200 psi (345-1380 kN/m²) are used the lime following the path of least resistance and forming a network of horizontal sheets interconnected by vertical or cross-cutting veins which after ion exchange and other reactions are thought to act as moisture barriers (WRIGHT, 1973; THOMPSON and ROBNETT, 1976). Another related technique has been used to improve foundations. Columns of lime, sometimes unslaked, are introduced into the soil by a rotating auger or by means of a special tool described as resembling a giant egg whisk (ASSARSON et al., 1977; BROMS and BOMAN, 1979). Columns have been successfully constructed to depths as great as 10m and under favourable circumstances addition of 5 to 10% lime has increased strengths by the order of 10 to 60 times with about 2/3 of the strength gain being achieved within 2 to 3 months (PAUS, 1979). The technique is reported to reduce settlement, increase bearing capacity and improve drainage and rate of consolidation.

Successful soil stabilization has been achieved by use of quicklime (CaO), hydrated lime or slaked lime-Ca(OH)₂, and dolomitic limes. Lime which contains only calcium is known as calcitic lime; when magnesium is also present the lime is termed dolomitic (Fig. 8.5). The mole ratio of calcium oxide to magnesium oxide expresses the degree to which a lime is calcitic or dolomitic. Quicklime is prepared by heating or calcining limestone to about 1200°C at which temperature carbon dioxide is driven off. The exact temperature of decomposition varies with

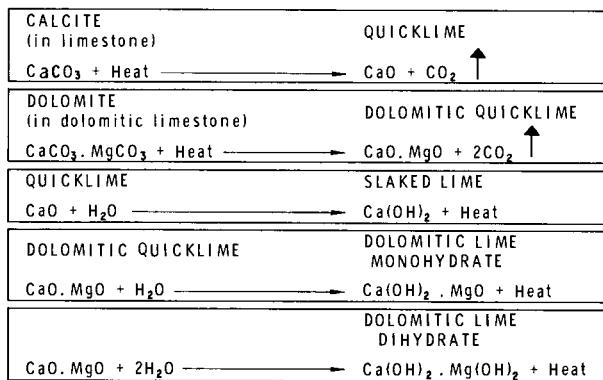


Fig. 8.5. Chemical reactions involving lime.

the partial pressure of CO₂. The reactivity of the lime is a function of the temperature and time of firing (HASLAM and HERMANN, 1926); of the two variables temperature has the greatest effect upon reactivity (RAY and MATHERS, 1928, p.419; AZBE, 1939). Lime prepared by low temperature firing is more reactive than lime

made at higher temperatures. If calcium hydroxide is fired quicklime may be prepared at as low a temperature as 500°C. When a high temperature is employed in the manufacture of quicklime it is sometimes described as "hard burned", whereas the low temperature products are described as "soft burned". Quicklime made by high temperature firing owes its reduced reactivity to sintering which gives the material a higher bulk density, reduced porosity, an increased crystallite size, and reduced surface area.

Calcium hydroxide or hydrated lime is formed when quicklime reacts with water. The reaction is exothermic and the process is termed slaking. If calcium oxide is allowed to react with moisture in the vapour phase small crystallites of calcium hydroxide (of the order of 250 \AA) are formed surrounded by what appears to be amorphous material on examination under the electron microscope. X-ray diffraction patterns of this material show conspicuous broadening of the powder lines (GILLOTT, 1967). Vapour-phase hydration is thought to occur via a topochemical reaction whereas a "through solution and crystallization" process is believed to operate when hydration occurs in liquid water (RAMACHANDRAN et al., 1964). The slaked lime produced by the two processes is known to differ in chemical reactivity. It is sometimes an advantage to use quicklime in stabilization because the uptake of water on slaking leads to faster drying of soil. The evolution of heat due to the exothermic nature of the hydration process also tends to speed-up chemical reactions and may be advantageous in cooler climates. In general however use of the hydrate is preferred.

Studies of reactions between hydrated lime and pure clay minerals have been reported. Samples of kaolin developed maximum strength on the addition of 4-6% of lime; the strength gain commenced immediately upon addition of lime. Montmorillonite and illite required treatment with lime in excess of 4-6% before there was a gain in strength. X-ray diffraction indicated that lime addition caused an immediate attack upon kaolinite crystal edges which was accompanied by a gain in strength. In the case of illite and montmorillonite strength gain was delayed until lime was added in an amount which exceeded that required for saturation of the interlayer positions with calcium (EADES and GRIM, 1960, p.62). Granular or aggregate bearing soils are commonly treated with 2-4% lime and clay soils intended to serve as sub-base for roads require treatment with 4-8% of lime based on dry weight of soil (CLARE and CRUCHLEY, 1957, p.100). A chart has been suggested by McDOWELL (1966) for the selection of lime content for soil stabilization (Fig. 8.6). Laboratory tests should be performed to establish the optimum amount for the particular conditions and to establish that a reaction leading to strength gain takes place between the particular soil and the lime. If excess lime is added it may have a weakening effect prior to its reaction possibly by acting as a low strength filler separating the mineral grains (LAGUROS et al., 1961, p.7). In this respect lime differs from cement as a soil-stabilization

material. There is generally found to be a linear relationship between the strength gained and the amount of cement added to soil, whereas strength gain falls off on increasing addition of lime. As the clay-grade content of a soil increases so to, in general, does the effectiveness of lime as a soil stabilizing agent. Unconfined compressive strengths of several hundred pounds per sq. inch after 28 days curing have been commonly reported (Fig. 8.7). For satisfactory strength development adequate compaction is required. Delay in compaction after lime application is apparently less critical than in the case of stabilization with cement.

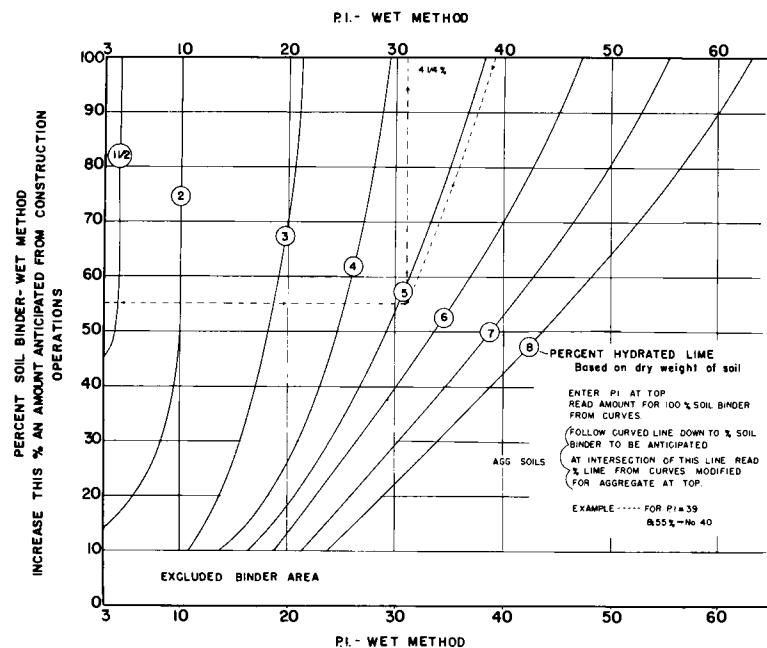


Fig. 8.6. Recommended amounts of lime for stabilization of subgrades and bases. Percent of relatively pure lime usually 90% or more of Ca and/or Mg hydroxides and 85% or more of which pass the no. 200 sieve. Percentages shown are for stabilizing subgrades and base courses where lasting effects are desired. Satisfactory temporary results are sometimes obtained by the use of as little as 1/2 of above percentages. Reference to cementing strength is implied when such terms as "lasting effects" and "temporary results" are used. Exclude use of chart for materials with less than 10%-no. 40 and cohesionless materials (P.I. < 3). These percentages should be substantiated by approved testing methods on any particular soil material. (Data supplied by McDowell, 1966).

Magnesian limes are generally prepared by firing dolomite. This term is employed both for the mineral which ideally contains equal molecular proportions of calcium and magnesium carbonate ($\text{CaCO}_3 \cdot \text{MgCO}_3$) and for the rocks which contain more than 50% carbonate of which more than half is the mineral dolomite

(PETTIJOHN, 1957, p.416). The magnesium-carbonate portion of the dolomite molecule decomposes at a lower temperature than the calcium carbonate so that when dolomite is fired to 900°C at atmospheric pressure the dolomitic quicklime formed contains equimolecular proportions of both magnesium oxide and calcium oxide ($\text{CaO}\cdot\text{MgO}$). Calcium oxide reacts with water much more readily than magnesium oxide which forms the hydroxide only very slowly at normal temperatures. The hydration product contains calcium hydroxide and (mainly) magnesium oxide. This is sometimes known as dolomitic lime monohydrate. If the burned dolomite is hydrated at high temperature and pressure by means of the autoclave the magnesium oxide hydrates as well as the calcium oxide. The product is then sometimes called dolomitic lime dihydrate (Fig. 8.5). When dolomitic monohydrate lime is used as the soil stabilizing agent the hydration of the periclase is thought to aid strength development even though the reaction is slow.

Three principal processes are thought to take place when lime is added to a clay-containing soil. These are: a rapid exchange reaction; a much slower reaction between the clay minerals and the lime; and carbonation of the unused calcium hydroxide by CO_2 present in pore solutions and gases.

If the exchange sites on the clay minerals are occupied by ions other than calcium, a rapid exchange reaction occurs in which many of the exchange sites become occupied by calcium ions. The lime treatment causes the soil to become more alkaline (pH rises)(CLARE and CRUCHLEY, 1957) and in the calcium system the clay minerals flocculate (RUSSELL, 1934, p.366; SCHOFIELD and SAMSON, 1953) so that the soil becomes more open textured. At constant moisture content the soil appears drier and more friable and is more easily worked. In clay soils there is generally an increase in the plastic limit and a decrease in the liquid limit so that there is a fall in the plasticity index (Fig. 8.8). The magnitude of the change in plastic limit is affected by the soil clay mineralogy. Montmorillonite soils show the greatest change, in illite-chlorite soils the effect is intermediate and the plastic limit is least affected in kaolinite soils (HILT and DAVIDSON, 1960, p.30). This order follows that of decreasing cation-exchange capacity (GRIM, 1953, p.129). It is evident that the amount of lime required to effect changes dependent upon exchange reactions is a function of both the cation-exchange capacity of the minerals and the nature of the ions occupying exchange sites prior to addition of lime. If organic materials are present in a soil they often interfere with lime stabilization. Organic compounds frequently have a high exchange capacity (see cation-exchange, Chapter 5) and are believed to compete with the clay minerals for the available calcium ions (LADD et al., 1960, p.83). It has been suggested that an organic precipitate surrounds the lime particles and isolates them from further reaction with the clay minerals (DUMBLETON, 1962, p.61). In general soil plasticity is reduced more by hydrated calcitic limes than by dolomite monohydrate.

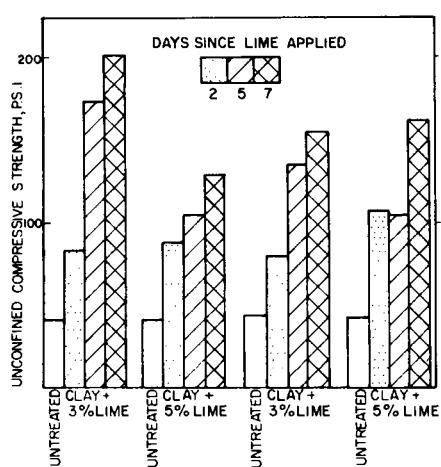


Fig. 8.7 Gain in strength of soil on treatment with lime. (Data supplied by National Lime Association, Washington, D.C.)

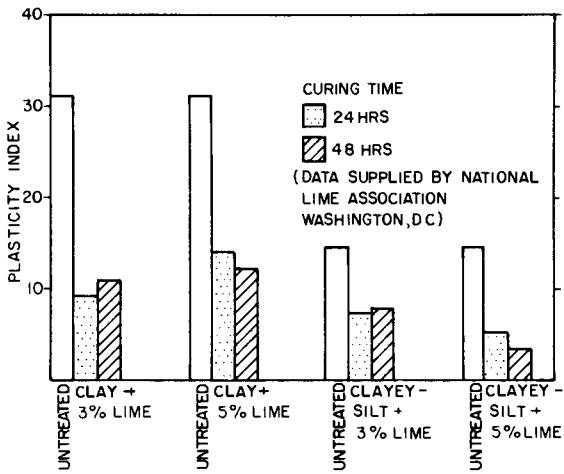


Fig. 8.8 Change in plasticity index of soil on treatment with lime. (Data supplied by National Lime Association, Washington, D.C.)

The mineralogical composition of the soil is known to affect the course of the soil-lime reactions and their bearing on engineering properties such as plasticity and strength. Montmorillonite- and kaolinite- containing soils develop strength more readily than do illitic soils and other constituents such as carbonates and amorphous constituents are thought to be important. The pH of the pore solutions has a significant bearing on reactions including those influencing strength-gain since it affects the solubility of both alumina and silica. The solubility of alumina is high at low pH, decreases rapidly above about pH3 to 4, continues to decrease slowly to about pH8 and increases rapidly again at higher values of pH. The presence of significant amounts of amorphous, reactive, alumina in a soil may not be beneficial. Reactions with the aluminates may use up significant amounts of the added lime forming calcium aluminate hydrates not all of which have good cementitious properties. In the case of silica the solubility increases steadily with rise of pH until at a pH above about 9 it increases rapidly. Hence, as is to be expected, formation of new cementitious minerals such as calcium silicate hydrates (EADES et al., 1962) is favoured by the alkaline conditions which result from addition of lime. The use of lime to water ratio in this regard has been suggested (SABRY and PARCKER, 1979).

Studies have been made of the effect on soil-lime stabilization of the addition of small amounts of other chemicals. Favourable results have been reported from the addition of 1-2% sodium hydroxide to clay soils stabilized with lime (DAVIDSON et al., 1960, p.49). The increased alkalinity is thought to favour an accelerated

attack on siliceous and aluminous compounds in the soil. The common ion effect may suppress ionization of the calcium hydroxide until sodium silicate has been formed. On eventual fall in pH this may react with the calcium silicate to form cementitious compounds (LAMBE et al., 1960, p.98). Confirmation of these earlier studies has been obtained in more recent work (O'FLAHERTY and GRAY, 1974). Addition of sodium metasilicate to lime stabilized soil led to a more rapid strength gain than was produced by Na_2SO_4 or NaOH ; addition of these compounds however gave more favourable results than were obtained with lime alone. Type of lime was not found to be a major factor though the importance of the nature of the soil was once more confirmed. Calcium hydroxide probably contributes to strength gain by reacting with carbon dioxide to form calcium carbonate. This has well-known cementitious properties and may function as a bond between the mineral particles of a soil.

The strength gain arises chiefly from chemical reactions between the lime, clay-grade minerals, and amorphous constituents in the soil. When these are absent or present in small amounts use has been made of lime together with a pozzolan. A pozzolan is defined as "a siliceous or aluminosiliceous material that in itself possess little or no cementitious value but that in finely divided form and in the presence of moisture will chemically react with alkali and alkaline earth hydroxides at ordinary temperatures to form or assist in forming compounds possessing cementitious properties" (AMERICAN SOCIETY FOR TESTING AND MATERIALS, 1980a, p.342). Pozzolanic materials such as certain forms of volcanic ash and diatomaceous earth, occur naturally and were employed by the ancient Romans. Artificial pozzolans include calcined clays and shales and pulverized furnace fuel ash which is known as flyash. This has been extensively employed as a pozzolan in lime stabilization of soils. As previously mentioned a lime-flyash slurry is sometimes injected into soils particularly in silts and sands. Appreciable work has been done to develop a procedure of mix design which optimizes the proportions of lime and flyash (ROSNER, 1978). In addition to its quality as a pozzolan some flyashes, such as some of those resulting from use of lignite coals, are self cementitious and may be used as a supplement or replacement for Portland cement (JOSHI, 1978; LAM, 1980). Strength gain and durability of soils mixed with lime and pozzolanic materials are reviewed in various publications of the HIGHWAY RESEARCH BOARD (1958; 1959). A manual on "Lime Stabilization Construction" is available from the National Lime Association, Washington, D.C.

Stabilization with phosphates and other compounds

Phosphoric acid has been used to a limited extent in soil stabilization. The mechanism is believed to involve an attack upon the clay minerals with release of aluminium hydroxide. Various aluminium phosphates are believed to form which act

as cementitious binders between the mineral particles of the soil. Among these aluminium metaphosphate is thought to be the most important since thus produced it is hard and water insoluble. Optimum moisture content for maximum compaction density is not necessarily the condition for maximum strength development on treatment with phosphoric acid. In alkaline soils such as those which contain calcium carbonate, an excessive amount of phosphoric acid is required as it must be added in excess of the amount needed to neutralize the alkali. The process has most promise for acid soils with high clay content. The procedure was described by LYONS (1957) and MICHAELS et al. (1958) and has been reviewed in a publication of the HIGHWAY RESEARCH BOARD (1962c) and U.S. WATERWAYS EXPERIMENT STATION (1960). The use of other compounds such as potassium chloride has also been investigated. Studies showed that addition of this compound to heavy clays caused a significant decrease in activity and apparently caused mineralogical changes linked with soil stabilization (FRYMAN et al., 1978).

Stabilization by electrokinetics

When an electrical potential gradient is applied to a soil across two electrodes the water commonly migrates towards the cathode (negative electrode). Migration in the opposite direction is also known. This phenomenon, known as electro-osmosis, has been studied as a means of soil stabilization. The migration of water is due to movement of the exchange ions associated with the clay minerals. These ions carry water with them so dewatering of the soil occurs. provided the water movement to one electrode exceeds the amount carried in the opposite direction by ions of opposite electrical charge.

Clay soils which lack strength due largely to presence of excess water show gain in strength when electrically treated due essentially to reduction in the water content. However, in the U.S.S.R. (TITKOV et al., 1965) it has been shown that new minerals with cementitious properties may form due to the ionic migrations and interactions which result from the imposed electric field. Principles concerning the utilization of the method and the decrease in swelling of highly expansive soils containing montmorillonite have been reviewed (MANCINI and O'BANNON, 1975).

MODIFICATION OF FROST HEAVING IN SOILS

Silts and lean clays are most susceptible to ice lens formation (see Chapter 6). Frost heaving develops when there is the correct combination of temperature, soil and water supply. Rate of temperature change and degree of supercooling, pressure, surface area (which depends on composition, fabric and soil type), amount of unfrozen water and depth to water-table are all important. Methods of reduction or prevention of frost heaving depend upon control of any or all of these variables. Probable effectiveness has to be balanced against cost.

The most obvious approach is to replace the fine grained soil with a material which is not susceptible to formation of ice lenses such as sands and gravels containing a minimum amount of fines and through which good drainage is possible. The required thickness is based on estimates of depth of frost penetration deduced either from experience or the freezing index. This method has been much used and is often combined with an improved system of underdrains (HIGHWAY RESEARCH BOARD, 1952). Exhaustion of readily available supplies of gravel close to the construction site and regulations of environmental protection agencies limiting exploitation of reserves in urban areas have led to increases in transportation costs which have always been considerable for such heavy materials. Hence alternative solutions to the problem have become more attractive economically. One approach is to thermally insulate frost-susceptible sub-grades (OOSTERBAAN and LEONARDS, 1965; YOUNG, 1965). A layer of insulating material is incorporated in the structure to limit the depth of frost penetration. Hence heave should not take place if freezing of the frost-susceptible sub-grade can be prevented. Recently, favourable results have been obtained by use of extruded polystyrene plastic foam with surface skins (PENNER et al., 1966) as insulating material in trial road sections in Canada. Particle board, cellular urethane plastics which may be formed in situ, and lightweight concrete made with Portland cement, which may be considered loadbearing have also been used (APOSTOLOPOULOS and SCHNEIDER, 1979). The low coefficient of thermal conductivity of sulphur [0.27 W/(m.K)] has led to trial use of this material as a foam (BETTER ROADS, 1975) and also as a binder in structural lightweight aggregate sulphur concrete employed as an insulating base material in roadway construction (GIFFORD and GILLOTT, 1979). Despite the soundness of the underlying concept of thermal insulation to limit formation of ice lenses in the soil application of the method has sometimes led to other problems of a practical nature. Heat loss from the pavement, due to radiation or other causes, is less readily made good by conduction from below due to the thermal barrier so more ice has sometimes formed on insulated sections of highway than on adjoining sections where there was no insulation. Hazardous driving has been attributed to this cause.

The potential economic advantages of changing the properties of the frost susceptible soil at the construction site has stimulated study of additives. Additives investigated have been intended to change the properties of the soil by increasing its strength, by preventing freezing of its pore water or by preventing moisture migration. LAMBE (1956) has summarized ways by which these objectives may be accomplished. Voids may be plugged by mixing in of impermeable material, particles may be cemented together, freezing point of pore water may be depressed by addition of salts such as calcium chloride, or waterproofers may be employed. Addition of calcium lignosulphate and sodium tripolyphosphate have been claimed to reduce the frost heave of silty soils (CRONEY and JACOBS, 1967). For the forma-

tion of ice lenses there is a minimum content of fine particles which must be present in the soil. An alternative to their removal is to aggregate the fines by use of flocculants or polymers which link particles together. The opposite approach is to add a dispersant. Dispersed clay particles can assume a more close-packed configuration and soil permeability is decreased. As voids are also reduced in size there is a tendency for freezing point of soil moisture to be lowered. Lambe found that soils composed of a wide range of particle sizes including adequate content of fines ("well-graded" in engineering terminology) responded most satisfactorily to treatment. The properties of uniform silts or clays were least readily changed. The use of dispersants and to a lesser extent soil waterproofers gave the most promise of being effective as additives in the reduction of frost heave (LAMBE, 1956, p.22).

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CHAPTER 9

CLAYS AS MATERIALS

Primitive man used clay freely to fashion articles for his daily use and ceramic articles and pottery are used by archaeologists as a means of identifying early cultures. Sundried bricks were employed for construction at an early date and excavations at Jericho disclosed structures dating from about 6,000 B.C. in the pre-pottery Neolithic period (DAVEY, 1961, p.22). Good quality ceramics were made at such centers of early civilization as Egypt, Sumer and Babylon. Fired bricks often covered with coloured glazes were used as a building material in Nineveh and Babylon. From the ninth to the sixth century B.C. decorated wall tiles covered with tin glazes were used by the Assyrians and Babylonians. Today clays rank among the most important nonmetallic raw materials both in terms of tonnage produced and commercial value of the products which are more numerous and diversified than ever before in history.

Much of the economic importance of clay in the modern world as well as its widespread use by early man arises from its plasticity and fired strength. The plasticity makes it possible to mould moist clay into useful shapes and what is more important this shape is retained on drying and after firing. On drying clays harden and shrink the volume decrease being approximately proportional to the water lost until the shrinkage limit beyond which there is little further reduction in volume. Weight loss continues after apparent shrinkage stops due to evaporation of pore water and finally due to loss of rigidly adsorbed water (FUNK 1974). The term "shrinkage limit" which is used in soil engineering seems to correspond approximately to the term "leather hard" employed by ceramists. Drying is usually carried out initially under warm humid conditions and the temperature is slowly raised to a value of about 120°C care being taken to minimise steep gradients. Further shrinkage takes place on firing together with other physical and chemical changes and the fired product develops increased strength.

Clays have other industrial uses in which retention of shape is unimportant. In the manufacture of Portland cement for example clays or other argillaceous rocks are often used as a source of alumina and silica. The calcareous clay known as marl was the raw material basis for many early cement plants. Clays are used to bond sands employed as moulds in foundries, in grouting, in drilling fluids employed in the petroleum industry, as catalysts, as paper fillers and coatings, in the rubber industry, in pelletising ores and in the pharmaceutical industry (GRIM, 1962). A potentially important new use for clays (especially kaolin and fire-clay types) is in the production of alumina or aluminium (AMPIAN, 1976, p. 253).



Fig. 9.1 A,B(p.286), C,D(p.287)(Legend see p.288).

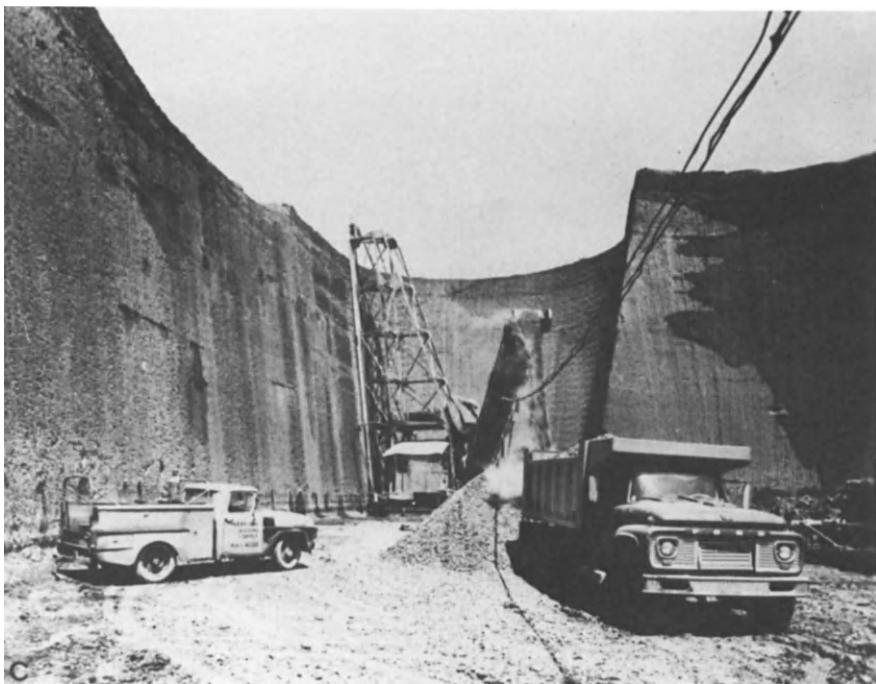




Fig. 9.1. Equipment for winning clays.

- A. Power shovel. (Photograph supplied by Bucyrus-Erie Co., South Milwaukee, Wisc.)
- B. Dragline excavating clay. (Photograph supplied by Northwest Engineering Co., Chicago, Ill.)
- C. Shale planer in operation. (Photograph supplied by Eagle Iron Works, Des Moines, Iowa.)
- D. Washing out kaolin by water jet delivered from high-pressure hose, Cornwall, England. (Photograph supplied by Anglo-American Clays Corporation.)
- E. Large draglines stripping overburden to expose bauxite for excavation. (Photograph supplied by Aluminum Company of Canada, Montreal.)

WINNING AND PRE-TREATMENT OF CLAY

A geological survey of a clay deposit to determine its nature, extent, mode of occurrence and quality should be carried out prior to its industrial exploitation. Clays are frequently worked in open pits as costs are lower than for underground mines. The method adopted depends upon the economics and geological nature of the deposit. Open pit mining has a significant environmental impact and therefore is increasingly subject to zoning restrictions and reclamation and disposal regulations (AMPIAN, 1976, p. 262). Various types of mechanical shovels and scrapers are used (Fig. 9.1 A-E) though well lithified deposits may require blasting. High pressure jets of water are employed in the working of the kaolin deposits in Cornwall, England.

The required use and economics determine the pre-treatment to which a clay is subjected. Clay required for the manufacture of structural clay products is generally used with as little pre-treatment as possible. Variation in the raw clay, however, causes variation in the product so procedures are followed to improve the uniformity of the raw material. Working a whole face in the clay pit followed by bulk blending of the clay in a large storage heap (Fig. 9.2) is one method adopted. A face may be worked on an incline and a proportion of all the clay beds exposed may be taken in each load removed by the scraper.

Some clays need grinding. This is accomplished by a variety of different types of commercially available equipment. Jaw crushers, hammer mills, ball mills and various types of roll crushers are used. Oversize pieces are removed and returned for further grinding by passing through screens of known sieve size. Grinding equipment is sometimes employed in conjunction with an elutriator, the whole operation being continuous. Air and water elutriators are employed for size classification. There are many applications for high quality clays and their greater value makes it economically worthwhile to use more refined methods of beneficiation to improve the physical or chemical purity of the raw clay. The colloidal properties of the clay minerals are exploited to separate them from the non-clay minerals. For example a deflocculated clay remains in suspension almost indefinitely whereas non-colloidal particles soon settle out. Large tanks can be used for this purpose and the refined clay drained off after an appropriate settling time.

The slurry may be separated into different particle-size fractions by centrifugal action. White clays are sometimes bleached by chemical means before the water is removed. If the clay is flocculated it soon sediments and the water can be siphoned off or decanted. Dewatering can also be accomplished by evaporation, filtration, centrifugal action or electro-osmosis. Iron materials have been removed by dry magnetic separation techniques for many years. Recently practical high-intensity gradient wet magnetic separation processes for removing weakly magnetic kaolin discolorants in fine mesh material have been developed (LAWVER and HOPSTOCK, 1974; IANICELLI, 1976). Froth floatation is much employed in concentration of ore minerals from gangue. This has been used for beneficiation of minerals such as feldspar which is often used in conjunction with clays in the ceramic industry. Kaolin of high purity has been produced commercially by ultrafloatation using powdered limestone as carrier of impurities which are removed in the froth (ANONYMOUS, 1963). Diagrams to illustrate some of the steps involved in mining and beneficiation of clay are shown in Fig. 9.3-9.5.

Principal steps in processing the various types of clay have been summarized as follows by AMPIAN (1976, p. 262):

Kaolin: crushing; blunging; rough sedimentation; water fractionation; ultra floatation; acid treatment; calcination; air floating; attrition grinding, delaminating;



Fig. 9.2 Shale stockpile in quarry, Ottawa. (Photograph supplied by Domtar Construction Materials Ltd., Ont., Canada.)

Ball clay: drying; shredding; pulverizing; air floating;

Fire clay: crushing; clacining; blending;

Bentonite: weathering, drying, grinding, sizing, granulation, additives for cation exchange;

Fuller's earth: blunging, extruding, drying crushing, grinding, sizing;

Common clay: crushing, blunging, extruding, drying.

RAW MATERIALS

Conditions at the time of genesis determine the composition and nature of a clay deposit. Mode of occurrence is also dependent on its geological history. This affects the procedure to be followed in exploitation of the clay; for example extent of consolidation often determines the type of machinery and method adopted for excavation. Numerical simulations which analyze the effects of consolidation parameters (permeability, compressibility) on the consolidation of nonhomogeneous (SCHIFFMAN and GIBSON, 1964) and of homogeneous clay strata (ALONSO and KRIZEK, 1975) have been proposed.

Clays which are composed dominantly of one type of clay mineral are relatively uncommon. Clays of this type include kaolin clays of which white china clay is an important example, montmorillonite clays which are termed bentonites and attapulgite clays. Clays composed of mixtures of more than one type of clay mineral together with non-clay minerals are much more common and are used commercially particularly in the structural clay-products industry and in cement and light weight aggregate manufacture. Clays are of considerable commercial value (Fig. 9.6).

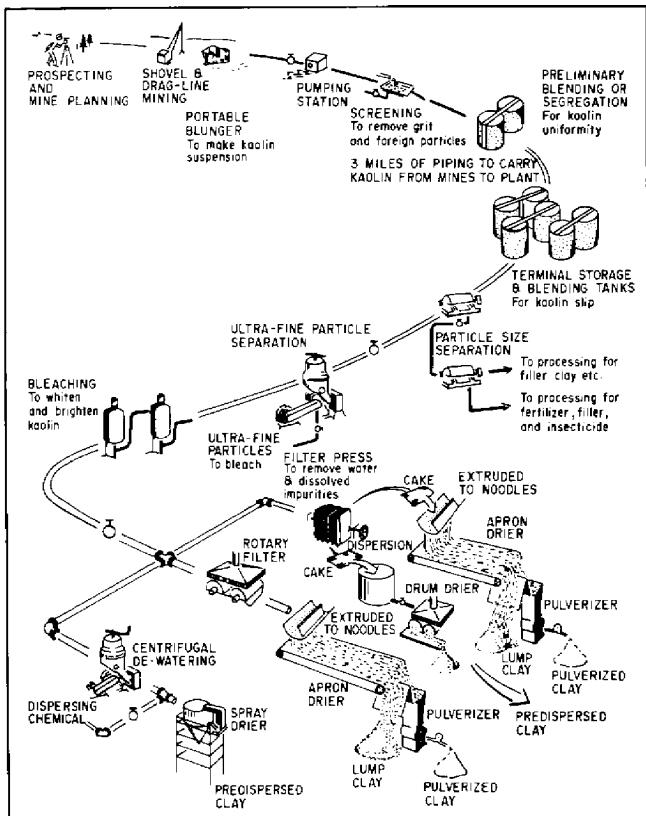


Fig. 9.3 Production of kaolin in Georgia.
(After MURRAY, 1963, p.17. Published by permission.)

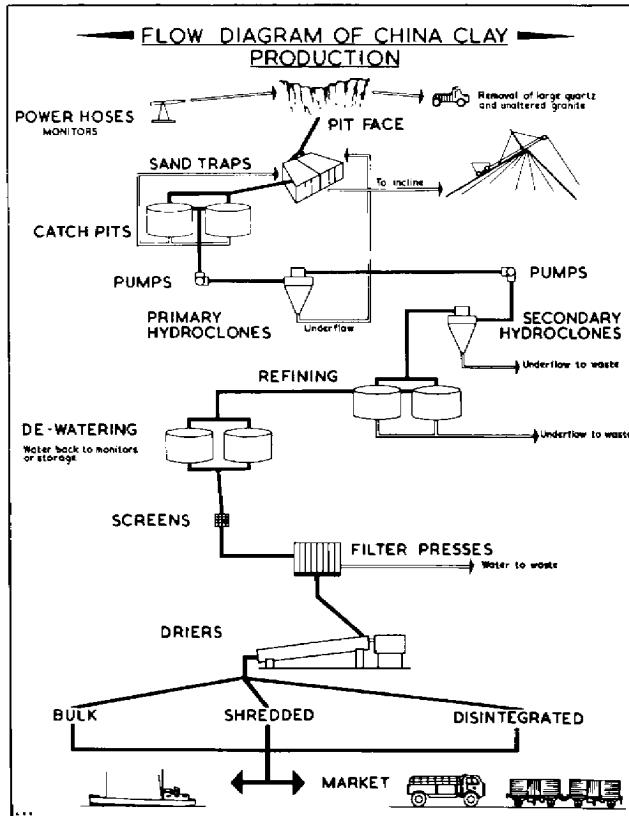


Fig. 9.4 China clay production, Cornwall, England.
(Diagram supplied by Anglo-American Clays Corporation.)

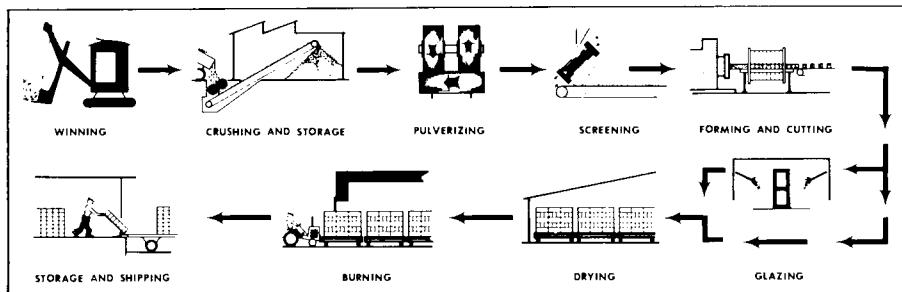


Fig. 9.5 Winning and processing clay for brick manufacture. (After CUTLER and MIK-LUCHIN, 1965, p. 402).

The word kaolin is derived from Chinese and the material was first commercially exploited in China. Economic deposits have been formed by weathering and sedimentary processes and by hydrothermal action. The important china-clay deposits of Cornwall, England, are of hydrothermal origin. They have been produced by the metasomatic alteration of granites (DAVISON, 1930). Important sedimentary kaolin deposits are found in Georgia and South Carolina, U.S.A. The source is believed to have been in a Piedmont area to the northwest. Early work suggested deep weathering and formation of kaolin at the source; uplift was followed by rapid erosion and deposition in the present location. According to KESLER (1956) the kaolin resulted from chemical weathering of feldspathic sands. Rapid erosion of crystalline rocks in the Piedmont led to formation of feldspathic sands which accumulated in a series of deltas. The kaolin formed by subsequent chemical decomposition of the feldspar due to weathering when parts of the deltas became exposed above sea-level. Kaolin enrichment resulted from winnowing and deposition in pools and lakes formed from cut-off river meanders, which were sometimes flooded by sea water. Sedimentation in fresh or salt-water is thought to have affected the density of the deposit due to the influence of electrolyte concentration on the flocculation state of the clay minerals. Hard and soft clay deposits are related to this cause (HINCKLEY, 1965). The suggestion that deposition in saline water resulted in a face-to-face type of arrangement of clay platelets and fresh-water deposition resulted in an edge-to-face orientation is, however, at variance with results of fabric studies on marine and fresh-water clays reported by other workers (MITSCHELL, 1956; ROSENQVIST, 1962). The clay is mined in open pits and transported to plants for refining. More than 5,000,000 tons of kaolin are used annually in the U.S.A. alone where the largest single user is the paper industry which utilized approximately 2,600,000 tons in 1977 (AMPIAN, 1977, p.290). Kaolin also has important uses in the rubber, paint, plastics, chemical, pharmaceutical and many

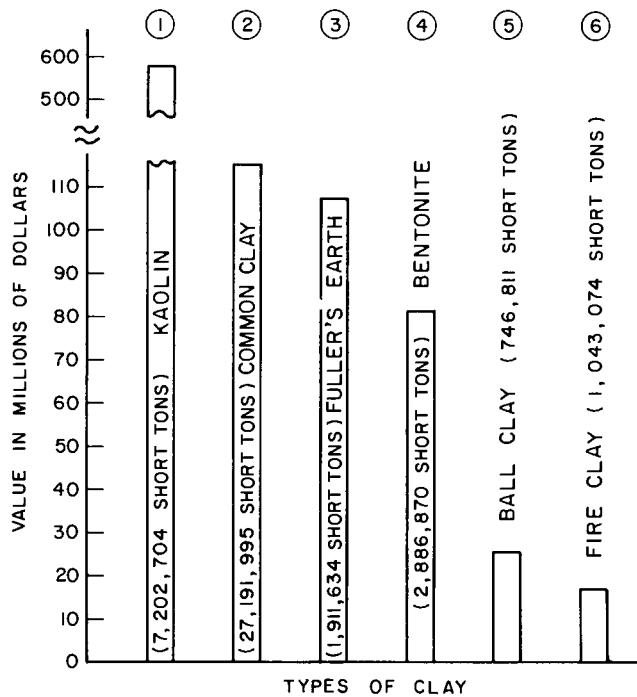


Fig. 9.6. Value of various clays sold or used in U.S.A. (Data from Minerals Yearbook, 1983 Vol. 1, Bureau of Mines, Washington, D.C., pp. 224-239).

other industries. As a filler in organic polymer systems, kaolinite may play an active role in modifying the properties of the polymer (THENG, 1979, p. 133-147). In the ceramics industry it is employed in the manufacture of whitewares such as insulators, sanitary ware, dinnerware and pottery, floor and wall tile and in refractories manufacture (Fig. 9.7).

Highly colloidal, plastic clays, found originally near Fort Benton in the Cretaceous of Wyoming, U.S.A., were termed bentonite. These clays are composed largely of montmorillonite with small amounts of quartz, feldspar, volcanic glass, organic matter, gypsum and pyrite. Bentonite was defined by ROSS and SHANNON (1926, p. 79) as "a rock composed essentially of a crystalline clay-like mineral formed by devitrification and the accompanying chemical alteration of a glassy igneous material, usually a tuff or volcanic ash". The term bentonite has unfortunately been applied to some relatively highly colloidal clays which contain no montmorillonite. Less confusion would be caused if the term was restricted to rocks of the sort described by Ross and Shannon. Geological features and mineralogical studies of bentonites from locations all over the world are described by GRIM and

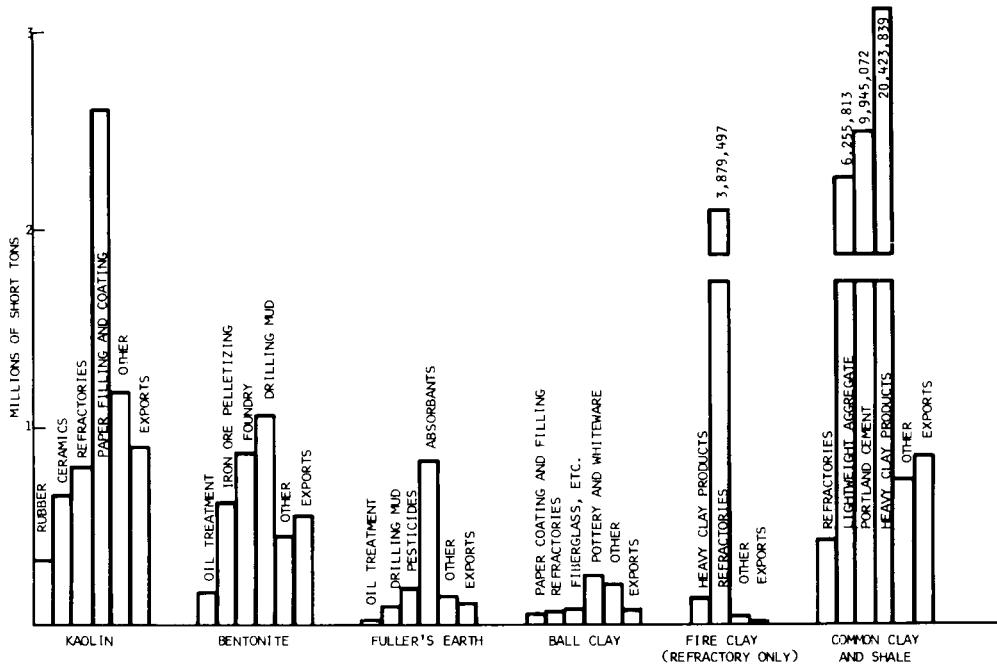


Fig. 9.7. Uses of various clays in the U.S.A. in terms of quantity. (Data from Minerals Yearbook, 1977, Vol. 1, pp. 290-291, Bureau of Mines, Washington, D.C.)

GUVEN (1978) in a review which also relates the properties of the clay to its diverse uses. Millions of tons of bentonite are now used annually (Fig. 9.7). An important application is the filtering, clarifying and decolourizing of animal and vegetable oils, and mineral oils and greases. Bentonite is employed with water as a bonding and plasticizing agent and with more water as a suspension medium. In foundries metals are often cast in moulds made principally of sand. The bentonite is added to give the sand increased plasticity and sufficient cohesion to retain its moulded shape at ordinary and elevated temperatures. It is also employed in the pelletizing of iron-ore and other substances. In this application the swelling characteristics of bentonites may be enhanced by conventional soda-ash additions or by calcium activation (BLEIFUSS, 1973). In another major use it acts as a suspension medium for removal of rock cuttings in well drilling. It is employed in sink-float separations and in medicine. Its high specific surface area is exploited in the manufacture of catalysts and as a carrier for chemicals and insecticides. Exchange reactions between the cations normally associated with montmorillonite and organic compounds such as surface-active agents have conferred a whole range of new and useful properties on the clay and the process is of con-

siderable industrial importance (JORDAN, 1963, p.304). Rare hectorite clays are found in the Mojave Desert Near Hector, California. They may be used as rheological additives, with applications as glaze suspending agents, as constituents in ceramic bodies, in weld rod coatings, foundry products and refractory mixes (JOUDREY, 1980).

Bauxite is the rock name employed for aluminium ore. It forms under tropical conditions of weathering with high rainfall and good drainage leading to hydrolysis and desilication of primary minerals with removal of alkalis and alkaline earths. The process is sometimes referred to as lateritic weathering though laterite is the iron-rich equivalent of bauxite produced under similar conditions. The principal minerals in bauxite are gibbsite Al(OH)_3 , boehmite AlO(OH) and its di-morph diaspore. The proportion of these minerals varies in different deposits and the iron-bearing mineral equivalents and clay may be present as impurities. Clayey bauxite may be beneficiated by washing. Australia has supplanted Jamaica as the world's major producer of bauxite. In 1983, ~ 32% of the world supply came from Australia, ~ 10% from Guinea, ~ 10% from Jamaica and ~ 9% from Brazil (Min. Yearbook, 1983, p.140-141). A bibliography relating to the worlds bauxite deposits has been published by FISCHER (1955). Its principal use is as an ore of aluminium, with smaller amounts being used in ceramics, refractories, in high alumina cements, in the chemical industry and as an addition to abrasives. Recent studies have shown that clay may be exploited as a source of alumina, since the carbothermal reduction of kaolin clay from $1360^\circ\text{--}1505^\circ\text{C}$ produces separately recoverable Al_2O_3 and SiC (BECHTOLD AND CUTLER, 1980). This process may become important as world bauxite reserves are depleted.

The majority of clay deposits are composed of a mixture of more than one clay mineral together with non-clay minerals. Such clays are generally not sold in the raw state but are used by the producers chiefly in the structural or heavy clay products industry and in cement manufacture (Fig. 9.7). To be economically attractive the deposit should be large and easily worked and located close to good transportation facilities and markets. The manufacturing plant is usually located nearby to minimise haulage costs which for such bulky materials can otherwise become high relative to the selling price of the manufactured product. For use in the manufacture of structural clay products the clay should be sufficiently plastic for satisfactory shaping, should not shrink excessively on drying, and should vitrify without excessive shrinkage at a fairly low temperature over a wide range. Non-clay minerals such as quartz are generally desirable as they reduce shrinkage. Limited amounts of alkaline and alkaline earth compounds are acceptable as they aid fusion and formation of vitreous bonding material. In excess they may have a detrimental effect as they tend to cause fusion at too low a temperature which is liable to lead to distortion of the product. Gypsum and pyrite

are present in some clays in a form which it is difficult to remove. These salts may be undesirable in the raw material owing to the possible formation of soluble sulphates in the fired products. Vanadium compounds also occasionally cause problems of a similar nature. Efflorescence, staining and sometimes deterioration of the product can result. Efflorescence in tile made from carbonate-free raw materials may be reduced by the addition of CaCO_3 . Increasing the firing temperature reduces efflorescence in tile and brick made from carbonate-rich material (IBERG and MERMENTHALER, 1972). Carbonates have generally been regarded as undesirable. On firing they are converted to the oxide (MgO or CaO) and if present in excess will cause a very short firing range¹. This increases the risk of either overfired products, which show excessive shrinkage, distortion and other effects due to fusion, or underfired products which are very soft and weak. Also the subsequent growth of hydration products can lead to deterioration of the article (SWALLOW, 1962). On the other hand, PETERS and IBERG (1978) found that finely dispersed carbonates in calcium-rich brick clays affected the properties of heavy clay products positively by reducing the tendency for strongly anisotropic fabrics to develop and by improving the pore structure.

The term fire clay is applied to certain clays which can withstand a high temperature without fusion. It has no definite connotation as regards the mineralogical composition of the clay. The seat earth's or underclays beneath the coal measures of the Carboniferous (Pennsylvanian) are extensively used as fire clays. It is thought that alteration of aluminous sediments in a swampy environment was responsible for the formation of these deposits. When diasporite and boehmite are present it also appears that these deposits have been changed considerably by reactions in presence of ground water (MURRAY and PATTERSON, 1975, p. 517). North American underclays were found by SCHULTZ (1958, p.367) to be composed chiefly of poorly crystallized kaolinite with illite, mixed-layer illite-montmorillonite, or more rarely illite-montmorillonite-chlorite, quartz and in many places a 14A mineral ranging from chlorite to vermiculite. In some fire clays studied by Brindley the disorder shown by the kaolinite was found to consist of random displacements of the structure by multiples of $b/3$ along the Y crystallographic axis. Differences between disordered and well-ordered kaolinite are described by BRINDLEY (1961). Fire clays are used mainly for heavy clay products and refractories (Fig. 9.7).

The highly plastic, white-firing ball clays are composed mainly of kaolinite (typically more than 70%), sericite micas and organic matter. They are of sedi-

¹Short firing range: a small change in temperature produces a large change in such properties as shrinkage, absorption and colour at temperatures where the material becomes hard and dense (J.G. Brady, personal communication, 1966).

mentary origin and usually much finer grained than kaolins (AMPIAN, 1976, p.254). Important deposits occur in the Kentucky-Tennessee ball clay district and in the United Kingdom (MURRAY AND PATTERSON, 1975, p.515). Ball clays are used chiefly for the manufacture of pottery, fiberglass, refractories, and for paper coating and filling (Fig. 9.7).

Fuller's earth is a term applied to clays which are able to decolourize oils. They were used in the cleaning of raw wool and are now employed as decolourizing and adsorptive agents, as drilling muds and as carriers for insecticides and fungicides. The term has no precise mineralogical meaning but such clays usually contain a high proportion of montmorillonite-saponite or attapulgite. Their decolourizing action apparently involves selective adsorption. There are deposits in England, the United States, Japan and elsewhere. Clays in which attapulgite* is the dominant clay mineral have important commercial uses. They are used in the refining of vegetable and mineral oils, as adsorbing agents in the chemical and pharmaceutical industry and as drilling muds in salt-water formations and at the high temperatures sometimes encountered in deep drilling (HADEN, 1963, p.287). Treated attapulgite clays may gain importance in the future as inorganic supports for enzymes in industrial applications (JOHNSON, 1977).

CLAY PRODUCTS

Clay products can be grouped into five major categories which in the United States accounted for about 70% of the commercial consumption of clay (Fig. 9.8). These categories are heavy clay products, portland cement, lightweight aggregate, refractories and fillers. These materials are products of the ceramic industry which also produces glass, whitewares, porcelain enamels, abrasives and special ceramics. Clays are used in many other products.

In the ceramics industry a mixture of clay, quartz and a feldspar or nepheline syenite is termed a triaxial body. This type of mixture is used in the fabrication of the classical products of the industry (Fig. 9.9). In the presence of water the clay confers plasticity and workability on the mix at normal temperatures during forming and is a reactive constituent during firing. The feldspar acts as a flux which is a substance which promotes fusion. The quartz is generally available at relatively low cost and imparts the desirable property to the mix of a reduced drying shrinkage. The tendency of the clay minerals to preferred orientation during forming is diminished. It probably plays a role in the development of mechanical strength in the fired product but also contributes to an increase in porosity and permeability.

*The name palygorskite has priority over attapulgite for the mineral with a ribbon-like structure of two pyroxene-like chains width (BAILEY, 1980).

Variation of the water content and state of flocculation or dispersion of the clay constituent changes the consistency of the mix. This possibility of changing the consistency is the basis of the four chief forming methods used in the ceramic industry. These are the dry press method, the extrusion method, soft mud moulding, and casting (NORTON, 1952, p.94). In general the least water is present in the mix used in the dry press method of forming and the most in slip casting. At the same moisture content, however, different clays have neither the same strength nor plasticity. This is dependent on the rheological and physico-chemical properties of the system and knowledge of these principles as they affect clay is used in controlling the behaviour of the mix during the fabrication process. For a particular clay there is an optimum moisture content for a given forming pressure. At, or near the optimum, fired strength reaches its maximum value and moisture absorption its minimum value (NOBLE et al., 1958). In casting methods a deflocculated clay suspension or slip is poured into a plaster-of-paris mould. Deflocculating agents are employed so that a minimum amount of water consistent with a fluid mass may be used. The water is withdrawn from the clay into the plaster by capillarity.

Pressing may induce deformation textures in the clay while settling and casting may cause the clay minerals to develop a depositional fabric. Orientation of the clay platelets and differences in moisture content in different parts of a formed ceramic body can have important and sometimes detrimental effects during drying and firing (MACEY, 1954; WILLIAMSON, 1960). In clay bricks formed by stiff mud extrusion, laminar voids caused by the flow of clay past the auger and through the die lead to lamination cracks which adversely affect the strength and durability

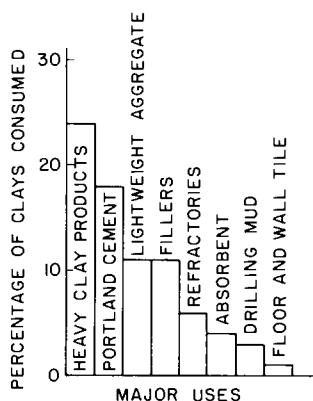


Fig. 9.8. Major uses of clay in the U.S.A. in 1983. (data from Minerals Yearbook, Vol. 1., p.239-240, Bureau of Mines, Washington, D.C.)

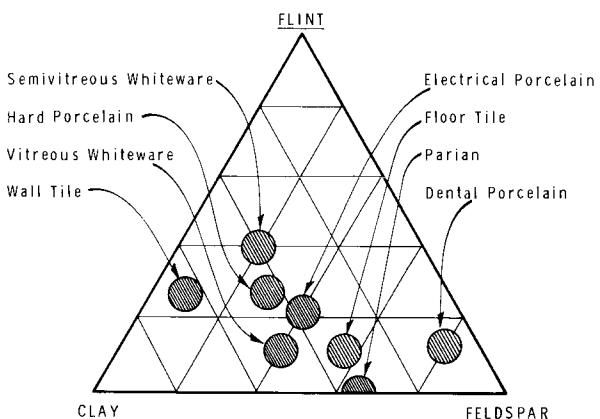


Fig. 9.9. Triaxial diagram showing composition of various whiteware bodies. (After F.H.NORTON, 1952. Elements of Ceramics. Addison-Wesley, Reading, Mass., p.125)

of the brick (RITCHIE, 1975). Special drying procedures are adopted in modern plants to minimise the harmful effects of moisture gradients. The strength of dried clay is important as it determines the precautions which have to be taken in handling ware prior to firing. Dry strength of articles in which there is a high colloidal clay content can reach values of several hundreds or even thousands of pounds per sq. inch (VAN VLACK, 1964, p.264).

Structural clay products or heavy clay products include building bricks, structural tile, lightweight clay block, sewer pipe and other products. A high porosity is required in certain structural clay products such as drain tile. Such articles are generally made at a relatively low firing temperature from raw materials in which there is a high proportion of non-clay minerals. Montmorillonite often gives the required high dry strength for small percentage clay component together with low temperature vitrification.

In the manufacture of Portland cement large tonnages of clay or other argillaceous deposit are used as a raw material. It provides a source of alumina and silica. Blast-furnace slag and pulverized fuel ash are also used as raw materials though in much smaller amounts (Fig. 9.10). The other principal constituent is lime which is commonly derived from limestone or other calcareous rock. Economic factors dictate that both high and low grade raw materials should be exploited. In modern cement manufacture this can generally be achieved by giving proper consideration to the proportioning and blending of the raw materials. Cement plants tend to be located near to good markets and in places where the two materials occur locally, economic considerations being of course a major concern. The composition of the raw mix has to be adjusted within narrow limits with respect to content of oxides of calcium, silicon, aluminium and iron. The amount present of such other constituents as magnesia and alkalies has to be maintained below a specified level. The origin and forms of alkalies present in cement clinker and their possible adverse effects on its phase composition is reviewed by Jawed and Skalny (1977). Lime, alumina and silica make up over 90% of the composition of commercial Portland cement. Detailed studies have been made of the phase relations between these three oxides (Fig. 9.11) and of the phase relations with MgO and Fe_2O_3 which also enter into the composition of Portland cement. From this phase data and from a knowledge of the oxide composition of the raw material the approximate composition of the cement clinker may be computed (BOGUE, 1955). Portland cement is composed of four principal constituents¹ which are tricalcium

¹In the shorthand notation employed by cement chemists the symbol C is used for CaO , S is used for SiO_2 , A is used for Al_2O_3 and F is used for Fe_2O_3 . Hence the four compounds are often written in the abbreviated form as C_3S , C_2S , C_3A and C_4AF .

silicate, $3\text{CaO} \cdot \text{SiO}_2$, dicalcium silicate, $2\text{CaO} \cdot \text{SiO}_2$, tricalcium aluminate, $3\text{CaO} \cdot \text{Al}_2\text{O}_3$, and a phase which is approximately tetracalcium aluminoferrite, $4\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{Fe}_2\text{O}_3$. These compounds are formed in the kiln at a temperature of 1,300-1,500°C. A reaction mechanism for the dynamic thermal synthesis of C_2S from CaO and SiO_2 above 1400°F has been proposed from kinetic studies (FIERENS and PICQUET, 1975 a,b). The thermal decomposition of C_3S has been studied below 1250°C and the effect of excess CaO , C_2S and several metal oxides has been determined (MOHAN and GLASSER, 1977 a,b). The clinker formed on firing is cooled and ground with added gypsum. This plays an important role in the hydration reaction.

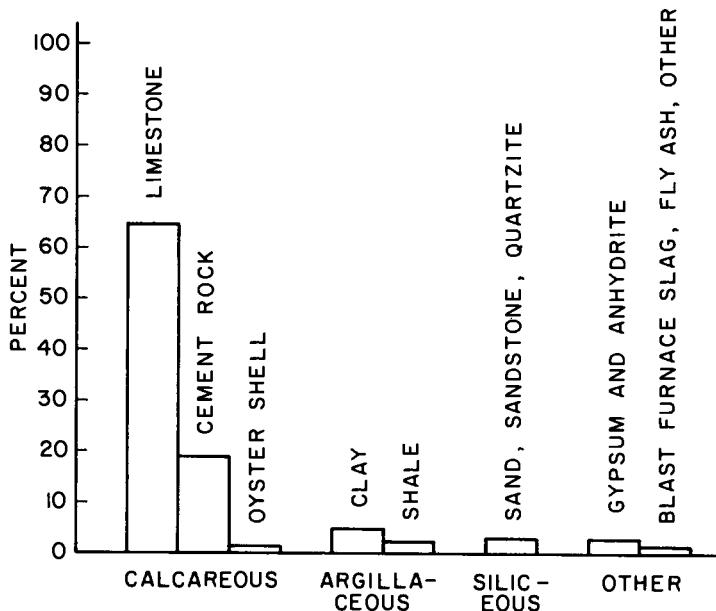


Fig. 9.10. Percentage of total output of Portland cement in terms of raw materials used. (Data from Minerals Yearbook, 1983, Vol. 1, p.184, Bureau of Mines, Washington, D.C.)

There are several modifications of Portland cement depending on the application. The AMERICAN SOCIETY FOR TESTING AND MATERIALS (1980, p.108) recognizes five types (Table IX-1). There are also other varieties of hydraulic cement such as masonry cement which is a mixture of Portland cement with finely ground limestone and other constituents, high-alumina cement and others. Cements are used extensively in the oil industry in well completion operations. A large range of admixtures and additives (including clays) are used to enable the cement to perform its intended use under a very wide range of temperatures and pressures and in the pre-

sence of adverse substances such as brines ((SMITH, 1976)). Clays also find wide application in the oil industry as drilling muds.

On firing certain clays have the property of swelling or "bloating". The material becomes porous and light in weight yet strong and durable. Such products may be used as light-weight aggregates in concrete. The mechanism of bloating hinges upon two essentials which are that a viscous melt must form during evolution of gas. For economic reasons the clay should soften at not too high a temperature. The clay has to be raised to the operative temperature rapidly. This temperature and the bloating characteristics of a clay may be assessed by an empirical test in which samples of the clay are removed from the furnace over a range of temperature, at which bloating is likely to occur (SHORT and KINNIBURGH, 1963, p.90). When clays are of the non-bloating variety bloating may often be induced by addition of iron compounds, alkalies, alkaline earths, flowers of sulphur, or carbon to the clay. RILEY (1951, p.123) has expressed the composition in

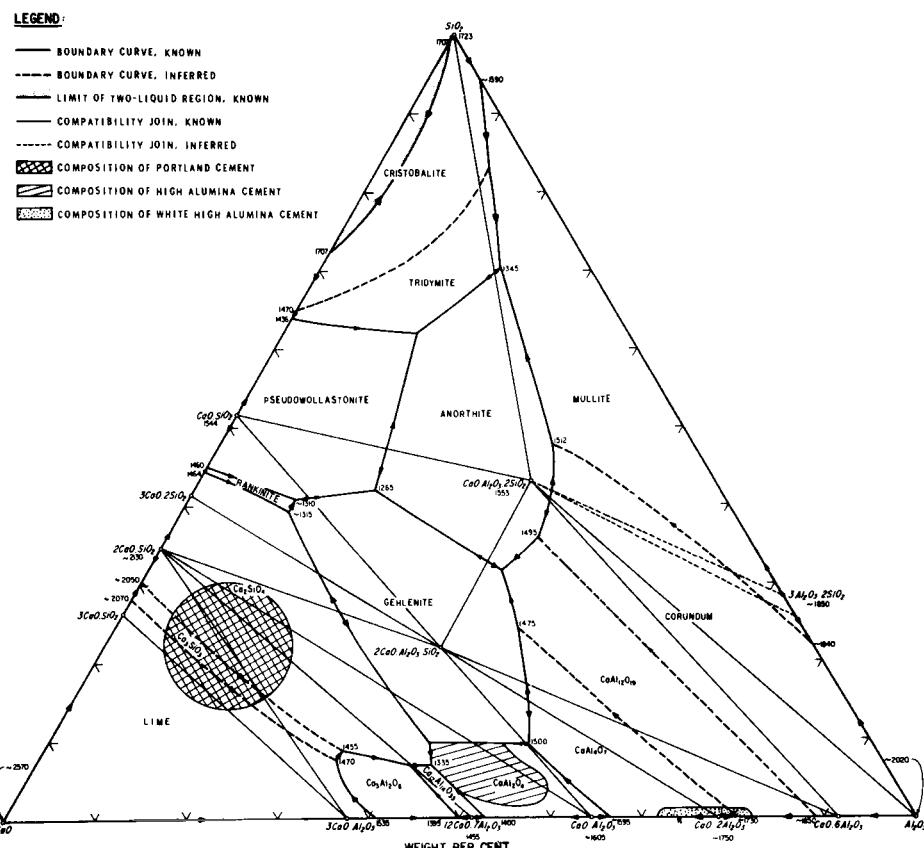


Fig. 9.11. Cement compositions in the lime-alumina-silica system. (After OSBORN and MUAN, 1960.)

TABLE IX-1

COMPOSITION OF VARIOUS TYPES OF PORTLAND CEMENT USED IN U.S.A.

| Description | Type I, general purpose | Type II moderate sulphate resistance and mod- erate heat of hydration | Type III, high early strength | Type IV low heat of hydra- tion | Type V high sulphate resis- tance |
|---|-------------------------------|---|-------------------------------------|--|---|
| Chemical requirements¹ | | | | | |
| SiO ₂ min per cent | | 20.0 | | | |
| Al ₂ O ₃ max per cent | | 6.0 | | | |
| Fe ₂ O ₃ max per cent | | 6.0 | | | |
| MgO max per cent | 6.0 | 6.0 | 6.0 | 6.0 | 6.0 |
| SO ₃ max. per cent | | | | | |
| When 3CaO.Al ₂ O ₃ is 8% or less | 3.0 | 3.0 | 3.5 | 2.3 | 2.3 |
| When 3CaO.Al ₂ O ₃ is more than 8% | 3.5 | | 4.5 | | |
| Loss on ignition, max. per cent | 3.0 | 3.0 | 3.0 | 2.5 | 3.0 |
| Insoluble residue, max. per cent | 0.75 | 0.75 | 0.75 | 0.75 | 0.75 |
| 3CaO.SiO ₂ ,max.per cent | | | | 35.0 | |
| 2CaO.SiO ₂ ,min.per cent | | | | 40.0 | |
| 3CaO.Al ₂ O ₃ ,max.per cent | | 8.0 | 15.0 | 7.0 | 5.0 |
| 4CaO.Al ₂ O ₃ .Fe ₂ O ₃ + 2(3CaO.Al ₂ O ₃) or solid solution | | | | | 20.0 |
| 4CaO.Al ₂ O ₃ .Fe ₂ O ₃ + 2CaO.Fe ₂ O ₃ | | | | | |
| max. per cent | | | | | |
| Potential phase composition² | | | | | |
| (Average values, per cent) | | | | | |
| 3CaO.SiO ₂ | 45.0 | 44.0 | 53.0 | 28.0 | 38.0 |
| 2CaO.SiO ₂ | 27.0 | 31.0 | 19.0 | 49.0 | 43.0 |
| 3CaO.Al ₂ O ₃ | 11.0 | 5.0 | 11.0 | 4.0 | 4.0 |
| 4CaO.Al ₂ O ₃ .Fe ₂ O ₃ | 8.0 | 13.0 | 9.0 | 12.0 | 9.0 |
| CaSO ₄ | 3.1 | 2.8 | 4.0 | 3.2 | 2.7 |
| MgO | 2.9 | 2.5 | 2.0 | 1.8 | 1.9 |
| Free CaO | 0.5 | 0.4 | 0.7 | 0.2 | 0.5 |

¹Reprinted with permission, from the Annual Book of ASTM Standards, Part #14. Copyright, American Society for Testing and Materials, 1916 Race Street, Philadelphia, PA. 19103.

²Data from BOGUE (1955, p.32).

terms of oxides, which will probably be compatible with the production of a high-temperature phase of sufficient viscosity to trap gases. Expanded shale aggregates may also be produced by a process involving sintering.

When vermiculite is suddenly heated to 300°C or more it exfoliates or expands due to a rapid generation of steam between the sheets of the layer structure. The increase in volume may be as much as thirty-fold in the direction normal to the cleavage and expanded product may have a weight as low as about 4-12lb./ft³ (64-192 kg/m³). It is used as an aggregate in concrete where thermal insulation is important and in the manufacture of light weight blocks.

Certain clays are used in the manufacture of a large group of refractories which are alumino-silicates. The history of the fused cast refractory industry is outlined by Humphrey (1977). A refractory is a material which can withstand high temperatures of not less than 1,500°C (BRITISH STANDARDS INSTITUTION, 1962, p.9) without softening or deformation. The raw materials include fire clay and bauxite. Minerals which contain alkalies or alkaline earths and which may act as fluxes should be absent or present in only limited quantity. Kyanite and sillimanite, alumino-silicate minerals of metamorphic origin, bauxite and alumina are sometimes added to fire clays in the manufacture of special refractories. Clays used as raw materials for monolithic refractories need a higher plasticity and higher green strength than those used for the manufacture of pre-fired products. Refractory clays are classified on the basis of the softening temperature expressed in degrees or in terms of the pyrometric cone equivalent. Other refractories include silica refractories, basic refractories, and special refractories. Some metals such as tungsten, molybdenum and tantalum are also employed as refractories. Refractories are employed for linings of blast-furnaces and open-hearth furnaces in the steel industry, for cement and ceramic kilns, and for other applications where resistance to high temperatures is required. Phase diagrams are effectively and extensively utilized in the refractories industry (e.g. WHITE, 1976) since the components are held at high temperatures sufficiently long for equilibrium to be established. A review of the development and use of these phase diagrams is presented by Osborn (1977).

In some regions where quarried stone and gravel is of poor quality or in short supply burned clay has been used in a role which is more usually fulfilled by rock products. For example calcined clay has been used in road building in Australia, and for airfield construction in the Sudan and Nigeria (LEGGET, 1962, p.612), as railway-track ballast and as riprap in the U.S.A. (LEGGET, 1962, p.256). Burned clay brick has also occasionally been used together with other materials as concrete aggregate at least since Roman times. Such uses of clay are technically sound and whether they achieve more widespread application is dictated by economic considerations.

CHANGES ON FIRING CLAYS

When heated the clay minerals lose most of their surface adsorbed water in the 100-120°C temperature range. The temperature at which water is lost by dehydroxylation varies with the nature of the mineral and any impurities, with the heating rate, the water-vapour pressure and other experimental conditions. Illites dehydroxylate between 350° and 600°C, montmorillonites dehydroxylate at about 500°C, the reaction going to completion by about 750°C, and kaolin minerals dehydroxylate in the 500-600°C temperature range. On further heating, clay minerals and related layer silicates pass through poorly crystallized transitional states before recrystallization to stable high-temperature phases. The nature of the transitional phases has been reviewed by BRINDLEY (1975).

Water vapour has been found to have a self-retarding influence on the dehydroxylation of kaolinite which BRINDLEY and MILLHOLLEN (1966) ascribe to the presence of a chemisorbed monolayer which reduces the area for dehydroxylation. On the other hand at water-vapour pressures above 400 p.s.i. (2.8 MPa) kaolin was found to show a decrease in dehydroxylation temperature attributed to a catalytic action of the water which facilitates the structural reorganisation (WEBER and ROY, 1965). Above the temperature of dehydroxylation kaolinite retains two-dimensional order in the crystal structure and the product is termed metakaolin. BRINDLEY and NAKAHIRA (1959 a,b) postulated that an Al-Si spinel-type phase was formed on heating to about 925°C. At a higher temperature of 1,050-1,100°C, they reported that the spinel was transformed exothermally into mullite with loss of silica which appeared as cristobalite. This reaction continued up to 1,400°C with the products developing better crystallinity (Fig. 9.12A). The dominant mechanism in the changes was considered to involve migrations of cations with adjustment of the oxygen framework the essentially close-packed arrangement of which is maintained to a temperature in excess of 925°C.

The nature of the transitional stage in the 900°-1000°C region is still being actively researched and debated. The primary question is whether the spinel-type phase formed when metakaolin decomposes is an Al-Si spinel or $\gamma\text{-Al}_2\text{O}_3$. Although WEISS et al (1970) reported the chemical isolation of the Al-Si spinel, a study using infrared spectroscopy by PERCIVAL et al (1974) showed that the spinel-type phase was largely $\gamma\text{-Al}_2\text{O}_3$. BRINDLEY (1975) subsequently concluded that the spinel phase is likely to be close to $\gamma\text{-Al}_2\text{O}_3$, but that the possibility of Si ions at the tetrahedral sites, could not be ruled out. This is in agreement with much recent evidence (LeMAITRE et al, 1975b; LEONARD, 1977; BULENS et al, 1978). However, the original hypothesis of an Al-Si spinel is strongly supported by other workers (CHAKRABORTY and GHOSH, 1978; CHAKRABORTY, 1979). The nature of the spinel could be influenced by the nature and purity of the starting material (BRINDLEY, 1975, p.122). The predominance of either kinetic or thermodynamic effects could also

THERMAL CHANGES AFFECTING LAYER LATTICE SILICATES

| | | | | | | |
|--|-----------------------------------|---------------------------------------|----------------|----------------------------------|---------------------------|-----------------------------------|
| A | Kaolinite | <u>About 500°C</u> Endothermic | Metakaolin | <u>About 925°C</u> Exothermic | Spinel + SiO ₂ | <u>1050°-1100°C</u> Exothermic |
| | <u>1050°-1100°C</u> Exothermic | Mullite (Composition uncertain) | + Cristobalite | <u>1200°-1400°C</u> | Mullite + Cristobalite | |
| (According to: Brindley and Nakahira, 1959) | | | | | | |
| B | | | | | | |
| Illite <u>200°-600°C</u> Anhydrous Modification <u>850°C</u> Spinel <u>1200°C</u> Mullite <u>1300°-1400°C</u> Fusion | | | | | | |
| (According to: Grim and Kulbicki, 1957) | | | | | | |
| C | | | | | | |
| (Anhydrous) Muscovite <u>1140°C</u> and less Leucite + Potash Feldspar + Mullite <u>1140°-1315°C</u> | | | | | | |
| <u>1140°-1315°C</u> Leucite + Mullite + Liquid <u>Above 1315°C</u> | | | | | | |
| <u>Above 1315°C</u> Leucite + Corundum + Liquid <u>About 1700°C</u> Complete Melting | | | | | | |
| (According to: Yoder and Eugster, 1955, p.229) | | | | | | |

Fig. 9.12. Thermal changes affecting phyllosilicates.

- A. After BRINDLEY and NAKAHIRA (1959b).
- B. After GRIM and KULBICKI (1957).
- C. After YODER and EUGSTER (1955).

determine what was observed in the spinel-type phase prior to mullite formation (FLANK, 1979, p.17). LEMAITRE et al (1975 a,b) proposed that metakaolin heated in the 900°-1050°C range can follow two parallel reaction paths. Specific mineralizers enhance either one route or the other. The model is represented in Fig. 9.13. The influence of crystallinity (BULENS AND DELMON, 1977) and the effect of mineralizers on various properties of fired kaolin bodies (LEMAITRE et al, 1976; LEMAITRE and DELMON, 1980) have also been discussed.

Different decomposition products have been reported on heating mica-type clay minerals. This is thought to result from failure to reach equilibrium, differences in initial composition and presence of other constituents notably water. According to GRIM and KULBICKI (1957) illite dehydroxylates between 200 and 600°C with an increase in height of the unit cell. A spinel appears above 850°C and increases in crystallinity and amount up to about 1,200°C when it is replaced by mullite (Fig. 9.12B). YODER and EUGSTER (1955, p.229) commented on the frequent lack of equilibrium in the observed decomposition products of natural muscovites and reported the sequence of mineral assemblages which should result from the equilibrium decomposition of anhydrous muscovite (Fig. 9.12C). Mullite decomposes to topotactically-related corundum when heated to about 1750°C in an open system (IWAI et al, 1980).

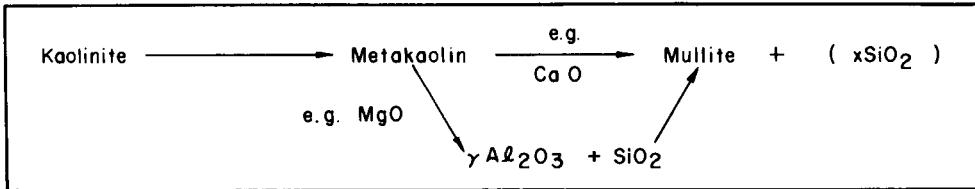


Fig. 9.13. Diagrammatic representation of thermal changes of kaolinite.

A commercial clay product is fired only long enough for the article to develop properties required for its use and equilibrium in the chemical or mineralogical sense is generally not achieved. Nonetheless phase diagrams are of great use and many which are of special concern to ceramists have been summarized (LEVIN et al., 1974; LEVIN and McMURDIE, 1975). Such data provide the first criteria for the deduction of the behaviour of the materials on firing and prediction of the composition and properties of the products. Phase transformations may be defined as either "reconstructive" or "displacive", depending on whether the two structures are very different, or whether there are only small displacements in atomic positions. An example of a reconstructive transformation is the conversion of quartz to tridymite in which strong Si-O bonds have to be broken - a slow reaction speeded up by fluxes in the manufacture of sand - lime bricks; displacive transitions occur in Na-Ca plagioclase feldspars due to structural collapse around a small cation (BUERGER, 1972; NEWNHAM, 1978, p.39-41).

Mineralizing agents such as fluorine or borates lower the viscosity and facilitate crystallization. Fluxes promote fusion and the presence of liquid is probably responsible for the greater facility with which chemical interactions often take place when such agents are present. Alkalies are particularly effective as fluxes and react with silica and to a smaller extent with alumina to form liquid at a temperature which may be several hundred degrees lower than the temperature at which liquid would form in their absence. Firing mixtures which contain mica-type clay minerals and feldspars liberates alkaline and alkaline earth oxides which act as fluxes. An increase in the proportion of such minerals leads to an increase in the proportion of glass and mullite develops at lower temperatures and in smaller amounts than in more kaolinitic mixes. Cristobalite forms at the expense of kaolinite (BRINDLEY and UDAGAWA, 1960, p.65) but when illite is present the fluxing action of interlayer cations is thought to be responsible for the generally observed reduction in amount of cristobalite and increase in glass content (SLAUGHTER and KELLER, 1959, p.707). Quartz tends to persist on firing and under these conditions is not readily converted to cristobalite (BRINDLEY and MARONEY, 1960, p.515; HOLDRIDGE, 1965, p.88). Cristobalite inclusions in a ceramic body may contribute to mechanical failure during temperature cycling due to the volume

changes which occur during the $\alpha \rightarrow \beta$ transition at 200-275°C and the irreversible nature of the initial $\beta \rightarrow \alpha$ inversion (WRIGHT, 1977).

The development of the glassy phase is associated with shrinkage of the article and the closing of pores. If heating is continued for too long this may lead to eventual bloating due to expansion of trapped gases or vapour (BRINDLEY et al., 1961, p.47). Refractories often contain corundum in addition to mullite and siliceous glass. In basic refractories such minerals as spinels (general formula AB_2O_4 in which A and B may be Mg or Al or other ions), forsterite and other silicates are often developed as fired product.

The firing process may involve sintering. This term refers to the formation of a weld or union between particles of powder at a temperature below the melting point. Sintering is generally accompanied by shrinkage and a decrease in void space and surface area. It was originally thought that sintering always took place in the absence of liquid but a fluid phase is now known to be present in some cases so the terms wet sintering and dry sintering have come into use. Viscous flow and ionic diffusion probably take place during wet sintering. Significant variables in the process are viscosity, surface tension and pore size. Particle rearrangement makes an important contribution to densification during liquid-phase sintering and hot pressing. Expressions describing rearrangement kinetics have been proposed (DiRUPO et al, 1979). The viscous mechanism is of major importance when there is a considerable amount of glass formed as is the case in the firing of a great many of the ceramic articles which contain clay. In dry sintering the mechanism involves a solid-state process driven by the reduction of total interfacial energy of the system. Initial, intermediate and final stages have been defined. It is considered that structural vacancies or point defects move in one direction while a corresponding movement of atoms or ions occurs in the opposite direction. As a result material is transferred from point contacts to form a connecting neck or bridge between particles which are drawn together (Fig. 9.14). Either the mass transport along the forming grain boundary to the "neck" region or the movement from the neck to the free surface regions have been found to be rate-controlling in the initial and intermediate stages (WONG and PASK, 1979, a,b). Most of the densification, and the greatest structural change occurs in the intermediate stage, due to a decrease in the number density of voids and grains associated with grain growth (ROSOLOWSKI and GRESKOVICH, 1975). The final stage is a closed-pore stage where grain growth invariably occurs. Sintering is an important process in the formation of certain single phase ceramics such as ferro-electric and magnetic ceramics.

The mineralogy of the raw material is related to the composition of the fired product and significantly affects the optimum conditions of manufacture and the properties of the fabricated article. The mineralogical changes which take place on firing are accompanied by an increase in strength of the product.

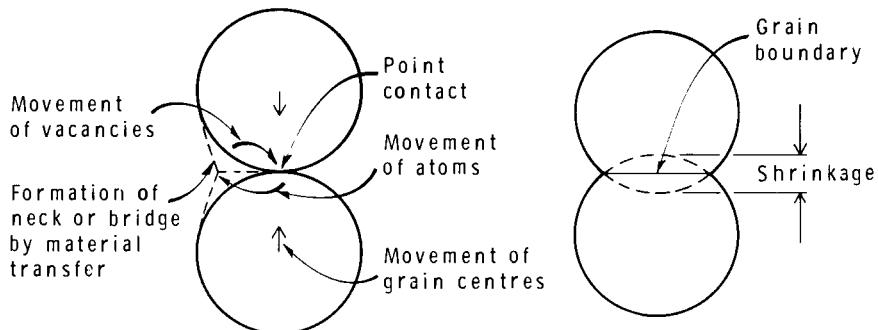


Fig. 9.14. Schematic illustration of sintering.

STRENGTH OF MATERIALS MADE FROM CLAY

It has been deduced from consideration of the forces between atoms that the tensile strength of almost all solids should be approximately one tenth of Young's modulus, i.e., about $E/10$ (COTTRELL, 1964, p.2). Materials ordinarily fail at much smaller fractional values of E than predicted by the simple theory. For example strong steels yield at about $E/100$ and many other common metals and alloys yield plastically at about $E/1,000$ and break at about $E/100$. The tensile strength of most commercial ceramic products is about $E/1,000$ and the breaking strength of ordinary glassware is similar. Strengths which approach much closer to the theoretical values have been achieved in glass fibres and whisker crystals which have a diameter of about 1μ m.

A fairly satisfactory explanation for the low strength of bulk materials which fail by brittle fracture is based on ideas proposed by GRIFFITH (1921). He suggested that structural flaws such as cracks lead to a concentration of stress which causes the material to fail at stresses well below the theoretical. In brittle materials such as glass at temperatures below those at which viscous effects become appreciable, it is now known that the flaws are generally formed in the surface due to abrasion, chemical attack or recrystallization. Stress concentration can also probably occur within a material as around pores and grain boundaries.

Recent work has shown that some non-metal single crystals, particularly those belonging to the cubic system, such as MgO , are ductile at room temperature when prepared by special techniques. Ionic crystals are, however, normally brittle. This is because brittle fracture involves both crack nucleation and crack propagation. Micro-cracks are believed to develop as a result of the coalescence of dislocations piled up at a barrier. Therefore plastic flow may result in crack nucleation in ductile materials. It is thought that the motion of dislocations is

impeded by grain boundaries in polycrystalline materials (KINGERY and COBLE, 1963, p.106) and also that cracks may result from the interaction of slip bands. Thus plastic flow as well as mechanical damage can lead to crack formation. The stress to initiate yielding as well as the state of the surface are both factors of importance in the mechanism of strength development (JOHNSTON, 1962).

In the high-temperature deformation of polycrystalline ceramics, grain boundary sliding and diffusional processes are especially important. In general, the most important variables (apart from stress and temperature) affecting deformation behaviour are considered to be micro-structure (grain size and porosity), composition and stoichiometry, crystalline perfection, and environment (e.g. irradiation, adsorbed water)(TERWILLIGER and RADFORD, 1974; RADFORD and TERWILLIGER, 1974).

Most fired clay products are composed of both crystals and glass. The glass may either form a continuous phase which surrounds and adheres to the crystalline components and incorporates the pores or it may be limited to interstices in a dominantly crystalline matrix. The important role of the glassy phase in determining the mechanical properties of fired clay products has been recognized for a considerable time (KRANER, 1929). Attention has been called to the state of stress in the glass and the stress distribution between the glassy and crystalline phases in considering strength development (MATTYASOVSKY-ZSOLNAY, 1957, p.302).

Mechanical properties are also thought to be affected by physical differences between the glassy and crystalline phases. For example there are differences in the thermal expansion coefficients which may result in micro-stresses within the fired product. Such internal stress concentrations probably represent points of weakness. Strain measurement by an X-ray technique has indicated that internal stresses do exist in ceramic systems and that their magnitude may exceed the bulk strength of the body (GROSSMAN and FULRATH, 1961). Mathematical expressions in which the forces in and around a crystal embedded in a glassy matrix are represented have been developed by LUNDIN (1959, pp.148-163), WEYL (1959), and SELSING (1961, p.419). An equation which relates strength to total porosity and nature of pores has been presented by BROWN et al. (1964).

Intergrowth and mechanical interlocking of the needle-like mullite crystals may also contribute to strength. ZOELLNER (1908) for example considered that the strength of porcelain is dependent upon the amount of mullite and upon the size and manner of intergrowth of the crystals. These factors are likely to be influenced by variations in original composition and firing procedure but there is little quantitative data as to the effects on properties of the fired product caused by changes in the character of the mullite (LUNDIN, 1964, p.97). SEM studies of fired china and ball clays showed primary mullite to be a pseudomorph after kaolinite which could persist to high temperatures before recrystallizing to the needle-like structure of secondary mullite (SCHÜLLER and KROMER, 1975). Studies on single phase mullite indicated that both polycrystalline and single crystal

samples gave high compressive strengths and high resistance to creep at 1400° and 1500°C (NOKKO et al., 1977). Modern work indicates, however, that the simple hypothesis of mechanical interlocking by itself is unlikely to account for strength development. Stress distribution between the components, stress concentration along structural flaws and other micro-structural features probably have a large influence on mechanical properties. Such factors have been reviewed by KINGERY and COBLE (1963) and in a publication of the NATIONAL BUREAU OF STANDARDS (1964). The scientific basis for the design of structural ceramics for specific applications including two approaches to materials development (tough vs. strong ceramics), assessment of ceramic performance and failure prediction is reviewed by EVANS and LANGDON (1976).

DURABILITY

When other qualities such as strength are adequate durability is often a key factor in the assessment of the economic value of a product. WEBSTER (1961) states that an object is durable when it is "able to exist for a long time with retention of original qualities, abilities or capabilities". Deterioration of materials made from clay or which contain clay can result from a variety of causes which include moisture expansion, chemical attack, and exposure to the weather. In refractory use molten slags and furnace gases may cause deterioration.

Dimensional changes in dried and fired clay products may result from moisture pick-up from the natural humidity of the surrounding air. Such dimensional instability may lead to cracking and loss in strength (ALVISET and LIGER, 1960; CLEWS et al., 1960). Deterioration of brick masonry (BUTTERWORTH, 1953, pp. 850-851; MCBURNEY, 1954), the crazing of glazed whiteware and the expansion of structural clay tiles have been attributed to this cause.

Moisture expansion of porous fired clay products is believed to begin during cooling by uptake of moisture from the kiln atmosphere. Expansion can result from a relaxation effect caused by a lowering of the surface energy of the solid due to the moisture adsorption or from chemical combination of the water with the material. According to SMITH (1955, pp. 314-315) the chief factors which affect moisture expansion are the accessibility of the inner surface, the surface energy and the bulk modulus of elasticity. Many authors have proposed that amorphous constituents are responsible for the moisture expansion of fired clay bodies as certain amorphous materials have a high specific surface area. In addition to expansion attributed to sorption of moisture at surfaces a continuing expansion has also been observed. This has been attributed to moisture penetration into the glassy phase. The alkali ions in the glass dissolve in water and are replaced by hydrogen ions. These attract water molecules into the spaces originally occupied by the alkali ions. This causes internal stresses as the water molecules are too

large for the volume vacated by the alkali. Disruption of bonds of the silica network is believed to take place accompanied by an increase in volume (WANG and TOOLEY, 1958, p.523).

In recent years the composition of the raw materials has been adjusted in the case of such fired clay products as wall-tiles which are subject to severe conditions favouring moisture expansion. In the United States wollastonite, pyrophyllite and talc have been introduced into the mixes and in Britain ground limestone and dolomite have been employed (HOLDRIDGE, 1965, p.100). Mineral phases such as anorthite, cordierite, gehlenite and pyroxenes occur in the fired products in addition to the more usual minerals such as mullite.

Soluble salts such as sulphates may be undesirable in fired clay products. In building bricks for example moisture migration may leach such salts from the interior of the brick and leave a white efflorescence on the surface when the moisture evaporates (Fig. 9.15). This is unsightly and it may also cause surface deterioration (HARDESTY, 1944, p.222). The source of the sulphur may be in the raw material. Clays sometimes contain gypsum and if this is present in small patches or thin veins it may not be readily separable from the clay. Alternatively, iron pyrites may be present in the clay. On firing this decomposes and gaseous oxides of sulphur which are liberated may react with bases in the clay to form sulphates. If there is sulphur in the fuel used for firing this may also provide a source of sulphur oxides (BUTTERWORTH, 1950; BROWNELL, 1958, p.266). If barium carbonate is added to the mix sulphates in the clay may be converted into insoluble barium sulphate. Ammonium-chloride addition has also been suggested as a means of control (BROWNELL, 1958, p.261) and other possible remedial measures have been discussed by COLE (1961). In masonry construction additives which reduced the porosity of the mortar, e.g. dispersing agents such as lignin sulfonate and maleic acid and pozzolanic additives, have been found to be effective in reducing efflorescence while also contributing to the strength (LIM and CUTLER, 1976). Green staining of structural clay products has been attributed to compounds of vanadium. This element is believed to be present in small amounts in many clays either in the structure of some of the clay minerals, as part of the adsorption complex, or in organic chemical compounds known as porphyrins some of which contain vanadium.

Fired clay products which are exposed to the weather undergo deterioration due to such effects as freezing and thawing. Frost action can also cause deterioration of concrete. In some cases the clay component in the aggregate may be involved in the mechanism of the process (DUNN, 1967). In general argillaceous rocks are not suitable as concrete aggregates. They tend to be soft and cause unsoundness in concrete. They frequently show directional properties with a strong cleavage or parting parallel to the direction of orientation of the platy minerals.



Fig. 9.15. Efflorescence on brick masonry, Ottawa, Canada.

As such rocks break-up easily the particle-size distribution of sized aggregate is liable to change on handling. They often show large changes in dimensions on wetting and drying. This may lead to formation of "pop-outs" as on moisture uptake aggregate particles near the surface of the concrete exert a swelling pressure. The clay content has been held responsible for the expansion in alkali of certain varieties of physically sound argillaceous dolomitic limestone. The proposed mechanism involves release of non-wetted clay from the carbonates when the dolomite is attacked by the alkali. The released clay then imbibes moisture and exerts a swelling pressure (GILLOTT, 1964). When such rocks are used as aggregate in concrete made with high alkali cement the expansion of the aggregate often causes the concrete to deteriorate (Fig. 9.16) (SWENSON and GILLOTT, 1960). The phenomenon is known as the alkali-carbonate reaction (HIGHWAY RESEARCH BOARD, 1964).

Certain siliceous aggregates have long been known to react expansively with alkalies causing durability problems in concrete. The "classical" variety involves amorphous, glassy or cryptocrystalline materials (MIELENZ, 1962, p.12) and is known as the alkali-silica reaction. Some rocks of the greywacke-phyllite suite are also alkali-expansive but aggregates of this sort show many differences in behaviour from those containing poorly ordered siliceous minerals such as opal. Because of the differences it has been suggested that expansive aggregates of this

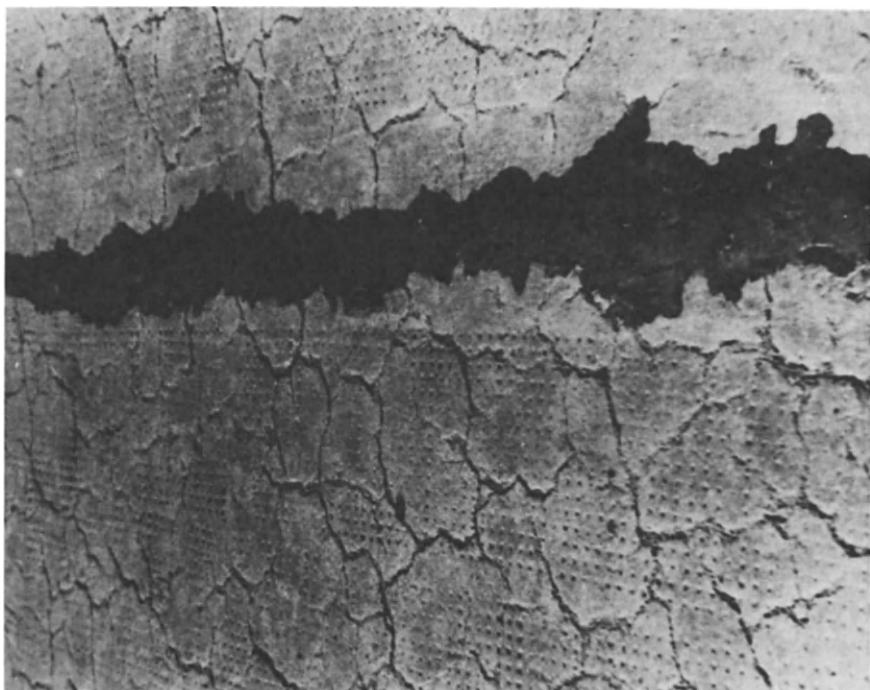


Fig. 9.16. Deterioration in concrete sidewalk with extrusion of joint filler.

sort be placed in a separate class termed alkali-silicate reaction. The differences in behaviour suggest that expansion is due to a different cause. Some gel exists but the evidence that it comes from strained quartz in the rocks is very indirect. Gel-like products observed may result from alkaline attack on other minerals. The evidence from scanning electron microscopy that alkali attacks some phyllosilicates and other minerals more rapidly than microcrystalline silica, is direct, comparative observation - exfoliation in some cases and dissolution in others. In studies to do with soil stabilization it is generally accepted that clays are attacked by $\text{Ca}(\text{OH})_2$ and it has been suggested that this reaction and one involving feldspars may contribute to alkali-aggregate reactions (VAN AARDT and VISSER, 1977 a,b). Certainly too, fabric has a major effect on the course of reactions in rocks. Alkali-aggregate reactions have been reviewed by a number of authors (GILLOTT and SWENSON, 1973; GILLOTT, 1975; DIAMOND, 1975, 1976; BROTSCHI and MEHTA, 1978) and in the proceedings of symposia on this topic the most recent of which was held in South Africa (National Building Res. Inst. C.S.I.R., 1981). The concrete deterioration which these reactions may cause can often be controlled by use of pozzolans. Some varieties of pozzolan may be produced by the calcination of clay (MIELENZ et al., 1951, p.322). Clay minerals have been shown to play

a role in other problems of concrete durability including the new material in which Portland cement is replaced by sulphur as the cementitious binder (JORDaan et al., 1978; GILLOTT, 1980).

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Chapter 10

THE MINERALOGICAL ANALYSIS OF CLAY

The crystalline mineralogical components of a clay are most readily identified by the powder method of X-ray diffraction analysis. This is generally combined with various auxiliary pre-treatments of the sample. Differential thermal analysis is also commonly employed and for certain uses such as the identification of non-crystalline constituents it is more sensitive than the X-ray method.

Other techniques which include electron diffraction, electron microscopy, and infra-red absorption analysis are also sometimes employed. They are most commonly used in specific research projects to provide detailed information not obtainable by the other more commonly employed techniques. Ion-exchange capacity is frequently determined. In general the mineralogical composition cannot be reliably deduced from the bulk chemical composition. The mineralogy is of fundamental importance to the understanding of clay behaviour at normal temperatures. In the industrial use of clay, however, high temperatures are often employed as in the manufacture of ceramics and cement; in such uses the elemental composition often becomes of prime importance.

ANALYSIS BY X-RAY DIFFRACTION

The analysis of the crystalline components in a material by X-ray diffraction is analogous to the fingerprint method of identification of humans. In X-ray diffraction analysis two parameters are determined. These are (a) the spacings between the planes of atoms in the crystals (the d-values), and (b) the intensities of the X-ray reflections from the corresponding planes. These two parameters are known for a great many crystalline materials and are published in the form of an index by the JCPDS-International Centre for Diffraction Data*. Identification depends on matching the experimentally determined dimensional and intensity values with those published in the index.

Various kinds of search manuals are available including those for inorganic and organic phases. Two manuals are required for search of the inorganic phases section of the file. One of these is arranged alphabetically and the other lists the most intense d-spacings. Listing of intensities is organized in two alternative ways according to either the Hanawalt or Fink procedure. Selected data for minerals are also available in two forms. In the earliest publication, "Selected Powder Diffraction Data for Minerals" data cards

*International Centre for Diffraction Data, 1601 Park Lane, Swarthmore, PA., U.S.A., 19081

are arranged in card number sequence together with a mineral name index. In the "Mineral Powder Diffraction File" cards in the book are arranged in alphabetical order by mineral name. The search-manual contains a Hanawalt numerical section, a Fink numerical section, a chemical name section and an alphabetical section by mineral name. Data are also supplied on magnetic computer tape and may be used with the automated powder diffractometers manufactured by several companies. Computer procedures of varying complexity and including search/match and phase identification, quantitative analysis, profile analysis and other routines are now commercially available. In some systems the first and second derivatives of peaks on the diffraction pattern are used to help recognize slight changes in peak profile caused by peak overlap and related causes. GLAZNER and MCINTYRE (1979) illustrated the principles by use of the APL language in identification of minerals in mixtures. More than one crystalline component is generally present in the sample and difficulty is often experienced in assigning sets of powder lines to particular components. It is for this reason that auxiliary pre-treatments and other analytical methods are so frequently used in clay-mineral identification.

Diffraction is the mutual reinforcement of a large number of waves. It occurs when any wave motion passes through a narrow opening. X-rays have wave-like properties and diffraction occurs when an X-ray beam passes through a crystal as the wavelength is of the same order as the spacings between the atoms. When there is no difference in wavelength between the incident and scattered radiation the transmitted X-rays are said to be coherent or unmodified. As a systematic relationship exists between the phases of the primary and the coherently scattered beams phase addition or reinforcement is possible. This constructive interference, which constitutes diffraction, can arise because of the regularly repetitive nature or periodicity of the crystal structure.

In addition to the effect which leads to diffraction many other complex processes take place when an X-ray beam interacts with matter (Fig. 10.1). Some of these processes such as the production of incoherently scattered radiation contribute to the "background" on which the diffraction pattern is superposed. If the incident radiation is of an appropriate wavelength considerable secondary fluorescent radiation may be emitted by an element in the sample. A very high background often results. Copper radiation induces this effect if iron is present in the sample. The problem may be avoided by use of X-rays of a different wavelength or by removal of the iron.

For in-phase scattering to occur the diffracted X-rays must satisfy a relationship known as Bragg's Law. An elementary proof of this relationship can be understood for a two-dimensional case by reference to Fig. 10.2. The difference in path length between a ray which strikes the surface layer of

atoms X and one which strikes the layer of atoms Y is:

$$\begin{aligned} D'B' + B'E' &= BB'\sin\theta + BB'\sin\theta \\ &= d_{hkl}\sin\theta + d_{hkl}\sin\theta \\ &= 2d_{hkl}\sin\theta \end{aligned}$$

If this path difference is an integral number of wavelengths the scattered rays ABC and A'B'C' will be in phase; this is the condition for constructive interference and beams scattered by different planes enhance one another. The condition for diffraction derived by Bragg is expressed in the equation:

$$n\lambda = 2ds\sin\theta$$

where λ = wavelength of X-rays, d = lattice spacing, θ = angle of diffraction, and n = order of diffraction.

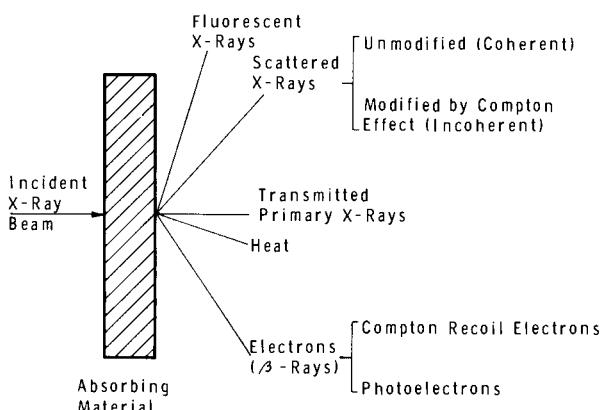


Fig. 10.1 Effects produced by interaction of X-rays with matter. (After Henry et al., 1951.)

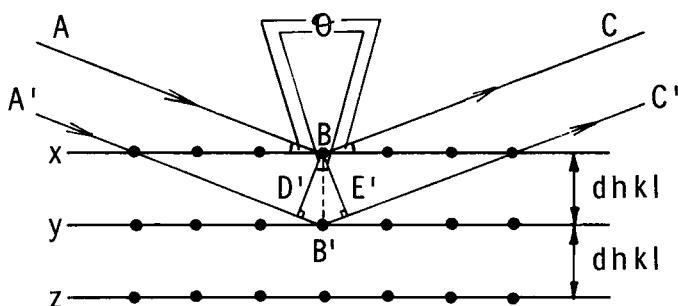


Fig. 10.2 Geometrical illustration of Bragg's law of X-ray diffraction by a crystal. x, y, z =planes of atoms in a crystal; A, B, C, A', B', C' =incident and diffracted X-ray beams; θ =diffraction angle.

The order of diffraction, n , may take any integral value but is limited by the proviso that $\sin \theta$ cannot be greater than unity. It represents the path difference expressed in wavelengths between rays scattered by adjacent planes. The term is commonly encountered in work dealing with clay-mineral identification where oriented samples which enhance basal "reflections" are employed. With such an experimental arrangement a series of orders of basal "reflections" such as 001, 002, 003, 004,... are frequently recorded. These "reflections" from the basal planes are of primary importance in the identification of the clay minerals. The term "reflection" is often used when reference is made to diffraction phenomena. The analogy between the reflection of light by a mirror and the diffraction of X-rays by a crystal is a useful though inexact analogy; the terminology is well established by usage.

An X-ray tube emits radiation of more than one wavelength but the "characteristic" radiation is of most importance. The value of this wavelength (which is not strictly monochromatic) is known with considerable accuracy for the elements used as target in X-ray generators. A set of values of the Bragg angle θ are determined in the diffraction experiment. Hence the corresponding set of values of the interplanar spacings "d" may be calculated from the Bragg equation. In practice these values are read from tables or printed on the chart automatically.

An X-ray diffraction pattern of crystalline material is not only characterized by the spacings of the reflections but also by their intensities. This results from structural considerations dependent on the nature and arrangement of the scattering material as well as on the direction of scattering. Hence the interplanar spacings, d , are dimensional characteristics of the crystal lattice; the intensities of the different reflections are dependent upon the atomic nature and arrangement. An X-ray diffraction pattern is recorded either by means of a camera employing special X-ray sensitive photographic film or by means of a diffractometer. The latter employs radiation counters connected to electronic recording equipment.

In the diffractometer a parafocussing geometry is employed (Fig. 10.3) in order to increase the intensity of the diffracted beams. A flat-plate sample holder is centrally located and is tangential to a focussing circle which passes through the effective X-ray focus and the inlet slit to the radiation detector. Both sample and detector rotate about a common axis but the gearing is such that the detector rotates at twice the angular velocity of the sample. By this arrangement the sample is maintained tangential to the imaginary focussing circle the radius of which decreases as the angle of diffraction increases. When the diffractometer is employed values of 2θ are read directly from the chart recording so by simply halving these values the Bragg angle θ is obtained. There are tables from which d-values are

obtained. In modern instruments this, and other information is printed directly on the chart. The peak heights are a direct indication of the intensity of the powder-diffraction lines.

Details concerning the operation of the diffractometer are given in textbooks on X-ray diffraction (KLUG and ALEXANDER, 1959; JENKINS and de VRIES, 1969). Diffractometer alignment has been discussed by PARRISH and LOWITZSCH (1959) and KITTRICK (1960). The effects of crystallite size on the diffraction pattern are considered by DE WOLFF (1958, 1959) and TRUNZ (1976) and methods of sample preparation by COPELAND and BRAGG (1958).

The platy clay minerals are characterized by long spacings between the basal planes of atoms. It is therefore essential to register reflections of 30 \AA^* or more on the recording. X-ray reflections from planes with such long spacings make only small angles with the main X-ray beam. Reflections from the long spacings found in clay minerals are not normally recorded by means of the Debye-Scherrer and Straumanis technique (Fig. 10.4) and a different geometry is employed in cameras used for work involving clay minerals. The spacings between the powder lines on photographs may be measured on a mm scale and

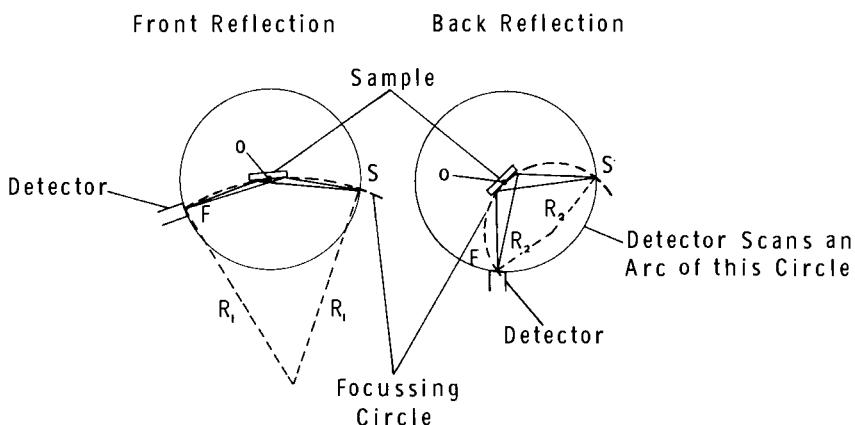


Fig. 10.3 Reflection geometry for diffractometer. R_1 and R_2 =radii of focusing circle for different 2θ angles; S=X-ray source; F=focus of diffracted X-rays; O=centre of diffractometer circle - sample rotates about O at half angular velocity of detector.

intensities estimated visually. The mm separation between the powder line and the direct beam is then converted into angular measure and the d-values obtained from tables based on the Bragg equation for the wavelength of the X-radiation used. Scales are available commercially, or can be constructed, by which d-values may be read directly from the film.

* $10\text{ \AA} = 1\text{ nm}$.

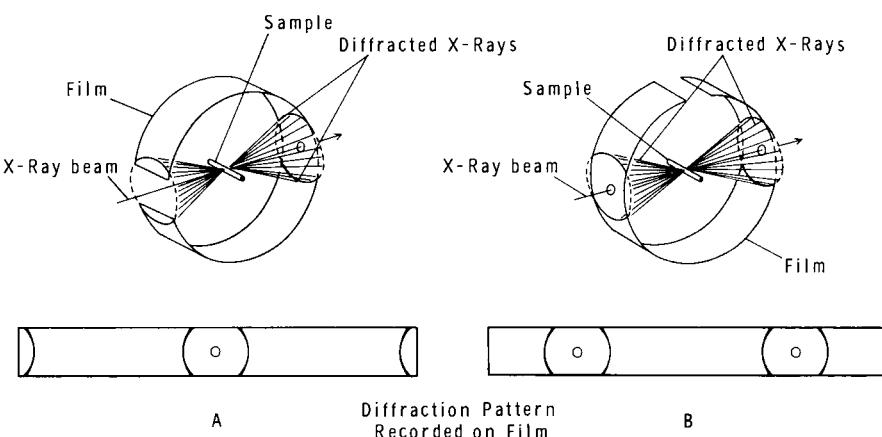


Fig. 10.4 Diffraction geometry of powder method. A. Debye-Scherrer arrangement. B. Straumanis arrangement.

In clay-mineral identification work the speed with which results can be obtained is often important. This arises since a large number of samples frequently has to be considered and several analyses generally have to be performed on the same sample after successive pre-treatments. The diffractometer is superior in this respect to the powder camera as d-values are obtained more rapidly and furthermore since it is possible to limit the angular range investigated one need only record that region in which significant diffraction effects are likely to occur. For example when a sample has been treated with glycerol or ethylene glycol one may limit the recording to the low angle region in which diagnostic changes in lattice spacing may be anticipated. On the other hand direct visual comparison between an unknown and reference diffraction pattern is easier when the pattern is recorded on film than on a diffractometer chart.

Clay-mineral analysis by X-ray diffraction is generally qualitative and gives only semi-quantitative information. More strictly quantitative clay-mineral analyses have been obtained in favourable cases and by the use of special techniques. The X-ray method is also used in crystal-structure analysis, to obtain information on the degree of disorder in the clay-mineral lattice, to follow changes in mineralogical composition induced by heat, and to derive data concerning the mean crystallite size of the minerals in a sample. X-ray amorphous material is not readily detectable by X-ray diffraction as it causes only broad, poorly defined halos instead of sharp maxima on the diffraction record. Preliminary X-ray analysis of the sample in the "as received" condition or after crushing (e.g. to pass a U.S. Standard 325 mesh sieve) often gives most information concerning the non-clay minerals.

DISAGGREGATION AND REMOVAL OF CEMENTITIOUS MATERIAL

A great many clay soils contain particles of sand or silt-size range. It is common practice to remove this coarser material by sedimentation or by a combination of sieve and sedimentation techniques. Different subdivisions within the clay grade have been adopted by different workers but commonly employed size fractions for mineralogical analysis are 2.0-0.2 μm and less than 0.2 μm ; a finer split at 0.08 or 0.04 μm is also sometimes analysed. Separation of samples within the less than 2 μm size range is most conveniently accomplished by centrifugal means (see Chapter 11). The minerals in clay soils are often joined together into aggregates which resist dispersion with a tenacity which varies with the factors responsible for the bonding. Unless the aggregations are broken down, small minerals which properly belong to the clay-size range may be removed in the silt- or sand-size fractions. Aggregations also reduce the perfection which can be achieved in the degree of parallelism between the platy particles in the oriented sample and so the basal X-ray reflections are weakened.

In a flocculated soil the clay minerals are united by attractive forces of an electrical nature. Disaggregation can sometimes be achieved by mechanical means involving agitation in water, use of the mortar and pestle or ultrasonic vibrations. Some workers have reported that the relative abundance of clay minerals separated by sonic treatment is not detectably different from that of clays separated by sedimentation (HEAKAL and HERBILLON, 1976). There is some indication however that easily cleavable minerals may suffer an appreciable reduction in grain-size when ultrasonic vibrations are used (GIPSON, 1963). Aggregations may be held together by cementitious compounds some of which are X-ray amorphous; non-crystalline coatings lower the peak-to-background ratio of the diffraction pattern. Carbonates, oxides and hydroxides of silicon and aluminium, and carbon compounds frequently act as cementing agents. Oxides or hydroxides of iron either alone or co-precipitated with similar compounds of aluminium have commonly been thought to have cementitious properties. Evidence has been presented, however (DESHPANDE et al., 1964, pp. 107-108), which indicates that iron compounds may not be important in the formation of clay mineral aggregations. Cementitious compounds have to be removed by a chemical pre-treatment before the clay can be properly dispersed.

Carbonates may be removed by use of acids but many clay minerals are affected by strong mineral acid. Replacement of exchangeable cations by H^+ ions from the acid is believed to be followed by release of Al^{3+} ions from within the structure of the aluminosilicates. Chlorites in particular are quite susceptible to attack by hydrochloric acid and certain smectites are known to be acid soluble. Weak organic acids and also ammonium acetate are likely to have less effect on clay minerals than the strong mineral acids.

Heating in a buffered solution of sodium acetate and acetic acid has also been recommended. Various types of ion-exchange resin have been employed and some of the acid soluble clay minerals such as hectorite appear to be little affected when separated from carbonates by this means (GILLOTT, 1963, p.765).

Organic material may be removed by oxidation with hydrogen peroxide (H_2O_2). The suspended sample is heated to about $80^{\circ}C$ and small amounts of 30% H_2O_2 are added. Frothing can be controlled by addition of alcohol or other commercially available preparations (KITTRICK and HOPE, 1963, p.321). Frothing is said to be less if sodium hypochlorite ($NaOCl$) is used as oxidizing agent (ANDERSON, 1963). Bromine has also been found to be a very effective oxidizing agent for removal of organic material (LANGEVELD et al., 1978). Most sediments contain some soluble organic matter and this reaches its greatest amount in oil-reservoir rocks. This may interfere with the mineralogical analysis by preventing dispersion of the clay minerals in water. Such constituents including hydrocarbons may be removed by detergent (PARHAM and MAST, 1963) or by subjecting the finely ground sediment suspended in organic solvents to ultrasonic vibrations.

Regardless of whether or not iron compounds have cementitious properties free iron is commonly removed. In the method proposed by MEHRA and JACKSON (1960, p.319) $Na_2S_2O_4$ (sodium dithionite, also known as sodium hydrosulphite and sodium hyposulphite) is used with a citrate-chelating agent to complex the ferrous iron and prevent precipitation of ferrous sulphide. As well as removing free iron the treatment facilitates removal of alumina and silica. About 1g of clay is treated with 40 ml of 0.3 M Na-citrate solution to which 5 ml 1M $NaHCO_3$ is added to stabilize the oxidation potential and pH. The suspension is heated to $80^{\circ}C$ and 1g of solid $Na_2S_2O_4$ is added. After stirring for 15 minutes 10 ml of saturated $NaCl$ and 10 ml of acetone are added as flocculating agents. The suspension is stirred, warmed and centrifuged with the supernatant being decanted for determination of the Fe, Al and Si extracted from the sample. Many other workers (MITCHELL and MACKENZIE, 1954; COFFIN, 1963) have proposed removal of free Fe by use of $Na_2S_2O_4$ together with different buffer reagents to control the pH at a variety of values under various conditions of temperature and reagent concentration. A technique employing a filter of ferro-magnetic stainless steel wool placed in a strong magnetic field has been used by SCHULZE and DIXON (1979). When passed in suspension through the filter, clay sized magnetic particles are trapped by the magnetic field.

Siliceous and aluminous compounds may be removed by the differential dissolution technique of HASHIMOTO and JACKSON (1960). Allophane and the free alumina and silica are removed by boiling an oven dry, iron oxide-free powder for exactly 2.5 minutes in 0.5N $NaOH$ in the proportions of 100 mg powder to 100

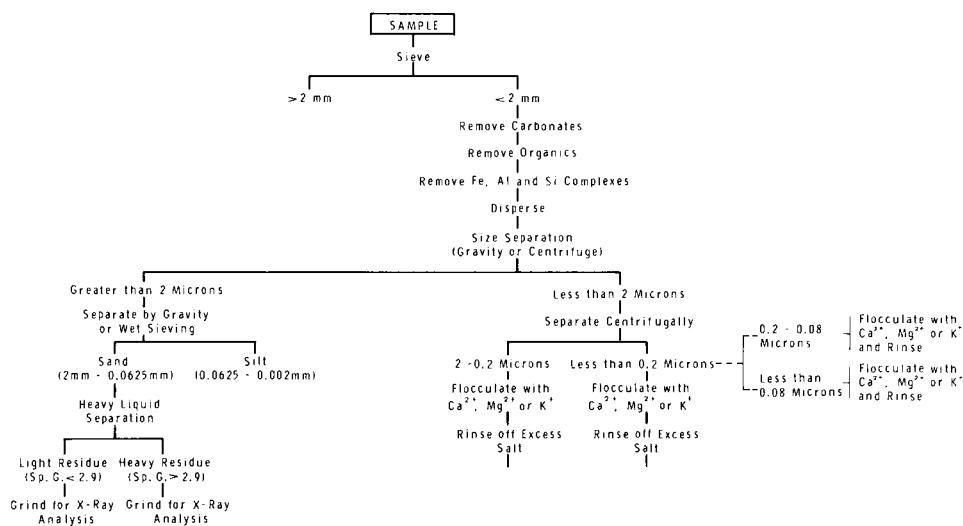


Fig. 10.5 Sample pre-treatment prior to X-ray analysis.

ml alkali. The solid and solution are immediately cooled and separated by use of the centrifuge. It is sometimes important to know whether the clay minerals themselves are affected by such a treatment and FOSTER (1953, p.151) has pointed out that one way by which this may be assessed is to compare the $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio of the bulk chemical analysis with the same ratio in the extract. Effect on exchange capacity may also be considered.

Minerals are generally dispersed following disaggregation by use of an agent such as sodium hexametaphosphate (calgon). The electrolyte content of the suspension may be changed so that repulsive forces between the particles become dominant. Dilute caustic soda solution, sodium carbonate, or ammonia is commonly employed. After dispersion and size separation the exchange sites on the clay minerals require saturation with a known cation as this affects the response to changes in relative humidity of swelling clay minerals such as montmorillonite. The clay suspension may be flocculated by addition of excess of the appropriate chloride solution. The supernatant liquid can be decanted after the sediment has had time to settle or the suspension may be centrifuged. The sample is generally treated several times in this way to make sure the exchange reaction has gone to completion. Excess salt is removed by repeated washing in distilled water until the clay tends to pass into dispersion or until a white precipitate of AgCl is no longer obtained when the washings are tested with AgNO_3 . Acetone facilitates the final stages of the

washing procedure as its presence favours flocculation. A desalting procedure for clay suspensions which combines ultrafiltration with dialysis has been recently developed (SCHRAMM and KWAK, 1980).

Chemical treatment prior to mineralogical analysis frequently leads to enhanced peaks on x-ray diffractograms but sometimes the clay mineral assemblage itself is altered and an artificially "weathered" sample is produced (BREWSTER, 1980). A schematic arrangement for pre-treatment of the sample prior to X-ray analysis is shown in Fig. 10.5.

MOUNTING AND TREATMENT OF SAMPLES FOR X-RAY ANALYSIS

The most useful information for clay mineral identification can be obtained from a sample oriented to enhance the intensities of the basal x-ray reflections. Since basal spacings are most diagnostic and orientation enhances intensities detection limits are improved. An oriented sample may be prepared on a glass slide by allowing a suspension of the clay to evaporate free from disturbance. This technique has the advantage of simplicity but suffers from the drawback that different clay minerals settle at different rates so segregation may occur and estimates of the relative proportions of the different minerals may be correspondingly affected. Alternative techniques intended to improve the perfection of the orientation of the clay platelets have involved the application of pressure (CODY and THOMPSON, 1976; BAJWA and JEMKINS, 1978), the use of the centrifuge (KINTER and DIAMOND, 1956), the smear of clay paste onto a glass slide (THIESEN and HARWARD, 1962) and suction onto unglazed ceramic tile or other microporous substrate (RICH, 1969; QUAKERNAAT, 1970).

Background due to scattered x-rays depends on the sample thickness and the nature of the material on which the sample is mounted. Glass often gives a relatively high background and this may be reduced by using a BT-cut quartz crystal oscillator plate (Fig. 10.6) (BUERGER and KENNEDY, 1958). When Cu-radiation is used silver membrane filters give no maxima up to $38^{\circ} 2\theta$ and also give a low background because silver has a high mass absorption coefficient in the Cu wavelength range (POPPE and HATHAWAY, 1979). Another approach to the reduction of background in the low angle region has been described by JOHNSON (1977). He attached a selectively heated thermistor to the zero suppression control in the ratemeter circuitry of the diffraction apparatus. This produced a logarithmic resistance response which approximates to the increasing level of background below about $2^{\circ} 2\theta$.

An X-ray diffraction pattern is generally recorded with the oriented sample in the air-dry state and also after it has had several auxiliary treatments. Many of the different clay minerals have similar silicate structures. Nonetheless they respond differently to chemical attack, heat, and changes in

relative humidity. Hence a comparison between the X-ray diffraction patterns recorded successively after each sample treatment facilitates correct identification.

Inspection of the d-values of the peaks on the diffractogram recorded from the air-dry sample will indicate the main groups of clay minerals that are present. The peak heights or areas give an indication of the approximate relative proportions. The spacings (d-values) of the basal reflections should also be examined to determine whether they can be resolved into integral series. Thus if there is a reflection at 10\AA the second order reflection should occur at 5\AA , the third order at 3.33\AA and so on. The relative intensities of these orders are affected by structural considerations. Regular mixed-layer minerals also give an integral series of orders of basal

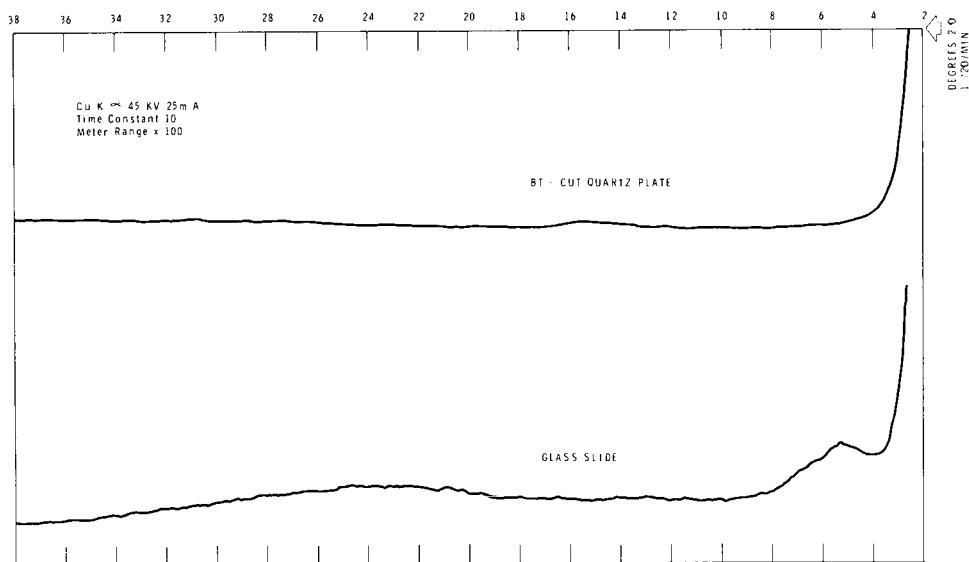


Fig. 10.6 X-ray scatter from BT-cut quartz plate compared with glass slide.

diffraction peaks which correspond to the sum of the spacings of the individual components. The nature of the components is determined by recording diffraction patterns from the sample following a series of treatments which generally include heating, saturation with organic liquids and saturation with different cations such as Mg^{2+} and K^+ . Random mixed-layer minerals show non-integral orders of reflections from the basal planes both before and after treatment with ethylene glycol or glycerol. Where two, or more, different types of layers are intergrown at random the angular positions of the (001) reflections are average values which result from the composite contribution of

all the types of layers in the intergrowth. In such cases it is not possible to account for the spacings of the observed peaks from a particular mineral simply by division of the fundamental repeat distance, $d(00l)$, by whole numbers. The actual angular position depends upon the relative proportions of the components in the intergrowth and on other factors (WEAVER, 1956). Detailed information on the nature of the interstratification such as the proportions of the components and their manner of distribution may be derived by the Fourier transform method of MacEWAN (1956, 1958). Computer techniques have been used which make possible rapid calculation of diffraction patterns in which degrees of irregularity of layers, structure factors and crystal size are varied. These calculated patterns are then compared with observed diffraction patterns until agreement is obtained. The principles of the calculation of the diffraction effects have been described by several authors (REYNOLDS and HOWER, 1970; PLANCON and TCHOUBAR, 1977).

Changes in relative humidity cause clay minerals with expanding structures such as smectites to show variation in the basal interplanar spacing; this causes corresponding changes in the angular position and intensity of the X-ray diffraction maxima. The basal spacing can be fixed by formation of a complex between the clay mineral and an organic liquid. The organic compounds normally employed are ethylene glycol and glycerol. Both are miscible with water but glycerol has a lower vapour pressure and is preferable as it evaporates less readily. After treatment an integral series of sharp basal X-ray diffraction maxima can be recorded. The glycol or glycerol may be applied to the oriented clay sample as a mist of fine droplets produced by an atomiser. Other methods are also used. The sample can be mixed on the slide with an excess of the organic liquid and left to evaporate. Drops can be placed round the edges of the slide so that the liquid slowly migrates into the sample. The glycol can be heated to 65°C and supplied to the sample as a vapour and glycerol treatment can be carried out similarly by heating at $100\text{--}105^{\circ}\text{C}$ (BROWN and FARROW, 1956). The sample can be leached with a dilute solution of the organic liquid (KINTER and DIAMOND, 1956, p.116). The hydration state of the mineral and nature of the exchange ion as well as the method of application of the organic solvating agent are sometimes important to correct clay-mineral identification. This was found to be so in the recognition of vermiculite (WALKER, 1958) and HARWARD and BRINDLEY (1966) found that beidellite can be distinguished from montmorillonite by giving proper consideration to these variables. Calcium or magnesium saturated montmorillonite dried at 105°C expands in glycerol vapour to about $16.7\text{--}17.7\text{\AA}$ whereas beidellites expand only to about $14.2\text{--}14.6\text{\AA}$ under these conditions.

The use of organic liquids can be avoided. The oriented sample may be allowed to come to equilibrium at a controlled relative humidity and a

diffraction pattern recorded while the ambient conditions are held constant; a stream of pre-conditioned air is supplied to the sample during the analysis. By employing conditions which vary from dry to wet the corresponding changes in interplanar spacing may be registered on the diffractogram (MILNE and WARSHAW, 1956).

The chief swelling clay minerals are smectites, vermiculites, swelling chlorites, and various mixed-layer minerals. Mg-smectites take up two monolayers of glycerol between the layers and develop a spacing of about 17.8\AA ; magnesium saturated vermiculite forms a complex with glycerol with a basal spacing of about 14.5\AA ; and swelling chlorites show a basal spacing of about 18\AA when treated with glycerol. Mg-smectites may therefore be distinguished from Mg-saturated vermiculites by this test (WALKER, 1958, p.311) but not from swelling chlorite. If the oriented sample is heated for about 1 hour to 600°C smectite and vermiculite both give an X-ray reflection at about 9.7\AA as the water and organic molecules in the interlayer region are driven off and the unsupported basal planes move closer together and the structure is said to have "collapsed". When swelling chlorite is heated, however, it gives an enhanced X-ray reflection at about 13.6\AA (STEPHEN and MacEWAN, 1950, p.82). Hence X-ray analysis of an oriented sample treated with glycerol followed by heat treatment makes distinction possible in favourable cases. The difference in the intensities of the 10\AA diffraction maxima before and after heating can be attributed to the collapse of the expandable clays. The optimum temperature of collapse of illite-smectite mixed-layer clay minerals is said to be about 375°C (AUSTIN and LEININGER, 1976). As an alternative to heat treatment contraction of the basal spacing of swelling clay minerals can also be effected by use of salts of large monovalent cations such as potassium chloride.

Chlorites are sometimes difficult to distinguish from kaolinite as the first 001 and third 003 order basal reflections may be weak and the second 002 and fourth 004 order chlorite reflections at about 7\AA and 3.5\AA , respectively, approximately coincide with the first 001 and second 002 order kaolinite reflections. The presence of chlorite may be confirmed by heat treatment. When heated to about 550°C for 1 hour the first order chlorite reflection at about 13.8\AA becomes sharp and of increased intensity. The higher order chlorite reflections disappear. The kaolinite reflections are also lost. Chlorites are more soluble than kaolinite in hot hydrochloric acid and may be removed in this way to make identification of kaolinite more certain. Various salts cause a shift in the basal spacing of kaolinite which is more readily affected than chlorite. The technique known as differential intersalting has been used as a means of identification (ANDREW et al., 1960; WADA, 1961). An intercalation procedure involving use of lithium dimethylsulfoxide to distinguish between kaolinite, chlorite and vermiculite has also been described

(ABDEL-KADER et al., 1978). Distinction between kaolinite and chlorite has also been made by resolving the second order kaolinite reflection at 3.58\AA from the fourth order chlorite reflection at 3.54\AA by employing high resolution conditions and a slow scanning speed during the recording of the diffractogram (BISCAYE, 1964). WARSHAW and ROY (1961, p.1483) have pointed out that mullite is formed when kaolinite is heated for 1 or 2 hours at $1,000^{\circ}\text{--}1,100^{\circ}\text{C}$ whereas thermal breakdown of chlorites at this temperature leads to formation of magnesium and iron-bearing minerals such as olivine or spinel. Mullite also develops at the expense of mica-type clay minerals though its temperature of formation is reported to be somewhat higher. As the temperature at which mineral transformations occur can be markedly altered by compounds which act as fluxes caution is needed in interpreting crystallization of mullite at these temperatures as a diagnostic criterion for the identification of kaolin, particularly in mixtures. Dickite differs from other kaolinite group minerals in that it often develops a 14\AA transitional phase when heated to temperatures of $550\text{--}700^{\circ}\text{C}$ at which dehydroxylation occurs (BRINDLEY and HSIEN-MING WAN, 1978).

Halloysite, when fully hydrated, gives an X-ray reflection at about 10.1\AA . If the mineral is dried at 100°C it dehydrates irreversibly and gives an X-ray reflection at about 7.2\AA . Halloysite when hydrated or partly hydrated will form complexes with organic reagents. The problem of its identification and distinction from kaolinite has been discussed by a number of authors (BRINDLEY et al., 1963; MILLER and KELLER, 1963; WADA, 1963).

Incomplete sheets of hydrated aluminium can occur in the interlayer space of clay minerals which normally show a variable basal lattice spacing. Such minerals occur in soils (SAWHNEY, 1958; BRYDON et al., 1961; DIXON and JACKSON, 1962) and have been prepared synthetically (BRYDON and KODAMA, 1966). Similar complexes of iron have also been reported (QUIGLEY and MARTIN, 1963). The complexes usually have properties intermediate or "intergradient" between those of vermiculite, chlorite and montmorillonite. The interlayer precipitate may interfere with both expansion and contraction of the clay-mineral structure when the usual procedures for characterization are carried out.

When such a mineral is present an oriented sample in the air-dry state commonly gives an X-ray reflection at an angle which corresponds to an interplanar spacing of about 14\AA . Solvation with glycerol may (BARNHISEL and RICH, 1965, p.633) or may not (RICH and OBENSHAIN, 1955, p.336; TAMURA et al., 1959, p.192), be accompanied by a shift in the 14\AA X-ray reflection to indicate longer lattice spacings. The 14\AA reflection is sometimes more intense relative to the 7\AA reflection than is usual when a chlorite is present. This recalls vermiculite but unlike this mineral the peak does not move to about 9.8\AA , when the sample is heated or saturated with potassium. Instead only partial

collapse of the structure is indicated and an X-ray reflection is registered from planes with a spacing somewhere between 10 and 14 \AA . A discreet reflection may not be registered at all as the 14 \AA peak sometimes develops a tail which extends towards higher angles (smaller d-values).

Various reagents have been employed to extract the interlayer aluminium so that the structure becomes free to expand or contract on appropriate treatment. Identification has depended upon X-ray analysis together with chemical analysis of the extract for aluminium and determination of the increase in cation-exchange capacity (FRINK, 1965). The suitability of the reagents used for extraction has been evaluated on the basis of the improvement in peak resolution on the X-ray diffraction pattern, effect on expansion and

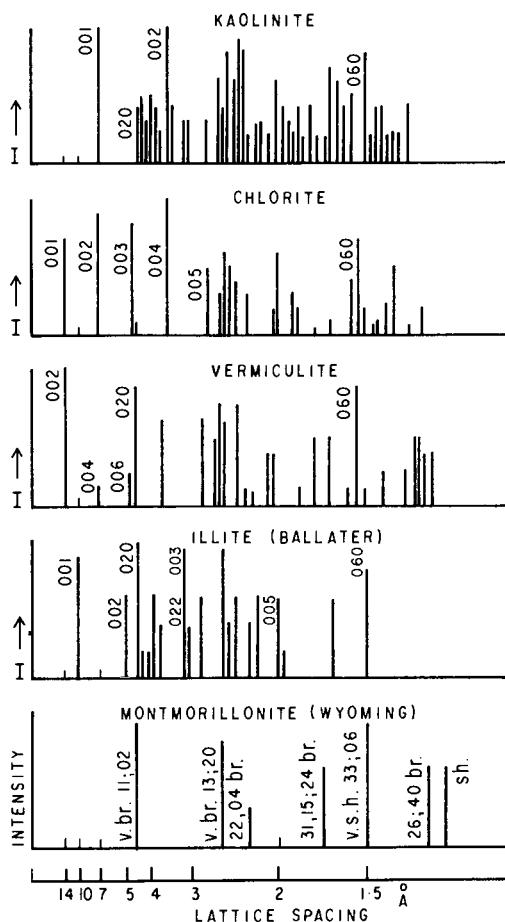


Fig. 10.7 X-ray reflections from some clay minerals. (Data from BROWN, 1961).

contraction properties of the structure and tendency of the treatment to destroy the minerals present. BROWN (1953) employed a mixture of KOH plus KCl. RICH and OBENSHAIN (1955) concluded that this tended to destroy vermiculite and recommended use of 1N KCl-0.1N HCl or 1N NH₄F. TAMURA (1958) employed sodium citrate and DIXON and JACKSON (1962, p.360), following a review of the various methods concluded that the most satisfactory results were obtained when the sample was heated to 400°C and then boiled for 2.5 minutes in a solution of 0.5N NaOH. Such intergradient clay minerals seem to be most common in soils undergoing weathering under acid conditions. Low organic content and frequent wetting and drying is also said to favour their formation (RICH, 1968).

TABLE 10.1

X-RAY IDENTIFICATION OF PRINCIPAL GROUPS OF CLAY MINERALS

| Technique | Information derived |
|--|---|
| Randomly oriented powder photograph (>2 μ m fractions) (<2 μ m fractions) | (a) Non-clay minerals (b) Clay Minerals { Dioctahedral 060=1.48-1.49 \AA { Trioctahedral 060=1.53-1.55 \AA (c) Clay mineral polytypes |
| Oriented sample (air dry) | (a) 14-15 \AA minerals { Chlorites { Smectites { Vermiculite { Intergrades (b) ~10 \AA minerals { Mica-type minerals (illites) { Hydrated halloysite (c) 7 \AA minerals { Kaolinite-Serpentine { Dehydrated halloysite { Serpentines |
| Oriented sample (Treated with glycerol) | (a) 17-18 \AA minerals { Smectites { Swelling chlorites (b) ~14 \AA minerals. Vermiculite (c) 10.5-11.0 \AA . Halloysite |
| Oriented sample (Heated 550-600°C, 1 h) | (a) Enhanced 14 \AA . Chlorites (higher orders vanish) (b) ~10 \AA { Smectites { Vermiculite (c) ~7 \AA minerals. Reflections vanish |

In addition to the X-ray analysis of samples oriented to enhance reflections from the basal planes (001) a diffraction pattern of a randomly oriented sample is required. This is commonly recorded on a Debye-Scherrer photograph. Powder

lines due to diffraction from planes with indices of type (hkl) and bands (hk reflections) due to diffraction from one dimensionally disordered structures are registered. By measurement of the d-value of the 060 reflection it can be determined whether dioctahedral, trioctahedral or both groups of clay minerals are present. The d-value of the 060 reflection is about 1.49 \AA for dioctahedral clay minerals and has a value of about 1.53-1.55 \AA for trioctahedral clay minerals; caution has been suggested in the use of this criterion for some minerals (TELLERIA et al., 1977). A consideration of the general hkl reflections may make it possible to distinguish between the various polytypes if mica-type clay minerals are present. The necessary criteria have been listed by LEVINSON (1955), YODER and EUGSTER (1955), SMITH and YODER (1956) and BROWN (1972). The non-clay minerals in the less than 2 μm fraction of a soil are also most readily identified by analysis of a Debye-Scherrer photograph.

A schematic illustration of the stages in the recognition of the principal groups of clay minerals is shown in Table 10.1 and interlayer spacings and approximate intensities of X-ray reflections in Fig. 10.7. More information concerning identification by X-ray diffraction has been given by CARROLL (1974).

QUANTITATIVE ANALYSIS

The relative proportions of the clay minerals in a sample can be approximately estimated from the relative intensities of the peaks on an X-ray diffraction pattern. The intensity of the diffraction pattern of a component in a mixture is proportional to its concentration. If a particular component is present in the same proportion in different mixtures, however, the intensity of the radiation diffracted by that component will not be a constant. It depends on the mass-absorption coefficients of the other components in the mixture.

Many of the methods of quantitative analysis by the X-ray method depend upon preparation of a calibration curve. A series of mixtures is made up composed of an increasing and known proportion of a reference clay mineral in a suitable dilution matrix together with a constant amount of a third component to be used as internal standard. Diffractograms are recorded from each of the mixtures and the ratio of the area of the peak from the reference clay mineral to that of the peak from the internal standard is calculated. The value of the ratio is plotted as a linear function of the weight fraction of the reference clay mineral in each of the mixtures. Once the calibration curve has been constructed it may be used to give the concentration of the required mineral in an unknown sample. The same proportion of the standard material is mixed with the sample, the peak ratio is determined and the concentration of the required mineral is read from the calibration curve.

The equations on which calculation of diffracted intensity is based generally require that the crystals have completely random orientation though there are similar relations for samples in which the crystals are perfectly oriented. These principles underlie quantitative analysis by the X-ray method. A sample in which the crystals are perfectly oriented would be much more satisfactory than a random sample because of the routine use of oriented samples to improve detection limits in clay mineral analysis. It is however not much easier to ensure perfect crystal orientation than complete randomness. Hence degree of preferred orientation is one of a number of factors which limit the precision of quantitative analysis of clay minerals by X-ray diffraction. Other problems arise from the choice of suitable internal standard and from the difficulty of obtaining reference samples of the clay mineral under investigation which are pure and truly similar.

A good internal standard should readily form a homogeneous mixture with the sample and this is not always easy with fine-grained and cohesive materials such as clay soils. CODY and THOMPSON (1976) list seven other requirements for a good internal standard. These are 1) that the crystallinity and particle size should be such as to give sharp diffraction peaks; 2) it should be readily available; 3) it should have strong peaks near those of the required mineral; 4) peaks from the standard should not overlap those of the required mineral; 5) it should not be present already in the samples being analyzed; 6) it should have a platy morphology, similar particle size and should orient to the same degree as the required clay mineral; and 7) it should be non-reactive to chemical and physical treatments used in clay mineral analysis and it should be stable to changes in relative humidity and other changes in laboratory environment. They conclude that molybdenum sulphide meets most of these requirements; other workers have used boehmite, aluminium powder, zinc hydroxide, etc.

The problems of obtaining suitable reference clay minerals for construction of the calibration curve arise from several causes. One problem is caused by variability in intensities of X-ray reflections from the same planes of related minerals due to isomorphous substitution and differences in chemical composition; another results from differences in crystallinity and a third arises because of differences in crystallite size. GIBBS (1967) made a serious attempt to overcome many of the difficulties of obtaining suitable reference minerals by separating minerals from the samples themselves; he then used the separated minerals as reference standards. The separation procedure is however very time consuming and doubt will often remain as to the purity of the reference material which has been obtained.

Other variables which need to be controlled for good reproducibility are the physical dimensions of the sample and method of calculation. Weighting

factors, peak intensity ratios, statistical procedures and various computer methods have all been used in quantitative clay mineral analysis with varying success. As a general conclusion it appears that if technique is standardized it is reasonable to expect a precision of at least $\pm 10\%$ particularly in comparative studies of a suite of related samples. Recent discussions of this topic have been published by DEVINE et al., (1972), SCHOEN et al., (1972), EDIL and KRIZEK (1972), CUBITT (1975), and CODY and THOMPSON (1976). Other attempts to achieve quantitative clay mineral analysis have been made by use of thermal methods and by calculation from chemical or elemental analysis (PEARSON, 1978).

THERMAL METHODS OF ANALYSIS

Significant physical or chemical changes generally take place at temperatures which are a characteristic for a particular compound. Thermal methods in which accompanying energy changes are recorded include differential thermal analysis (DTA) and differential scanning calorimetry (DSC). Thermal methods which depend on measurement of weight change include thermogravimetry (TG) and derivative thermogravimetry (DTG). In other methods dimensional change or thermoluminescence is measured. In some commercial apparatus more than one set of measurements is made at the same time on the same sample. Typically DTA and evolved gas analysis are performed simultaneously or DTA, TG and DTG curves may be plotted on the same chart. Standard texts describing the equipment for thermal methods of analysis and its use in applied clay mineralogy and related fields are available (MACKENZIE, 1970; WENDLANDT, 1974).

In DTA and DSC the composition of a sample is inferred by matching the measured temperatures at which the thermal changes occur with known values. Standard samples may be analysed under the same conditions as the unknown and the two sets of thermograms compared or the temperatures at which peaks occur on the thermogram of the unknown may be matched with published data. In a mixture a component can be detected when present in a concentration of about 1 or 2% or more so that as analytical tools these methods have a similar sensitivity to X-ray diffraction. When a quantitative analysis is required the amount of sample used must be weighed accurately.

In DTA a sample and thermally inert reference material such as alumina calcined to a temperature of at least 1200°C are heated side by side at a constant or reproducible rate, commonly $8-12^{\circ}\text{C}/\text{min}$, and the temperature difference between the two materials is recorded. If the sample undergoes a reaction which absorbs heat its temperature becomes lower than that of the inert reference and an "endothermic" peak is registered. When heat evolution occurs in the sample it becomes temporarily hotter than the reference and an "exothermic" peak is produced. Some arrangement is made so that the temperature is known at which these changes take place. The thermal changes

are registered by means of thermocouples in the sample and reference material. In most modern equipment the temperature differences are recorded graphically by means of an electronic recorder after suitable amplification. Photographic recording is occasionally employed. Electronic means are also generally used to control the heating rate (Fig. 10.8). Provision is commonly made for control of the atmospheric composition in which the sample and reference are heated; with some types of equipment this may be varied during the course of an analysis. Pressures above and below atmospheric and controlled cooling to temperatures below ambient may also be employed. DSC is a similar technique but the sample and reference are kept at the same temperature and the amount of energy required to maintain this balance is measured as a function of temperature or time. Enthalpy is proportional to the area under the curve and the differential heat flow is proportional to peak height.

Factors which affect thermal analysis include heating rate, packing of sample, dilution of sample, crystallinity of the minerals, pre-treatment of sample, particle size of sample, furnace atmosphere and design and composition of the sample holder (BAYLISS and WARNE, 1962; MACKENZIE and MITCHELL, 1962).

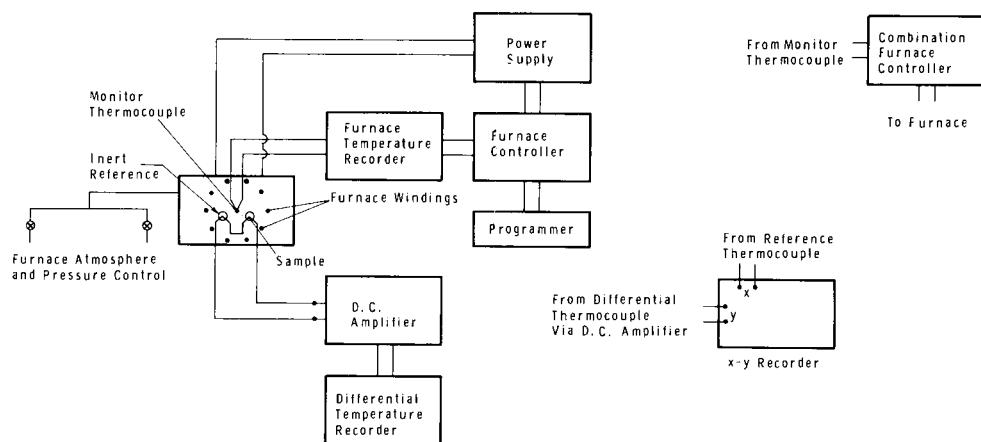


Fig. 10.8 Two alternative arrangements for DTA instrumentation.

In the case of kaolinite, for example, the degree of disorder in the crystals has been shown to affect peak temperature and peak height. By maintaining a standardized procedure of sample preparation and analysis SMYKATZ-KLOSS (1975) was able to use changes in the DTA curves to estimate the relative degree of disorder and to distinguish kaolinites from different localities. The importance of a standardized procedure of sample pre-treatment has frequently

been emphasized. For example saturation of exchange sites with a known cation has been recommended because the different hydration properties of exchange ions have been found to affect the form of the thermograms. Ca-saturation is generally satisfactory but TAN and HAJEK (1977) reported that the intensity of both the 530° and 1000°C peaks was lower for Ca-kaolinite than for Na-, H-, or Al-kaolinite. In this case the size and shape of both the endothermic and exothermic peaks was affected by the different exchange ions but not the peak temperature. In addition to standardization of exchange ion before thermal analysis of clays preconditioning to a known relative humidity, such as 55% over a saturated solution of Mg(NO₃)₂.6H₂O, is strongly recommended.

Differential thermal analysis has been employed most commonly for qualitative analysis of clay minerals but some attempts at quantitative analysis have also been made (SAND and BATES, 1953; CARTHEW, 1955b). The major thermal effects associated with the clay minerals occur in three temperature ranges. There is a low temperature region from 50 to 200°C where endothermic peaks occur associated with the loss of surface water. There is a mid-temperature region from about 450 to 700°C where endothermic peaks occur due to the loss of OH ions which form an integral part of the alumino-silicate structure. The high temperature region is above about 800°C and is associated with an endothermic peak due to the final breakdown of the clay-mineral structure and an exothermic peak or peaks resulting from crystallization of new phases.

The size of the peaks in the low temperature region reflects the amount of adsorbed water and more than one peak may occur if water bound with different energies is present. Well crystallized kaolinites generally have a small peak or none at all but hydrated halloysite is an exception and shows quite a large peak at about 120°C; this peak is irreversibly destroyed by drying or heating the sample above 100°C. Serpentines also show a small endotherm in the low temperature region. The 2:1 type clay minerals show larger endothermic peaks in this region and smectites often have a complex peak system depending on the degree of hydration and nature of the exchange ion. The chlorites may or may not show peaks in this region depending on the particle size. Palygorskite generally displays two peaks in the low temperature region the first of which is the larger and sepiolite shows a large endotherm at about 150°C which is sometimes double. If colloidal constituents are present, such as gels of silica, alumina or iron they too lose associated water endothermally and cause a peak or peaks in the low temperature region of the thermogram. If large low-temperature endothermic peaks (particularly if coupled with a sharp exotherm at about 1000°C) cannot be accounted for by minerals detected by X-ray diffraction these peaks are a good indication that gels are present.

Many of the clay minerals show an endothermic peak in the 500-600° range

associated with loss of structural hydroxyl ions. If more than one type of clay mineral is present these peaks tend to overlap. Well crystallized kaolinite gives a peak at about 600°C , halloysite dehydroxylates at about 560°C , chlorite gives a peak or peaks at $550^{\circ}\text{-}650^{\circ}\text{C}$ and illite gives a peak at about $500^{\circ}\text{-}550^{\circ}\text{C}$. Montmorillonite gives a peak at about 700°C though some minerals of variable interlayer spacing show the peak at the lower temperature of $550^{\circ}\text{-}650^{\circ}\text{C}$. The temperature at which this peak occurs may often be shifted by use of different pressures of water vapour during the analysis. The serpentines and chlorites may be distinguished on the basis of peaks registered in this temperature range (NELSON and ROY, 1954, p.343; PHILLIPS, 1963). Antigorite and chrysotile display the endothermic peak at a temperature of about 700°C which is followed by an exothermic peak associated with formation of forsterite. In chlorites there is a gap of about 100°C between the endothermic peak at about $550\text{-}675^{\circ}\text{C}$ and the exotherm at about $805\text{-}875^{\circ}\text{C}$. This exotherm is often preceded by an endotherm. Loss of hydroxyl at two different temperatures from the chlorites may reflect the difference in structure which exists between hydroxyl ions in the silicate layer and hydroxyl ions in the brucite layer. Palygorskite gives a single or double peak at $350^{\circ}\text{-}600^{\circ}\text{C}$ and sepiolite gives two peaks at about 300°C and 500°C .

Most of the clay minerals have an endothermic reaction in the $800\text{-}1,000^{\circ}\text{C}$ range and this is often followed by an exotherm attributed to recrystallization. This is generally larger for kaolinites than for 2:1 type minerals. Palygorskite and sepiolite generally give an endothermic peak at about 800°C followed immediately by an exotherm attributed to formation of clinoenstatite. Other peaks associated with formation of high temperature phases occur in the temperature range from $1,000^{\circ}$ to $1,400^{\circ}\text{C}$ (WAHL and GRIM, 1964). Thermograms of some of the principal clay minerals are shown in Fig. 10.9.

Thermogravimetry (TG) is the analytical technique concerned with measurement of weight changes in samples on controlled heating or cooling. In DTG the first derivative of the thermogravimetric curve is recorded. A precision balance is employed and the temperatures or times are recorded at which weight changes occur in the sample. Reactions which involve only energy changes such as crystal inversion, crystallization, fusion, and certain types of solid-state reactions are therefore not detectable by thermogravimetry although they are detectable by DTA and DSC.

The method has value in clay work since very many reactions which affect clays on heating are accompanied by evolution (or more rarely absorption) of a gaseous component. As described in connection with DTA adsorbed and structural water are lost by clay minerals on heating and these changes are of course accompanied by a corresponding loss in weight. Water is also lost by gypsum on

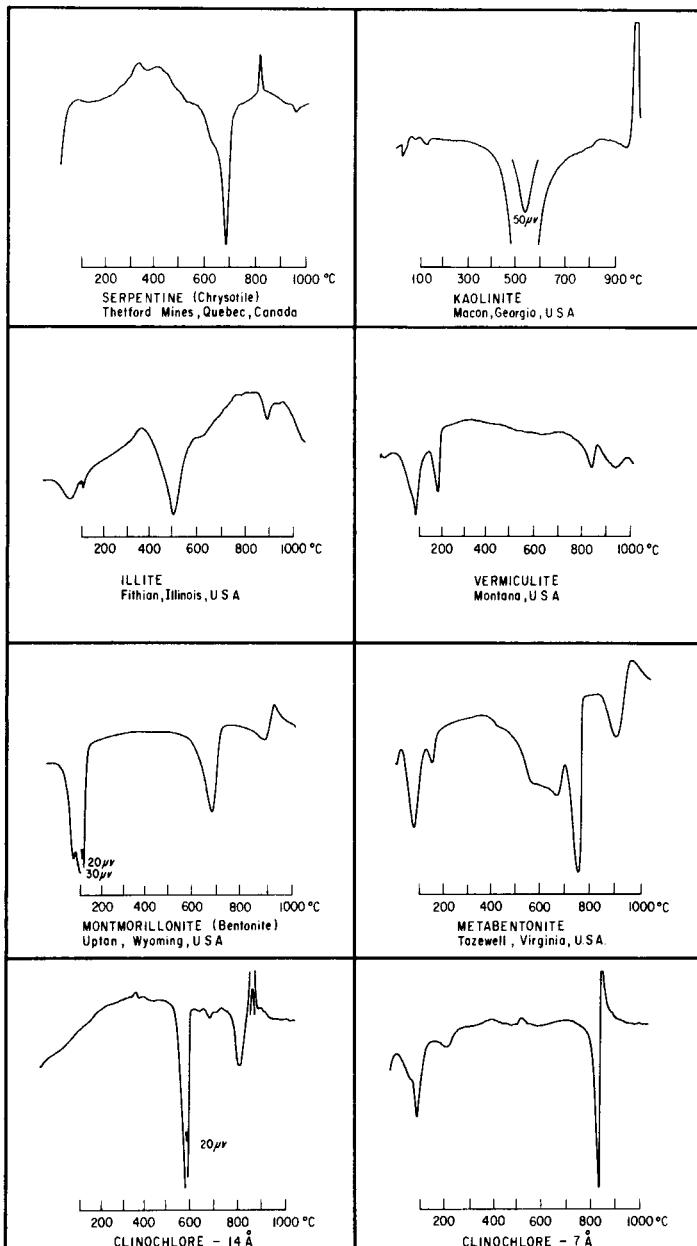
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Fig. 10.9 Thermograms of some of the principal clay minerals.

heating and by the hydrated, X-ray amorphous silica, alumina and iron compounds. Carbonates dissociate with loss of CO_2 . Some oxidation reactions in which oxygen is absorbed from the air are accompanied by a gain in weight.

Thermal methods of analysis are useful tools in clay-mineral analysis since the information often supplements that obtainable by X-ray diffraction. There are, however, limitations to its usefulness. Overlapping of peaks is the greatest drawback to a full analysis by these methods alone. Full control of atmospheric composition and pressure and use of more than one technique greatly increases versatility but does not yet give these methods full self-sufficiency as an analytical procedure for clay-mineralogical work.

INFRARED ANALYSIS

Infrared radiation forms part of the electromagnetic spectrum and includes a range of wavelengths which are longer than those of visible light but shorter than those of the radio range. The wavelengths lie between about 0.7-500 μm ($14,000\text{-}20 \text{ cm}^{-1}$). The infrared spectrum has been subdivided into near infrared with a wavelength range of 0.7-2.8 μm ($14,000\text{-}3,600 \text{ cm}^{-1}$), fundamental region with a wavelength range of 2.8-33 μm ($3,600\text{-}300 \text{ cm}^{-1}$) and far infrared with a wavelength range of 33-500 μm ($300\text{-}20 \text{ cm}^{-1}$) (LEE SMITH, 1979). The exact values of the ranges quoted vary somewhat in different texts. The region which has been most investigated in mineralogical work lies in the range of wavelengths between about 2.5-50 μm ($4000\text{-}200 \text{ cm}^{-1}$). Infrared spectra are generally recorded as curves showing percent absorption or transmission as ordinate versus frequency as abscissa. Frequency is commonly expressed in terms of the wavenumber, ν , in units of waves per cm (cm^{-1}). The wavenumber is derived from the wavelength, λ , (expressed in μm) by use of the following relation:

$$\nu = \frac{10^4}{\lambda}$$

Hence a wavelength of 1 μm corresponds to a wavenumber of 10,000 cm^{-1} , a wavelength of 10 μm = 1000 cm^{-1} and 100 μm = 100 cm^{-1} . Therefore absorption band positions are generally expressed in wavenumbers (cm^{-1}) but may be quoted in wavelengths (μm).

The natural vibration frequencies of atoms in molecules and crystals are in the infrared range. When a material is exposed to monochromatic infrared radiation varying with time so that a range of frequencies is covered absorption occurs at those frequencies which coincide with the frequencies of vibration of molecules or groups in the compound. Characteristic infrared spectra are associated with a number of molecular groups such as CO_3^{2-} , OH^- , SO_4^{2-} . Interatomic vibrations are generally classified into two chief types: stretching vibration modes and bending or deformation vibration modes. There

are sub-divisions within these two modes. In addition to fundamental absorption bands weaker absorption bands may also appear. There are those which are multiples of the fundamental frequency and are known as overtones; others occur at frequencies which are the sum or difference of two or more fundamental frequencies and are known as combination bands. In layer-structure silicates such as the clay minerals infrared absorption bands cannot be assigned and interpreted simply on the basis of nearest neighbour ion interaction. There is commonly also a substantial effect from next nearest neighbour ions or ions in the second coordination sphere.

Infrared spectra are subject to distortion caused by anomalous dispersion resulting from differences in refractive index at interfaces (Christiansen effect) and to scattering of the radiation associated with this and other processes. These effects are minimized if the particle size of the sample is less than that of the wavelength of the radiation being used. The clay size range is therefore satisfactory but silt-and sand-sized particles are too coarse. Wet grinding, filing, ultrasonics and mechanical impact devices have been recommended to reduce particles to the appropriate size range ($<2\text{ }\mu\text{m}$). Chemical pretreatments are sometimes used such as removal of organic matter and iron and saturation of exchange sites with a known cation such as potassium. Quite frequently samples are analyzed in the "as received" condition with little pretreatment other than grinding. Additional spectra may be recorded after heating at about 105°C to remove surface water, after chemical treatments and after heating to a high enough temperature to cause dehydroxylation of the clay minerals. Specimen preparation has been discussed by a number of authors including WHITE (1977). Infrared spectroscopy has been applied to two major kinds of problems in clay mineralogy. It has been used as an aid to mineralogical identification and in crystal chemical and structural investigations.

The results of infrared analysis are of greatest significance in identification when there is ambiguity in the interpretation of the X-ray diffraction pattern. For example there is often uncertainty in the positive recognition of kaolin when chlorite is present. This distinction can be made quite readily by infrared analysis as the kaolin minerals show a band at $3,698 \pm 2\text{ cm}^{-1}$ not shown by chlorites (KODAMA and OINUMA, 1963, p.242). It is often not easy to identify the specific species of a clay-mineral group. Infrared spectroscopy has been used for this purpose in analysis of the chlorites (TUDDENHAM and LYON, 1959), the kaolinites (LYON and TUDDENHAM, 1960) and the serpentines (BRINDLEY and ZUSSMANN, 1959). Poorly crystalline and amorphous constituents in soils are difficult to identify and infrared spectroscopy is useful in this regard. For example imogolite, a poorly crystalline mineral, may be recognized by an absorption band at 348 cm^{-1} and distinguished from

allophane, with which it is often associated. The presence of other clay minerals, which also have absorption bands in this region, can be recognized because they have other bands elsewhere in the spectrum (FARMER et al., 1977). Infrared spectra of some typical phyllosilicates are shown in Fig. 10.10 A,B.

The amount of infrared radiation absorbed depends on concentration and sample thickness or put another way on the number of absorbing molecules so that quantitative analysis is sometimes possible. This has generally given a rather low precision of the order of $\pm 15\%$ (SAND and ORMSBY, 1954, p.282) though greater accuracy has been claimed in some cases (LEHMANN and DUTZ, 1959). Factors which affect precision include particle size and shape, degree of crystallinity, orientation of crystals, chemical composition, the presence of amorphous material and the nature of the embedding material (HLAVAY et al., 1977; ROUSSEAU, 1978).

In structural and crystal chemical investigations infrared spectroscopy has given information on type of bonding and orientation of bond axes (SERRATOSA and BRADLEY, 1958; SERRATOSA et al., 1963; LEDOUX and WHITE, 1965). The substitution in a certain coordination of an ion of different charge can cause changes in intensities or frequencies of the absorption bands (STUBICAN and ROY, 1961b, p.625). This effect was found to be marked when ions of different charge were substituted in the octahedral layer of dioctahedral clay minerals (STUBICAN and ROY, 1961c, p.49). Mechanisms of mineralogical change have been investigated such as those induced by heat (STUBICAN and GUNTHARD, 1957, p.542; FRIPIAT et al., 1960) or acid treatment (GRANQUIST and SUMNER, 1959, p.306). Dehydration, dehydroxylation, clay-organic, and exchange reactions have also been studied by means of infrared spectroscopy (ROY and ROY, 1957; HOFFMAN and BRINDLEY, 1961; HELLER et al., 1962; ROSENQUIST, 1963; WEISS, 1963; CZARNECKA and GILLOTT, 1980). There are now a number of good texts on infrared spectroscopy some of which include reference collections of spectra of well-characterized mineral specimens (FARMER, 1974; VAN DER MAREL and BEUTELSPACHER, 1976; SMITH, 1979).

CHEMICAL ANALYSIS

A full chemical analysis gives the composition in terms of elements and is generally expressed as oxides on a percentage basis. There is a variety of methods whereby this information is obtained. The classical procedures involve dissolving the sample by some process such as fusion in sodium carbonate or sodium hydroxide or heating with hydrofluoric and sulphuric acids. The quantities of the elements present are determined by precipitation of various compounds which are estimated gravimetrically. Procedures for chemical analysis have been described in standard texts (GROVES, 1951; SHAPIRO and

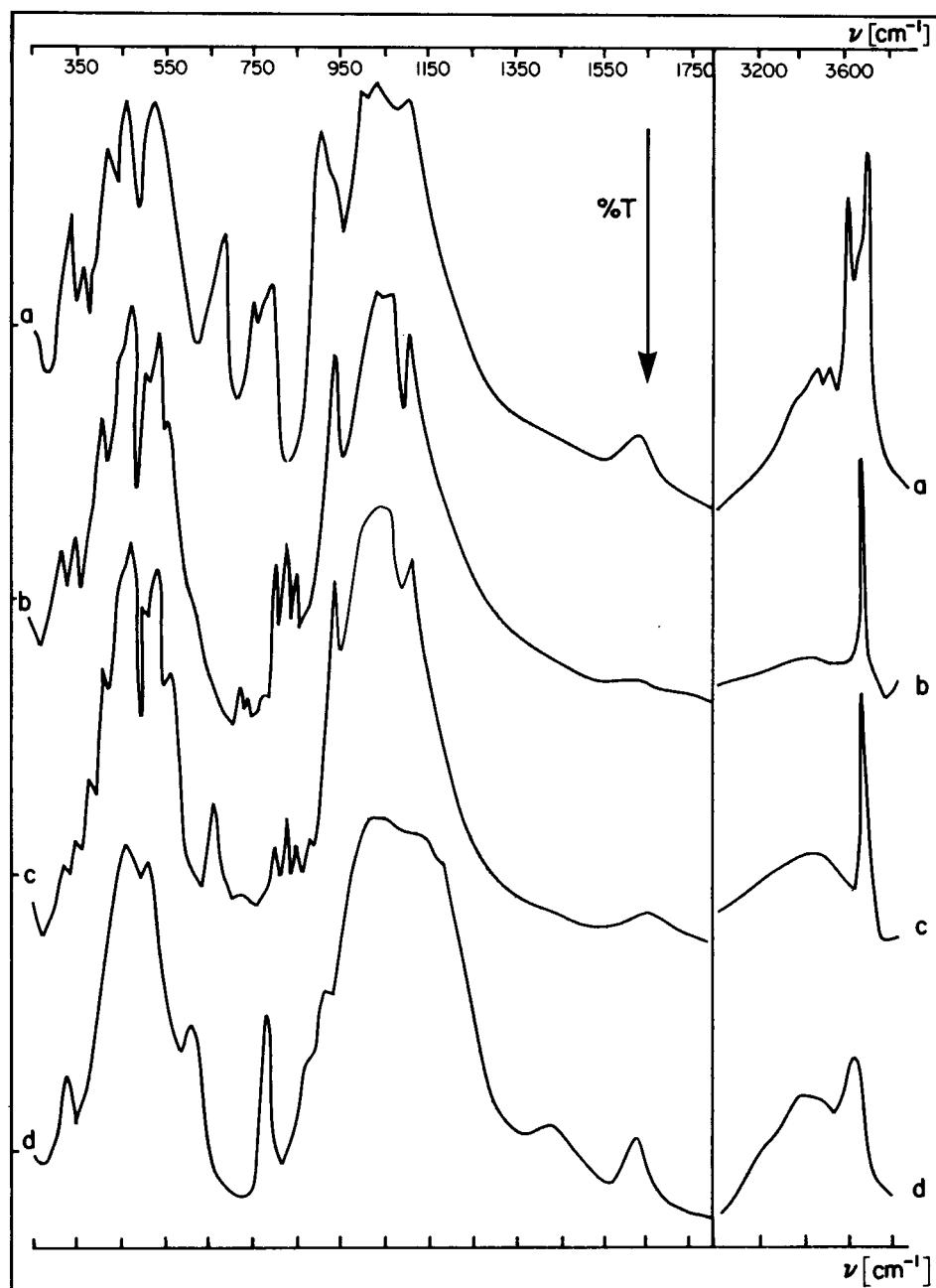


Fig. 10.10A. Infrared Spectra (KBr pellets) of typical phyllosilicates:
 a) Ca-kaolinite b) pyrophyllite c) talc.
 d) Ca-montmorillonite. Spectral regions: 250-1800 and 3000-3800 cm^{-1}

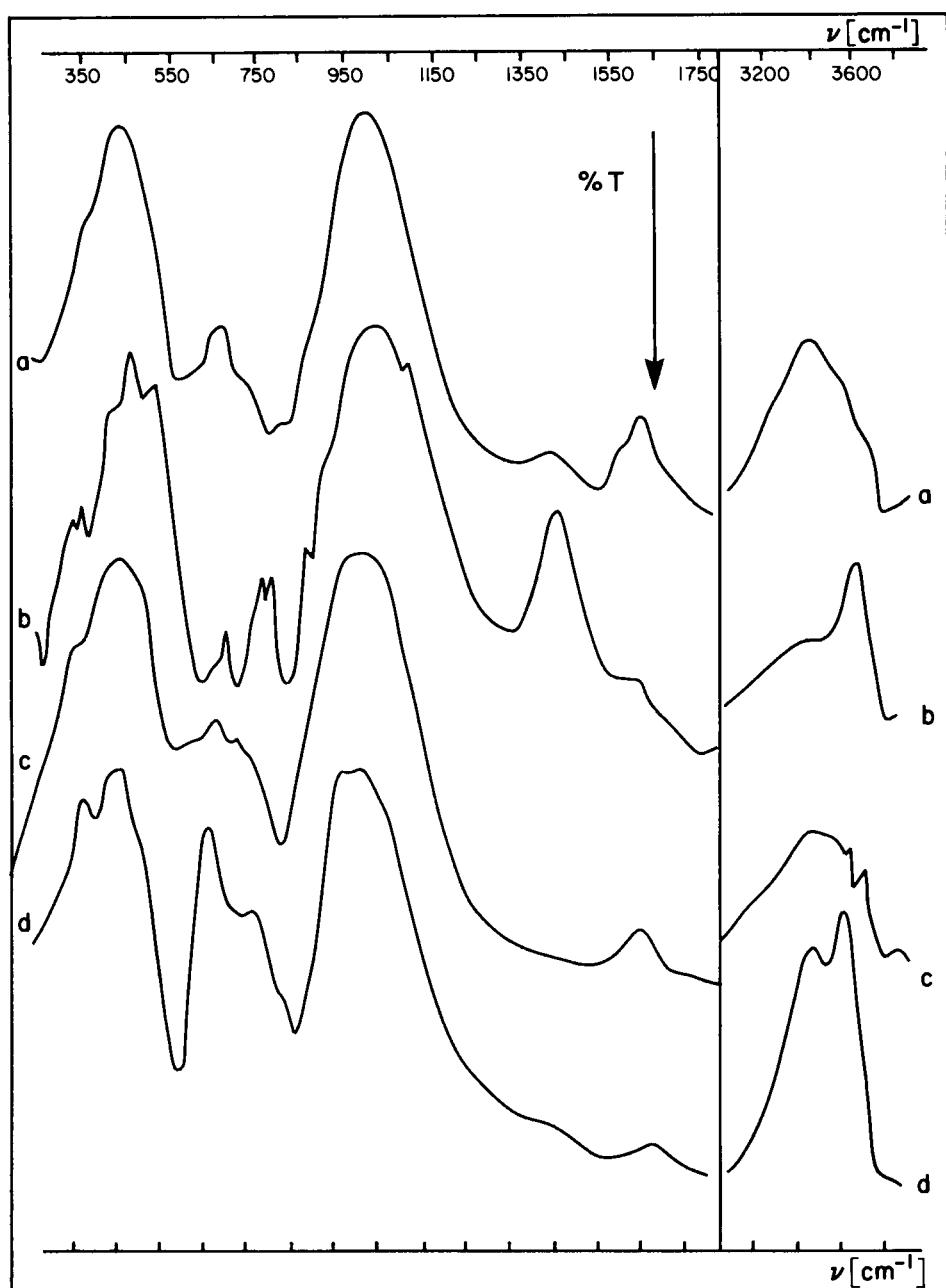


Fig. 10.10B. Infrared spectra (KBr pellets) of typical phyllosilicates:
 a) vermiculite b) Ca-illite c) biotite
 d) Ca-chlorite. Spectral regions: 250-1800 and 3000-3800 cm^{-1}

BRANNOCK, 1956; BLACK, 1965; JACKSON, 1975). There are other techniques by which the composition in terms of elements may be determined. These include spectrographic analysis, flame photometry, chromatographic analysis, X-ray fluorescence analysis (LIEBHAFSKY et al., 1960; TUNCER et al., 1977), and other methods (DEMORTIER and HOFFELT-FONTAINE, 1976).

The elemental composition is of great importance in connection with the behaviour of clays at high temperatures. For example the alumina/silica ratio together with the total alkali content often gives an indication of refractoriness. Similarly the chemical composition may give an indication of the bloating characteristics. Chemical analysis is carried out routinely in cement manufacture in the control of composition of raw material and finished product. Mineralogical composition may be computed from the chemical analysis. The results of such calculations are sometimes of value for comparative purposes (NICHOLS, 1962) and when only restricted groups and amounts of clay minerals are present results may compare favourably with those obtained by other methods (PEARSON, 1978). In general the determination of the proportions of clay minerals in a soil from chemical analyses is unreliable owing to the variable composition of clay minerals.

When a full chemical analysis is not required it may be useful to estimate the free oxides or iron and aluminium. The term "free" is often used in a general sense to describe simple compounds such as oxides or hydroxides which are not chemically combined in the silicate structure of a clay mineral and which may or may not be amorphous to X-rays. Other useful chemical information to do with clays is pH, loss on ignition, hygroscopic moisture, CO₂ due to carbonate, organic matter, inorganic carbon, exchange capacity, nature of exchange ions and percent saturation with alkali ions.

There are a large number of methods for determination of cation-exchange capacity which is the sum total of the exchangeable cations in a soil sample. Techniques which are widely used depend upon saturation of the exchange complex with a single ion such as NH₄⁺, Na⁺, Ba²⁺, Ca²⁺ or K⁺. The amount of cations adsorbed may be found from the difference in composition of the initial and final solutions or by other methods. Neutral ammonium acetate, alkaline sodium acetate and alkaline barium chloride plus triethanolamine have been commonly used reagents (CHAPMAN, 1965). Many others have been used or recommended for certain purposes including buffered nickel (II) ammine complexes and a silver-thiourea complex (BARRETT and WICKHAM, 1978; CHHABRA et al., 1975). Cation exchange capacity has also been determined by techniques based on electrodialysis, X-ray fluorescence, differential thermal analysis, atomic absorption spectrophotometry, flame photometry, and nephelometry (ADAMS and EVANS, 1979)- a method based on measurement of the light scattered by a turbid solution.

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Chapter 11

PHYSICAL ANALYSIS OF CLAYS

Physical analysis involves measurement of both vector and scalar parameters. Fabric elements were subdivided on this basis by SANDER (1939, p.297). Vectorial data indicate directional properties. When there is a parallel orientation between linear or planar elements they are said to possess a preferred orientation. This may result from deposition, growth or deformation. Orientation is defined by the angular relationship of the linear or planar elements to a set of chosen orthogonal axes termed fabric axes. Scalar data include such features as grain shape, size, size distribution, porosity, and surface area. Because many of the properties of clays depend upon the colloidal dimensions of the particles and upon their arrangement, physical analysis is of great importance to the understanding of clay behaviour.

ANALYSIS OF ARRANGEMENT AND ORIENTATION IN CLAYS

If the clay minerals assume a preferred orientation their markedly anisotropic nature causes the mechanical and bulk physical properties of the clay to vary with direction. A preferred orientation may be detected by measurement of the physical properties in different directions in a sample of clay (KAARSBERG, 1959; PENNER, 1963; WINKELMOLEN, 1972). The techniques which are likely to give the most complete information include observation with the petrographic microscope using polarized light, observation by means of the electron microscope, or X-ray diffraction analysis. By use of the optical microscope the general orientation of the clay minerals can often be observed together with their distribution and arrangement relative to other constituents. The distribution, shape and arrangement of pores may also be investigated. The higher resolution of the electron microscope makes it possible to study in more detail the arrangement of the sub- μm -sized constituents in small areas. A statistically satisfactory analysis of clay-mineral orientation in soils may be achieved by X-ray diffraction techniques.

With soft materials such as clays special procedures have to be adopted in order to preserve the original fabric. In the first place an "undisturbed sample" is required on which the field orientation has to be marked. The sample should be packaged to prevent drying. On arrival in the laboratory soil samples, sealed in wax or other material, are often stored in a fog room. Sampling inevitably causes some disturbance but specimens from the centres of core segments or block samples may be expected to be of the best quality. A

good procedure is to examine specimens oriented normal and parallel to sedimentary bedding though other orientations may give additional information.

The most commonly used techniques of analysis require moisture replacement or removal and sectioning or surface exposure. Moisture replacement followed by sectioning is the common procedure in preparation of samples for observation on the optical microscope. Moisture removal and exposure of a surface by fracture are the common procedures in preparation of samples for examination on the electron microscope. Cutting and grinding are sometimes used in sample preparation and again it is important to consider ways of safeguarding the original fabric from damage.

Samples for microscopic study have been prepared from dried clays and from dried clays impregnated with compounds such as epoxy (MARTIN et al., 1979). The unknown effects of drying on particle arrangement cast doubt on the suitability of the procedures for the investigation of the natural fabric of many clays. Other techniques have been developed (MITCHELL, 1956; TOURTELLOT, 1961) in which drying is unnecessary. In one method the clay is impregnated with a water-soluble high molecular weight polyethylene glycol compound (Carbowax 6000, produced by the Union Carbide Corporation and available from Fisher Scientific). The wax melts at 55°C and the clay is immersed in the melted wax held at about 60°C. Time is allowed for the natural water in the clay to form a uniform mixture with the wax by slow diffusion. The time required depends upon such factors as the size of the specimen, its water content and the bulk density. MITCHELL (1956, p.696) allowed 3 days and MARTIN (1965) found 21 days to be adequate for a 1½ inch diameter sample. When cool the wax-impregnated clay has a hardness similar to that of talc. There are disadvantages to the use of polyethylene glycols. GREENE-KELLY (1971) reported up to 20 per cent shrinkage during impregnation and Carbowax, like many polymer compounds of this type, tends to crystallize in the form of spherulites. This structure can sometimes be seen in thin sections of Carbowax-impregnated samples which implies that damage to the clay fabric is a strong possibility. This particular drawback can be largely overcome if the Carbowax-impregnated clay is cooled rapidly by immersion in Freon supercooled in liquid nitrogen (GILLOTT, 1973). Other compounds and techniques have been used for preservation of fabric in unconsolidated sediments. For example CONWAY (1982) has described the use of a polyester resin-acetone mix after water replacement with acetone and other methods have been described (GREENE-KELLY, 1973; GILLOTT, 1973).

A flat surface is required for X-ray analysis or for bonding to a glass slide if the specimen is to be studied microscopically in thin-section. The flat surface is produced by grinding the specimen, held either by hand or in a jig on a plate glass surface, with No. 600 carborundum powder using kerosene

or toluene as a vehicle. When a microscopic thin-section is to be made the flat surface of the sample is bonded to a glass slide by an adhesive such as "cooked" Canada balsam which has been redissolved in toluene or xylene. This has the disadvantage that several months may be required for the balsam to harden and a clear epoxy resin which cold sets in about 12 hours or less when mixed with a suitable hardener may be employed instead. The remainder of the slide preparation procedure is similar to that employed for making microscopic thin-sections of rocks except that the organic vehicle instead of water is employed in the grinding process.

The petrographic microscope

If two points are sufficiently close together there may appear to be only one point. The ability of a microscope to separate clearly two such points for observation is defined as the resolving power of the microscope. Resolution is given by the following equation:

$$d = \frac{0.61\lambda}{n \sin \alpha} = \frac{0.61 \lambda}{N.A.}$$

d = linear separation of two points, λ = wavelength of the radiation, n = refractive index of the medium between light source and objective lens, α = half aperture angle of cone of light rays received by the objective, N.A. = numerical aperture. Resolution in the light microscope is chiefly limited by diffraction, spherical aberration and chromatic aberration, though coma and astigmatism are also important. The theoretical limit upon resolution is about two-tenths of a micrometre when an oil immersion objective is employed.

The standard microscopic thin section prepared for petrographic study is about 30 μm thick. It thus contains a great many layers of overlapping crystals when the material is composed of particles in the μm or sub- μm -size range. In microscopic viewing there is a thin layer within the object in which all points appear to be sharply in focus. This layer is termed the depth of focus. Depth of focus is approximately inversely proportional to the numerical aperture of the objective and is not much greater than the resolution at high magnifications. Outside the boundaries of this layer, light is scattered diffusely and this makes it difficult or impossible to observe particles close to the limit of resolution if the section is too thick (a section should not be thicker than about 10x the resolving power). In practice it is difficult to obtain sections of clays which are sufficiently thin though there are techniques for making ultra thin sections of materials.

Even though clay minerals are commonly too small for individual study under the optical microscope their orientation and distribution may be investigated due to the aggregate effect on polarized light. Should there be a difference

in orientation between different clay mineral varieties, however, this cannot in general be detected by optical means since only the average composite effect can be observed. When a randomly oriented anisotropic crystal is rotated between crossed polarizers the transmitted light is extinguished four times at 90° intervals during a complete rotation of 360°. This occurs when the vibration directions in the mineral coincide with the vibration directions of the polarizing material in the microscope. When fine-grained crystals such as the clay minerals have a parallel arrangement the composite interaction with polarized light resembles that of a large single crystal.

A microscopic thin-section cut normal to the plane of preferred orientation of the clay minerals extinguishes the light four times in a 360° rotation when the vibration directions of the clay minerals coincide with the vibration planes of the polarizing material in the microscope. When there is more than one direction of preferred orientation extinction bands appear to sweep across the plane of the thin-section as the stage is rotated. If the plane of the section coincides with the basal surface of the platy clay minerals, however, the section will show dark or low grey colours under crossed polarizers for all positions of rotation of the stage. When the clay minerals have a random arrangement sections oriented at different angles with respect to the sample will appear similar and there will be no position of uniform darkening or extinction on rotation of the slide between crossed polarizers.

A photoelectric cell has been used by MORGENSTERN and TCHALENKO (1967) to obtain a quantitative measure of the intensity of the light transmitted through a sample on the petrographic microscope. They interpreted the degree of particle orientation by comparing the observations with predicted birefringent behaviour of an aggregate deduced from a model distribution function of the particle orientation.

The electron microscope

The electron microscope has proved to be a very useful tool for studying clays because it makes it possible to resolve the individual particles. It has been used in studies of fabric, particle size-shape relations, morphology, interstratified layer relationships, growth mechanics and clay mineral identification (GILLOTT, 1969; BOHOR and HUGHES, 1971; OLIVIER and SENNETT, 1973; YOSHIDA, 1973; BASSIN, 1975; OSIPOV and SOKOLOV, 1978; TOMPKINS, 1981; KELLER, 1982). These studies in turn have increased knowledge of the physical and chemical environments of clay deposition, diagenesis and deformation behaviour. The addition of analytical attachments such as the energy dispersive x-ray analyzer, auxiliary stages and image analyzing computers capable of giving information on porosity, pore size distribution, etc. have further increased the potential of electron microscopy.

In the electron microscope an electron beam performs a similar function to that of visible light in the ordinary microscope. Visible light has a wavelength of 4,000-7,600 Å whereas the electron beam employed in the electron microscope has a very short wavelength of the order of 0.05Å. Consideration of the equation giving resolution shows that this leads to a great increase in potential resolving power. Resolution of spacings in the Angstrom-range have been reported and a useful magnification of 100,000 times or more is readily achieved by modern electron microscopes. Magnetic and electrostatic lenses in the electron microscope perform a similar function to glass lenses in the light microscope (Fig. 11.1). With many instruments it is possible to obtain an electron diffraction pattern from an area previously imaged on the viewing screen. A camera is incorporated so that the image or diffraction pattern may be photographed.

The electron beam is generally transmitted through the sample. In the scanning electron microscope (Fig. 11.2) a reflection geometry is employed. The electron beam is focussed to a fine point of the order of 100 Å and is scanned over the surface of the sample stimulating emission of secondary electrons which are collected and amplified. The output is fed to a cathode

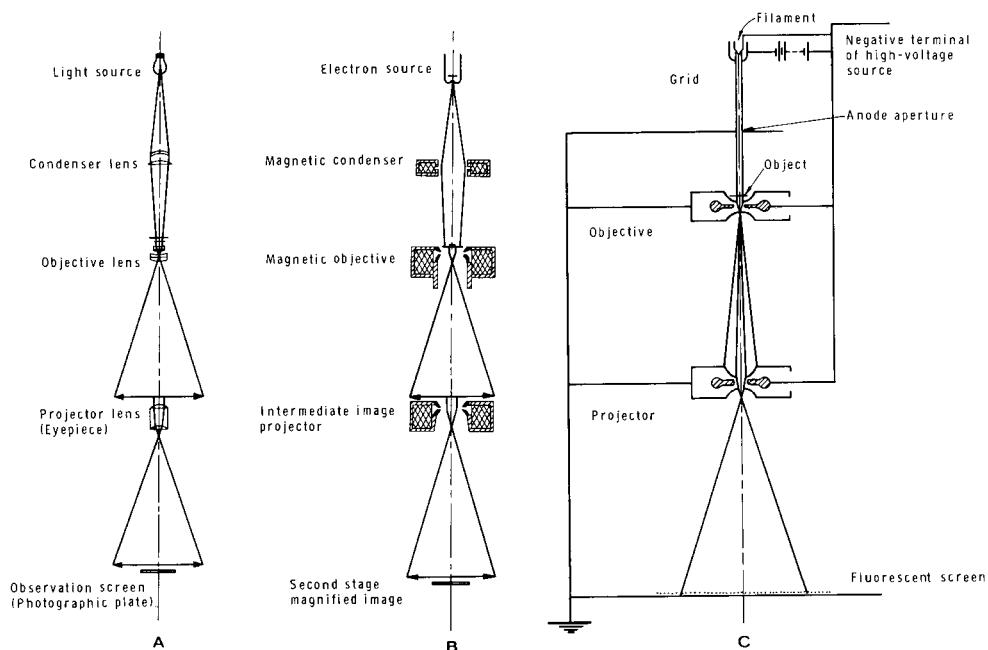


Fig. 11.1 Comparison of arrangement and ray paths in light and electron microscope. A. Light microscope. B. Magnetic electron microscope. C. Electrostatic electron microscope. (After ZWORYKIN et al., 1945, pp. 86,89.)

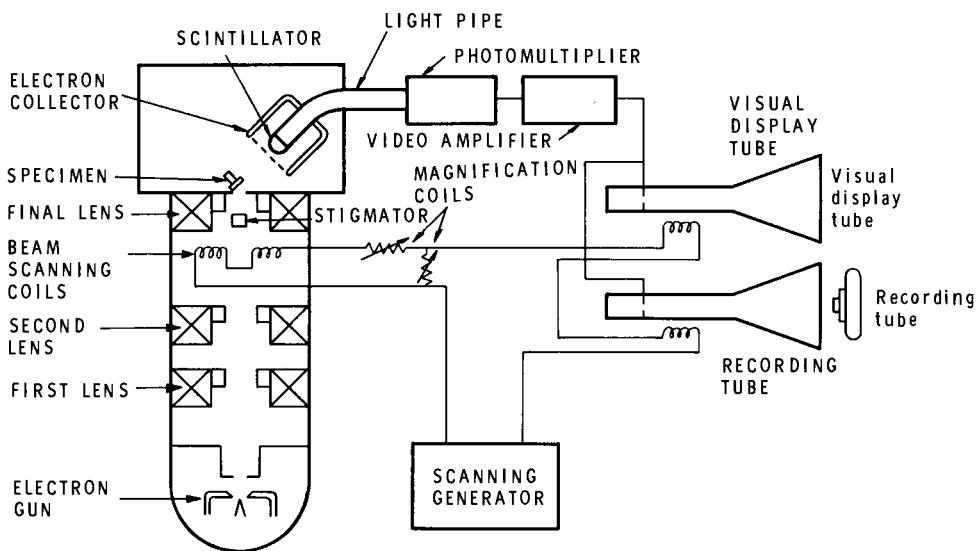


Fig. 11.2 Schematic diagram of scanning electron microscope. (After OATLEY et al., 1965, p.187).

ray tube the spot of which is deflected in synchronism with the scan of the initial electron beam on the specimen surface. In practice, at least two cathode ray tubes are employed: one for direct viewing and one for photographing the image. The visual display tube has a long persistence screen, whereas the cathode ray tube used for photographic recording has a high resolution screen with a short afterglow. The image formed has a magnification which depends upon the ratio of the lengths of the final and initial scanning movements. The resolution has been improved to less than 100 Å (OATLEY et al., 1965, p.194) but it is not as good as that of transmission electron microscopes. It is adequate for many purposes however, and the large depth of focus of the electron optical system makes possible examination of rough or even curved surfaces. Hence the greater perspective and almost stereoscopic image often yields more information than can be obtained with the optical microscope even at magnifications at which detail can be resolved by optical means.

A thin layer of metal such as evaporated gold has to be deposited on the surface of a non-conducting material such as clay to prevent an electric charge building up on the surface which otherwise causes a serious loss of resolution. It is sometimes necessary to remove the metallic coating from the specimen so that it may be observed or analyzed by other techniques or so that it may be subjected to other experiments. Gold may be removed by amalgamation

with mercury if a dry process is required or by dissolution in sodium cyanide solution if the specimen can withstand treatment in a liquid (SELA and BOYDE, 1977). Because of the poisonous nature of cyanide, in particular, it is often simpler to coat the specimen with aluminium accepting the small loss in image quality; this metal is readily dissolved in solutions of NaOH, KOH or NaOCl.

Sample preparation techniques, vary with the information sought, the nature of the sample, and the experimental arrangement (KAY, 1965; GREENE et al., 1974; KING and BANHOLZER, 1978). Electron microscopes function under conditions of high vacuum into which the object under examination must be placed and so it must be degassed and the moisture removed. Clays have been dried in air at ambient temperatures, at elevated temperatures in the oven, in steps at successively lower relative humidities (TOVEY and WONG, 1973), by air drying after replacing the water by a more volatile fluid with a lower surface tension than water, by freeze drying and by critical point drying. Surface tension forces become large on drying and may cause distortion of delicate structures. It has been suspected that this may cause originally platy particles to roll up and display a tubular morphology; similarly fabric may be damaged due to alteration of the original particle arrangement. Air drying is not generally recommended and certainly the fabric of some soils when air dried appears more dense and significantly different from that of the same soil when freeze dried (Compare Fig. 4.14a with 4.14 c,d). Air drying or one of its variants may however suffice for soils in which the natural moisture content is below the shrinkage limit.

When water is removed by freeze-drying the sample is frozen and the water is evaporated by sublimation under vacuum. A small sample is rapidly cooled in liquid nitrogen to a temperature of -150° to -160°C. It is better to immerse the sample in cooled Freon or isopentane rather than directly in liquid nitrogen as this forms a layer of gas surrounding the specimen which slows down the cooling rate. A very rapid lowering of temperature is desirable as this restricts or prevents growth of ice crystals which damage fabric; comparison has shown that freeze-dried, delicate samples, such as flocculated bentonite, when supercooled in Freon appear very different from the same material when supercooled directly in liquid nitrogen (GILLOTT, 1975). The rate of drying by vacuum sublimation is generally fast enough to keep the sample frozen owing to the transfer of the heat of sublimation of ice. In some cases melting may occur owing to slow diffusion of water vapour through clay. To prevent this the sample may be mounted on a pre-cooled copper block or surrounded by a cooled outer jacket.

Freeze drying seems to cause little change in total porosity but there are grounds for believing that pore size distribution may be altered (MURRAY and QUIRK, 1980). When water freezes ice 1 generally forms and there is an

increase in volume of about 9%. Thermal gradients are another possible cause of differential changes in dimensions which may lead to build-up of stress and fabric damage. The freezing point of water close to surfaces is significantly depressed so water in small pores will not freeze at 0°C. Changes in solution concentration due to growth of ice crystals on outer surfaces of the specimen, in cracks or larger pores may cause moisture movements due to osmotic effects. Similarly desorption of unfrozen adsorbed water on mineral surfaces and its migration down the vapour pressure gradient towards the sites of ice crystal growth may lead to build-up of hydraulic pressure (LITVAN, 1972). Growth of larger ice crystals at the expense of smaller ones and expulsion of impurities to ice crystal grain boundaries are other probable causes of fabric damage. Cryoprotectants such as chloroform, camphene, tertiary butanol and hydrophilic polymers have been used by biologists in attempts to overcome these problems (FRANKS, 1977). Damage due to formation of ice crystals may be prevented if the pore water is converted to ice glass. This phase change involves a smaller increase of volume than that which accompanies crystallization so possible damage from this cause is also reduced.

Rapid cooling, high viscosity in the liquid state near the freezing point and depression of the freezing point by addition of appropriate solutes favour solidification in the glassy state. It has been reported that a cooling rate of $10^4^\circ\text{C sec}^{-1}$ is required to form ice glass if no cryoprotective agents are present. Even when Freon supercooled in liquid nitrogen is used as the freezing agent such a rapid drop in temperature is unlikely over more than a very limited volume due to poor conductivity in the sample. At best ice glass may be expected to form throughout only very small samples or in the surface layers of larger samples. High viscosity to favour ice glass formation has been used experimentally by biologists to protect the fine structure of living cells from cryoinjury. They introduced such compounds as glycerol, dimethyl sulphoxide, ammonium acetate, polyvinyl pyrrolidone and sucrose to increase the viscosity of tissue fluids. So far this procedure seems not to have been used in work with clays. Devitrification of ice glass is reported to occur at about -130°C (MERYMAN and KAFIG, 1955) i.e. close to the recrystallization temperature which in many materials is found at about half the melting point in °K. Rate of sublimation is however extremely slow below this temperature due to the low vapour pressure of ice so in practice higher temperatures have to be used.

Replacement of pore water by an organic compound such as amyl acetate has been suggested as a way to overcome some of these problems (BOYDE and WOOD, 1969). Many organic compounds solidify in the vitreous state more readily than water and have a relatively higher vapour pressure just below their freezing points. Hence solidification in the glassy state and sublimation

without devitrification should be much more readily achieved. Another technique commonly used by biologists is to freeze-etch the sample. A surface layer of ice held at a very low temperature is sublimated by passing an even colder metal close above the sample. The temperature gradient leads to rapid sublimation of the ice. Thus the part of the sample examined by the electron microscopist, namely the surface, is dried under very favourable conditions.

An alternative method for removal of water makes use of the critical point at which temperature and pressure the specific volumes of a liquid and its vapour are the same and there is no difference between the two states. As the phase boundary disappears no fabric damage due to surface tension forces should result when the liquid changes into vapour and is allowed to escape. The water may be removed directly though dehydroxylation or other mineralogical changes may take place because the critical point of water is at a rather high temperature and pressure (374°C , 22.5 MPa) and supercritical water has a high activity. To avoid this problem water may be replaced by a miscible liquid with a lower critical point. Liquid CO_2 has been used in biology (ANDERSON, 1950, p. 570) because the critical point occurs at a low temperature (31°C , 7.6 MPa) and for similar reasons it has been adopted for work with clays (GILLOTT, 1969; GREENE-KELLEY, 1973). A drawback is that water is immiscible with liquid CO_2 so the pore fluid has first to be replaced by another liquid which is miscible with liquid CO_2 . Amyl acetate, dioxane and methanol have all been used. The sample is generally immersed in a series of increasingly concentrated solutions of the organic liquid or, for samples which disintegrate readily, the initial stage of water replacement may be accomplished by vapour exchange. Problems due to initial disintegration are sometimes lessened when the sample is immersed directly into alcohol. The liquid CO_2 is introduced to the sample in a pressure vessel which allows for a continuous flow until exchange is complete. The CO_2 is allowed to escape to atmosphere after the temperature and pressure have been raised above the critical point. Critical point drying also has inherent limitations and fabric damage may result because of such causes as build-up of pressure due to low sample permeability. Despite such possible drawbacks various authors have expressed greater confidence in this method than others (LAWRENCE, 1977; MURRAY and QUIRK, 1980).

In the electron microscope bombardment with the electron beam raises the temperature of the sample so thermal decomposition is a possibility. Most minerals are not seriously affected under normal conditions of operation. The penetrating power of the electron beam is very low at an applied voltage of 50-100 kV so the thickness of samples to be examined by transmission is limited to about 1,000-2,000 Å depending on the atomic number of the atoms in the sample (COSSLETT, 1951, p. 47). The penetrating power of the electron

beam becomes greater as the potential is increased and high voltage microscopes are used at voltages in excess of one million V. Thicker samples of the order of 1 to 2 μm may be examined and possibly samples enclosed within a small sealed cell so that drying may be unnecessary.

A mechanical grinding and polishing technique by which glass-ceramics have been reduced to the required thinness for examination in a commercial transmission electron microscope has been developed by DOHERTY and LEOMBRUNO (1964). If modified somewhat the technique should be applicable to clays. Sectioning of bulk specimens by ultra-microtomy has been carried out with much success in biology. Diamond knives are available so that hard materials may also be sliced by this technique. Soil samples generally need embedding before ultrathin sections can be prepared. Unless the impregnating agent is water-miscible the sample has to be dried and so the previously discussed factors relating to moisture removal have to be considered. Gelatin, Durcupan Fluka, Vestopal and very low viscosity epoxy resins introduced under vacuum have been employed.

It is often difficult to prepare samples of the actual material which are sufficiently thin to be viewed by transmission. Replica techniques are often employed. A replica is a thin film which is transparent to electrons and which reproduces the surface details of the sample. In the single-stage replica technique the surface of the sample is coated with the replicating material which, when removed, gives a negative impression of the surface. In the two-stage technique a first impression or negative replica of the surface is used as the base for a second or positive replica. The two materials employed have to be each insoluble in the others' solvent. In general the sample has to be dried before replication and once again the nature of the sample and drying procedure have to be considered. Replica methods are extremely useful in textural studies.

Shadowing techniques have greatly facilitated the interpretation of the textural detail of surfaces. This results from the enhanced contrast seen in the image in the electron microscope. Shadowing also sometimes makes it possible to obtain depth or height measurements of surface features from measurements of shadow length and shadowing angle. In principle the technique involves coating the specimen with a very thin film of metal which is deposited on the surface from a source at an oblique angle. The deposition is carried out in a high vacuum before the specimen is examined in the electron microscope. As the metal atoms arrive at an acute angle topographic highs in the specimen surface intercept a greater proportion of the metal atoms and cast shadows, where metal deposition has been thin or absent, on the side away from the source of metal during deposition (Fig. 11.3). When the shadowed

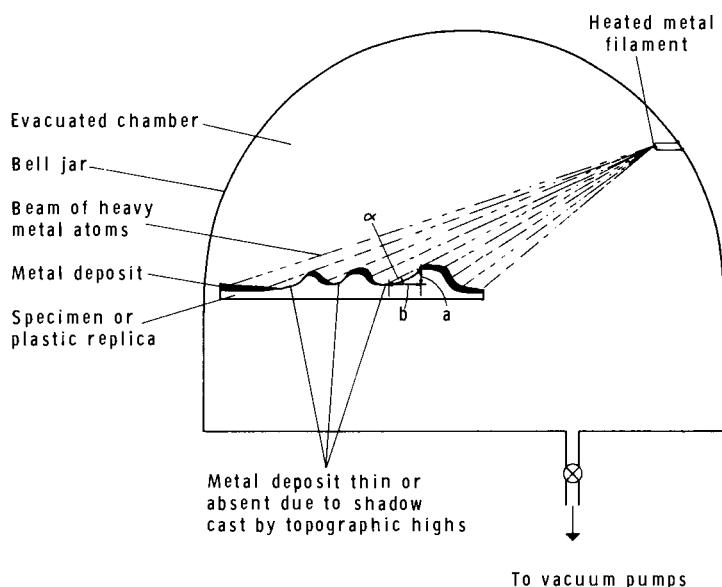


Fig. 11.3 Principle of shadow-casting technique. α =angle of deposition; a =height of surface feature= $b \tan \alpha$.

sample is viewed in the electron microscope the differential scattering of the electrons, which results from the varying thickness of the metal film, reveals elevation changes of the original surface. Metals of high atomic number such as chromium, gold and platinum are commonly employed for shadowing.

Platinum and its alloys are popular because of their low granularity and ease of evaporation (McKEE and BROWN, 1977). Modifications to standard procedures and special techniques for decreasing granularity and improving resolution have been described (GOODHEW, 1977). Among these are simultaneous deposition of a metal and non-metal such as platinum and carbon and replacement of light elements by heavy elements on the exchange sites of clay minerals.

Replicas and samples examined in the scanning electron microscope provide information about a surface. Hence it is essential that the surface examined be as representative of the fabric of the bulk material as possible. Cutting a clay is thought to drag particles from their original position and is not recommended. Grinding may be employed but is not practicable unless the water is replaced by an impregnating agent and this is in itself undesirable. Surfaces may best be exposed by fracture. This can generally be accomplished when the sample is in the undisturbed state at the natural moisture content or after drying. If the water is to be removed by freeze-drying the sample may

be frozen and then cleaved on a chilled metal block under liquid nitrogen by a sharp blow from a chilled chisel.

More elaborate freeze fracturing procedures have been used in work with biological materials and polymers (HAGGIS and PHIPPS - TODD, 1977; SLEYTR and ROBARDS, 1977 a,b). Exposed surfaces sometimes become contaminated by loose material. This may be removed from robust samples by cellophane peeling and from more delicate samples by an electrostatic cleaning technique described by HULBERT and BENNETT (1975). Differential etching and decoration have been successfully used in other fields to improve contrast and to expose detail not otherwise accessible to observation. Chemical etching, electrolytic polishing and ion bombardment (TSONG and BARBER, 1973; CARTER and COLLIGON, 1968) have been used but these techniques have not been much exploited in work with clays.

Excellent photographs of soil fabric may be obtained by use of the scanning electron microscope (see Ch. 4). This instrument has several important advantages for fabric studies compared with transmission instruments. These are:

- (1) As the principle involves reflection from the sample surface the difficulty of making a very thin section is avoided.
- (2) The surface is examined directly and the large depth of focus makes it possible to examine rough surfaces.
- (3) It produces an almost three dimensional image.
- (4) The resolution, though less than that of the transmission electron microscope, is adequate for much soil fabric work.
- (5) The magnification may be varied from about 20x to about 100,000x.
- (6) There is a long working distance with the sample positioned at one end of the electron-optical column so that access to the specimen is easy. The large specimen chamber makes it possible to insert extra apparatus or attachments.

Elemental analysis by energy dispersive methods is nowadays almost always used in conjunction with observation of shape and texture. Stages which make it possible to carry out *in situ* experiments such as heating, cooling and deformation of samples have been developed. The present trend is to employ additional analytical techniques and to adapt quantitative methods of image processing to fabric studies.

X-ray diffraction

X-ray methods for the investigation of crystallographic orientation in polycrystalline materials have been widely employed in metallurgy. The same techniques have been used, but much less extensively, for the study of clays. The diffraction geometry may involve transmission through, or reflection from

the sample and sometimes both arrangements are employed. The diffraction pattern may be recorded either on film or by means of a diffractometer. As in other X-ray methods in which X-ray intensity data are required the diffractometer often yields the quantitative information most rapidly.

Diffraction of characteristic X-radiation transmitted through a thin stationary section of a fine-grained polycrystalline material in which the crystallites are randomly oriented gives a photograph which has a similar appearance to a Debye-Scherrer pattern. When the crystallites have a preferred crystallographic orientation the Debye-Scherrer rings show a discontinuous intensity distribution around the circumference. The segments where there are intensity maxima correspond to directions to which a high proportion of crystals contributed diffracted rays due to the preferred orientation. A detailed analysis of the extent and direction of the preferred orientation of the crystals is possible.

In diffraction methods employing a reflection geometry orientation of the platy clay minerals enhances the basal reflections but decreases the intensity of reflections from lattice planes oriented in other directions such as those parallel to the prism zone. Hence the intensity of a basal 001 reflection relative to that of a prism 0k0 reflection when expressed as a ratio gives a measure of the degree of orientation. BRINDLEY and KURTOSSY (1961, p.1206) employed the ratio of reflection intensities of 001 to 060 and of 002 to 060 and MARTIN (1965) employed the ratio of 002 to 020 for this purpose. A similar procedure was used by QUIGLEY and THOMPSON (1966) who estimated degree of particle parallelism in samples of Leda clay by measurement of the 001 peak height of illite relative to background radiation.

A more complete representation of the spatial orientation of the crystals may be made on a pole-figure diagram or orientation diagram. This is a planar projection representing a polar or meridional section through a reference sphere. Normals to crystallographic planes from a sample located at the centre intersect the surface of the sphere in points. These points are projected to the plane of the great circle on which crystallographic orientation is to be represented (Fig. 11.4). Although a stereographic projection (Wulff net) is angle true it causes aerial distortion. In a Lambert-Schmidt projection equal areas on the surface of the reference sphere remain equal on the planar projection. Regions of equivalent density distribution of points on the projection are joined up by contour lines. The use of shading makes symmetry in the orientation of the fabric elements more readily apparent (Fig. 4.12). For plotting a pole figure it is preferable to use the equal area (Lambert) net as this preserves the ratio of areas which exist on the reference sphere and facilitates comparison of contoured diagrams (TURNER and WEISS, 1963, p.50). In the Schmidt or grid method of contouring

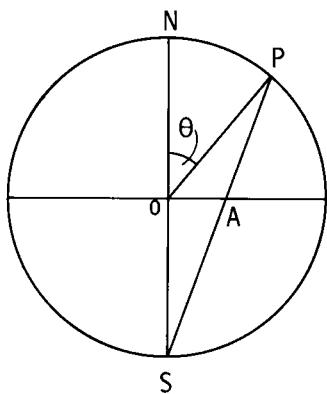
the point diagram is overlaid on a predetermined grid (TURNER and WEISS, 1963, p.61). Circles which in area are 1% of the projection are centred on grid intersections and the number of points within a circle is counted. Contour lines enclose areas in which the density of plotted points is greater than some chosen value represented by the next lowest contour line. An alternative procedure has been discussed by FLINN (1958) and computer programmes have been devised.

The intensity data for construction of a pole-figure diagram may be recorded photographically or electronically by means of counters. A series of photographs with the sample orientation changed successively is generally needed but the number may be reduced by use of a special type of moving film camera (STARKEY, 1964). When electronic counting equipment is employed the most complete information can be obtained by use of the pole-figure (texture) goniometer available commercially from several manufacturers. Alternatively a standard powder diffractometer may be used and the crystal orientation investigated by the inverse pole-figure technique (HARRIS, 1952; MUELLER et al., 1958). Diffracted intensities from the sample are compared with those from a randomly oriented sample with an equal number of grains. The random intensity value is obtained experimentally or by calculation. The relative intensities are called texture coefficients. The inverse pole figure gives a description of the crystallite orientation distribution for a single direction of the sample. The detail on the diagram is less and the orientation distribution with direction of the sample is not so complete as given by a set of standard pole figures. Results are, however, obtained more quickly. Fig. 11.4 illustrates the principles of pole figure projection and details are given in the literature (JETTER and BORIE, 1953; CULLITY, 1978; HIGGS et al., 1960; TAYLOR, 1961; INTERNATIONAL TABLES, 1968; AMERICAN SOCIETY FOR TESTING AND MATERIALS, 1982a).

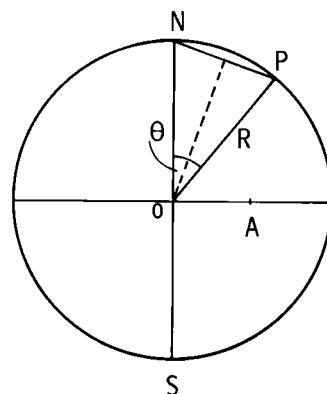
In work involving clays it is difficult to obtain a sample with random orientation for comparison with the specimen. Most clay minerals are not of constant composition and this introduces uncertainty into calculations of diffracted intensities. Diffraction peaks tend to be weak and background high in clay studies thus reducing the statistical significance of the data. Nonetheless the X-ray procedure offers the most complete method of fabric analysis available at the present time.

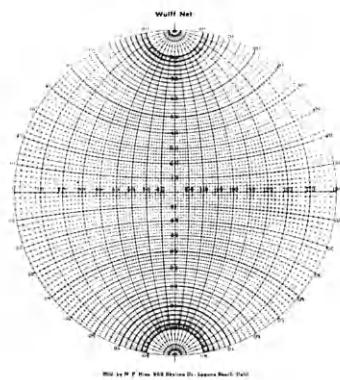
ANALYSIS OF SHAPE OF MINERALS

The shape of the clay minerals has been established mainly by use of the electron microscope. Fine particles such as clay minerals tend to form agglomerations which, except near edges, show few distinguishing features under the electron microscope. Adequate dispersion is therefore necessary both for observation of shape and measurement of size and size distribution.

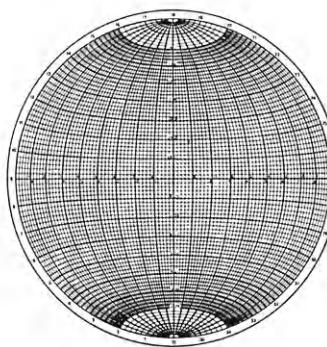


A = Stereographic projection of P

A = Lambert projection of P

$$OA = \sqrt{2} R \sin \frac{\theta}{2}$$


STEREOPROGRAPHIC PROJECTION NET



SCHMIDT - LAMBERT EQUAL AREA PROJECTION NET

Fig. 11.4 Comparison of Wulff (stereographic) with Lambert (equal area) projection net.

As described in Chapter 10 commonly used dispersing agents are dilute solutions of Na_2CO_3 , NaOH and sodium hexametaphosphate (calgon). Various organic reagents have also been used such as gelatin and a eutectic mixture of camphor and naphthalene. Ultrasonic treatment has been used to break-up agglomerations but is better avoided whenever possible because of the risk of damage to the clay crystallites.

When drops of aqueous dispersions are allowed to air dry on a coated electron microscope grid or stub the particle concentration increases and aggregation of particles occurs. The drying of suspensions also poses similar problems to those discussed in connection with sample preparation for fabric studies. Air drying, freeze drying and critical point drying have all been used and various other modifications to standard techniques have been proposed (JERNIGAN and McATEE, 1975; McATEE and LAMKIN, 1979). Direct adsorption from suspension onto a film to which the particles adhere has been suggested. Particles stick to gelatin because it is hygroscopic (PERRIE and PEACH, 1973) and to Cytochrome C or cetyl pyridium bromide because they have a charge opposite to that of the clay minerals (GREENE et al., 1973; NEUMANN, 1976). Deposition from toluene onto special filter paper (KING and BANHOLZER, 1978) and collection as a fine spray from an atomizer are alternative procedures.

Photographs of the shapes and sizes of the principal clay minerals have been published in many articles and several books (BEUTELSPACHER and van der MAREL, 1968; BORST and KELLER, 1969; SERGEYEV et al., 1978). Clay minerals are plate-like, lath-like to fibrous, tubular or irregular (Fig. 11.5). Well crystallized kaolinite and dickite often form hexagonal plates and pseudohexagonal books. When less well crystallized these minerals form elongate plates and laths; halloysite frequently has a tubular morphology. Illite forms irregular flakes or laths the amount of warping increasing with increasing interstratification; illite is often intermixed with other clay minerals. Glauconite may resemble poorly crystallized illite and also occurs as pellets. Montmorillonite commonly occurs as very small platy or lath-shaped particles of poorly defined shape and as wavy and crumpled sheets. Sepiolite develops lath-like or fibrous forms. The poorly crystalline mineral allophane generally occurs as irregular spherules consisting of aggregated and deformed rings or hollow spheres with an external diameter of 35 to 55 Å. The wall is made up of defect kaolin-like layers with pores and openings permitting passage of water (HENMI and WADA, 1976; PATTERSON, 1977). Imogolite forms fine tubular paired threads of the order of 100 to 300 Å in diameter and several micrometers in length (WADA and GREENLAND, 1970). A technique for the identification of individual clay mineral particles from a rotation selected area electron diffraction pattern has been described by NOBLE et al. (1972).

The shape and texture of particles may be analyzed quantitatively by the Fourier method used by EHRLICH and WEINBERG (1970). They defined shape as the maximum projected area of the grain in planar section. The coordinates of points on the periphery of the planar projection are determined by means of a digitizer. The number of points digitized and the magnification of the grain determines the resolution. The shape and texture are expressed in terms of a

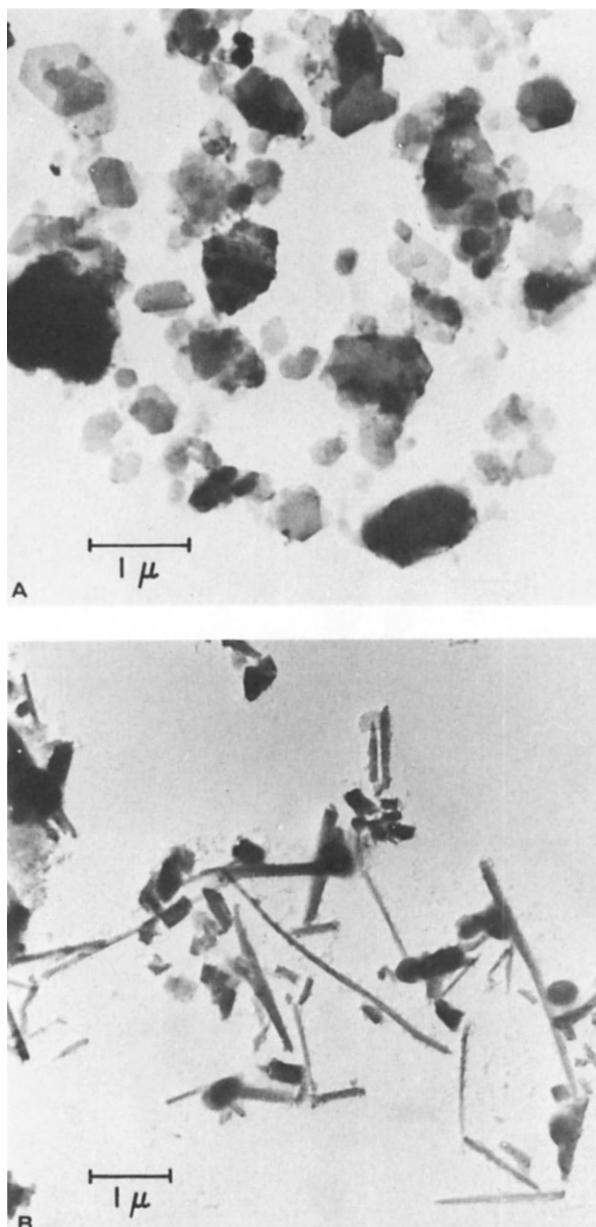
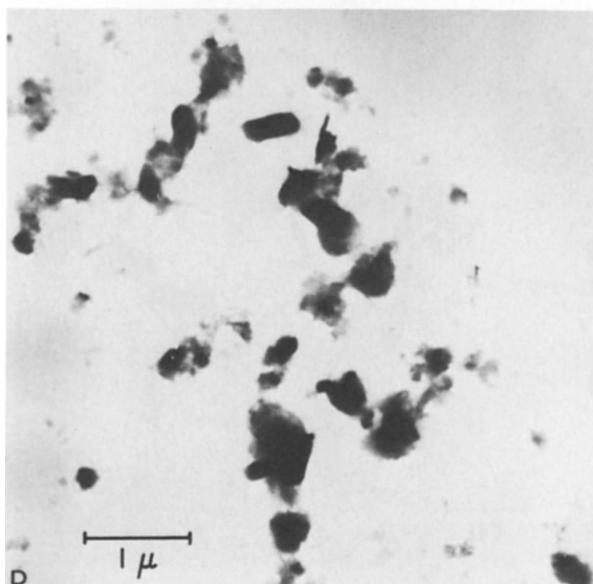
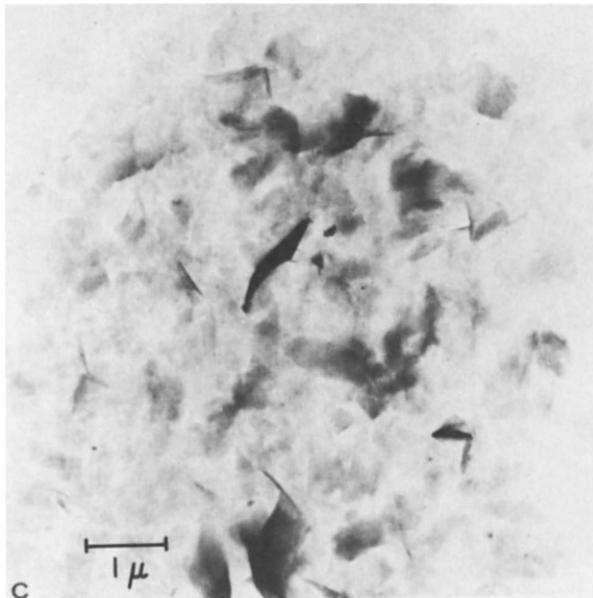


Fig. 11.5 Electron micrographs of some clay minerals.
A. Kaolinite in hexagonal plates. Georgia, U.S.A.
B. Halloysite in elongate crystals believed to be tubular. North Carolina, U.S.A.



C. Montmorillonite in thin plates of irregular shape, some apparently bent, and fragments which may be shards.
Wyoming, U.S.A.

D. Illite in irregular flakes and laths. Fithian, Illinois, U.S.A.

Fourier series by a computer programme. The data may be analyzed statistically and results compared from grain populations within or between different samples. The method has been mainly applied to sand-sized particles but presumably could be extended to particles in the clay-size range.

Information on the shape of crystallites can sometimes be obtained from a consideration of the variation in width of the X-ray diffraction-powder lines (KLUG and ALEXANDER, 1954, p.518). The profile of powder lines is, however, affected by factors other than differences in dimension of the crystals such as lattice imperfections. Owing to complexities of interpretation the X-ray method has been little used for shape determination of crystals.

Factors such as dispersion in sample-preparation procedure and high vacuum conditions during examination may sometimes affect the information obtained by means of the electron microscope but uncertainties in interpretation are less than in most other methods of shape determination of materials which are too fine-grained for resolution in the optical microscope.

PARTICLE-SIZE ANALYSIS

The particle-size distribution of the fine fraction of soils is commonly found by sedimentation methods; this is generally combined with a sieve analysis of the coarse fraction ($> 74 \mu\text{m}$, 200 mesh sieve). There are a great many methods available for particle-size analysis and these have been classified under six major headings by the Society for Analytical Chemistry (1963) (Table 11.1). Most of these methods have been employed in the grain-size analysis of soils but those involving a relative motion between the particles and fluid have been used most widely for the fine fractions. Nearly all soils are composed of particles which have a range in sizes and the size distribution may be represented graphically. A common method is to plot cumulative weight percentages as ordinate versus the logarithm of size as abscissa employing semi-logarithmic graph paper (Fig. 11.6).

In soil engineering the term grading is used to describe the particle-size distribution. A soil with a wide range of particle sizes is said to be well-graded. Boulder clay, till and landslide deposits are often of this type (Fig. 11.6E). Soils in which the particle-size range is more restricted are termed graded (Fig. 11.6 A-C). When there is a narrow range of particle sizes a soil is said to be uniform (Fig. 11.6 D). This terminology is different from that used by geologists. To them a graded sediment is one in which the grains are chiefly of the same size range; graded bedding is a special type of stratification in which there is a gradation of grain-size from coarse below to fine above (BATES and JACKSON, 1980, p.269).

Ambiguity can be avoided by describing the particle-size distribution in terms of sorting. This can be expressed in numerical terms by use of various

TABLE 11.1
TABULATED CLASSIFICATION OF METHODS OF MEASUREMENT OF SIZE DISTRIBUTION AND SURFACE¹ (AFTER SOCIETY FOR ANALYTICAL CHEMISTRY, 1963, p.156).

Measurement of size distribution

| | | |
|-------|---|--|
| (I) | Relative motion between particles and fluid | |
| | Fluid static (sedimentation) | Sedimentation pipettes Sedimentation columns Density variation Sedimentation rate Fractional decantation |
| | Fluid moving (Elutriation) | Liquid Gas |
| | Centrifugal | Hindered settling Gravimetric Absorptiometric Radiometric |
| (II) | Image formation | |
| | Light beam | Optical microscope Flying-spot principle |
| | | Individual sizing and counting Automatic sizing and counting |
| | Electron Beam-Electron microscope | |
| (III) | Scattering of radiation | |
| | Light beam | |
| | X-ray beam | |
| (IV) | Diffraction of radiation | |
| | Light beam | |
| (V) | Electrical properties | |
| | Conductivity | |
| (VI) | Sieves | |
| | Woven wire (standardised) | |
| | Recent techniques (not yet standardised) | |

Measurement of surface

| | |
|-------|----------------------------|
| (I) | Permeability to fluid flow |
| | Liquid flow |
| | Gas flow |
| (II) | Adsorption methods |
| | Gases and solutes |
| | Static |
| | Dynamic |
| (III) | Absorption of radiation |
| | Light beam |
| | Penetrating radiation |
| (IV) | Optical measurement |

¹ Reproduced by permission of the Society for Analytical Chemistry.

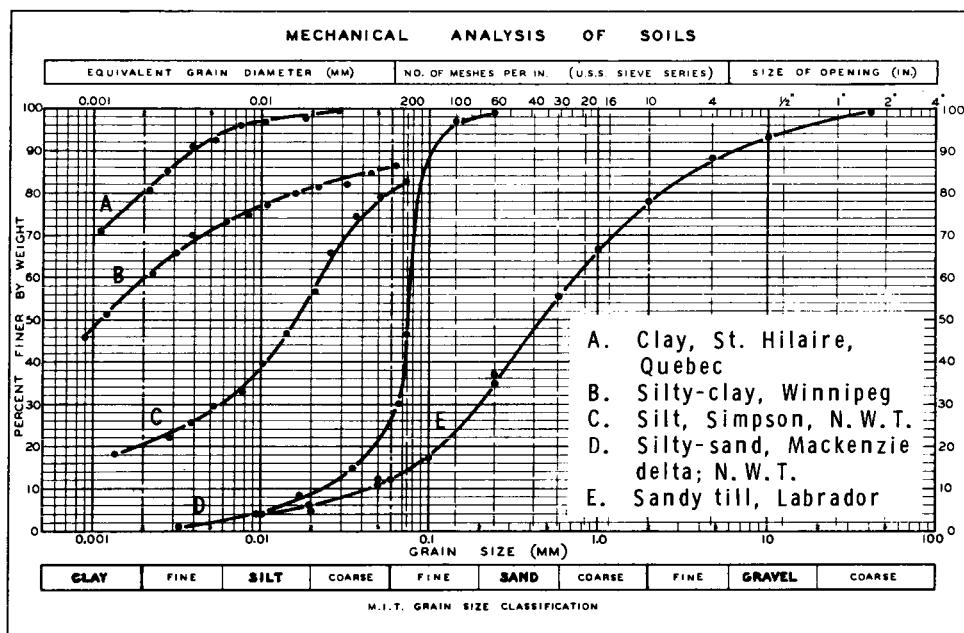


Fig. 11.6 Cumulative particle-size analysis.

coefficients such as the coefficient of sorting, S_0 , which is the square root of the ratio of the quartiles, $\sqrt{Q_3/Q_1}$, where $Q_3 > Q_1$. The quartiles are the values of particle size taken from the cumulative percentage curve at the 25% and 75% intersections. A well-sorted sediment is one in which there is a narrow particle-size distribution (Fig. 11.6D).

The methods of size analysis involving relative motion between particles and fluid are based upon Stokes' law:

$$V = \frac{2}{9} \cdot \frac{gr^2}{v} \cdot (p - p')$$

where V = velocity of fall, p = density of the particle, p' = density of the liquid medium, v = viscosity, g = force of gravity, and r = radius of spherical particle. The dimensions of the particles are commonly given as the equivalent spherical diameter. This is the diameter of a sphere with the same density and same rate of free fall as the particle. If this diameter is calculated from the velocity of fall by means of Stokes' law it is sometimes referred to as the Stokes' diameter. Stokes' law applies strictly only to spherical particles with smooth surfaces. Most clay minerals are platy or elongate and surface roughness due to solution pits or impact is likely. The effects of shape and texture on settling velocity have recently been

reconsidered and experimental results using modern techniques have been compared with calculated values derived from modified equations. Reasonable agreement was reported and it was also observed that mica settles at orientations which are neither perpendicular nor parallel to the gravitational vector (KOMAR and REIMERS, 1978; DOYLE et al., 1983). The specific gravity of the clay minerals varies from about 2.55 (halloysite) to about 2.9 (chlorite). When considered as sedimenting units the density is affected by the solution in the hydrous double layer so the value used in the calculations is only approximate. Hence the fundamental data obtained are settling velocities rather than particle diameters from analyses of the type which involve sedimentation. The hydrous double layer also affects the size and shape of the units.

Stokes' law requires that particles fall independently of one another and of the walls of the vessel. In practice errors due to interference between particles are considered to be very small if a concentration of 50 g of clay soil per litre or less is employed. The particles should be large enough that their rate of fall is not affected by Brownian movement. Hence particles in the colloidal size range, which includes most clays, do not fulfill this requirement. In order to carry out a size analysis based upon motion between particles and fluid the soil has to be dispersed. After dispersion, however, the size of the particles probably bears little resemblance to that in the original soil or sediment. In many soils and sediments the primary particles are aggregated. The degree to which the aggregations are broken up depends upon their nature and the dispersion procedure adopted. Most of the clay minerals have a marked cleavage so that dispersion may not only break up aggregations of minerals but may also fracture and cleave the actual crystallites themselves. Agglomerations of mineral particles may be disaggregated by various chemical pretreatments (see Chapter 10). Despite the limitations soil-size analysis is widely carried out and methods based on Stokes' law are the most popular.

Among the methods of particle-size analysis based on Stokes' law the pipette method and the hydrometer method are two of the most commonly used techniques (Fig. 11.7). The pipette method is regarded as a standard method of fine analysis by the BRITISH STANDARDS INSTITUTION (1975). The hydrometer method though sometimes regarded as a subsidiary method (BRITISH STANDARDS INSTITUTION, 1975) is simpler and since results for many soils are about the same as those obtained by means of the pipette method it is probably more commonly used.

In the pipette method the pretreated and dispersed sample is placed in a 500 or 1,000 ml graduated cylinder and allowed to come to temperature equilibrium either in a water-bath or air conditioned laboratory. The

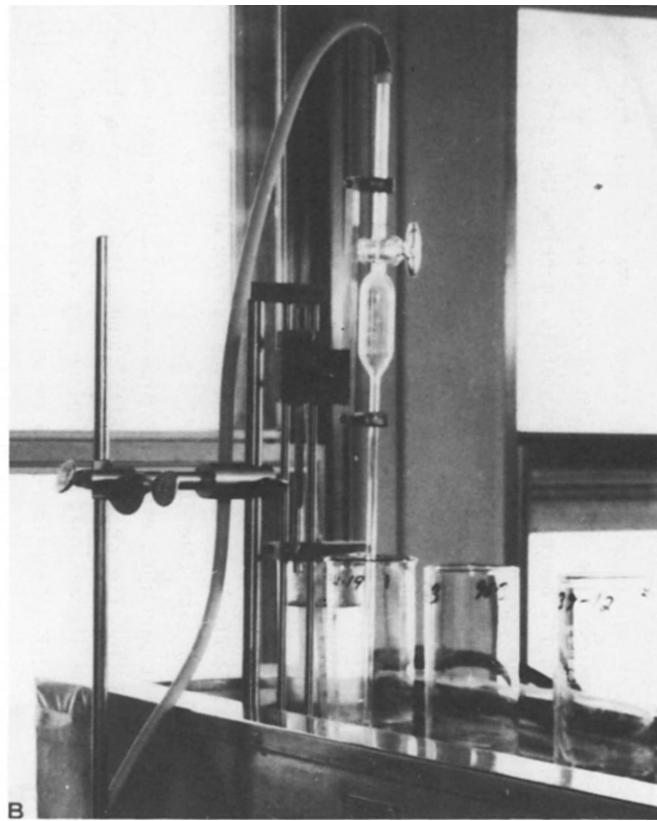
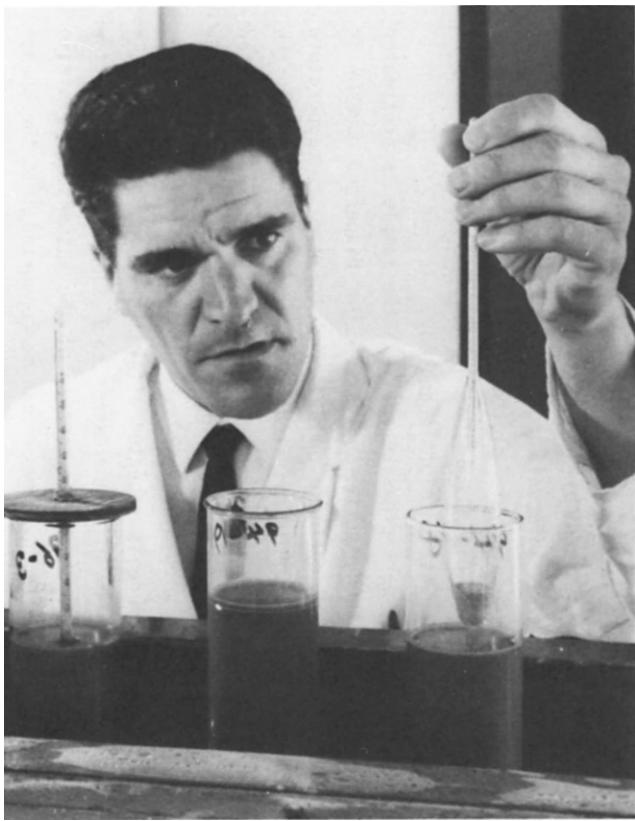


Fig. 11.7 Hydrometer (A) and pipette (B) used for particle-size analysis.

suspension is thoroughly shaken-up prior to start of the analysis usually by an end-over-end method of agitation. A stop clock is started and after the elapse of the pre-determined time interval the first sample is extracted by means of the pipette which is lowered to a depth of 10 cm below the surface of the suspension. Further samples are withdrawn after increasing time intervals. The amount of solid in each of the aliquots of suspension withdrawn is determined after the material has been dried to constant weight. In the usual procedure the volume of suspension withdrawn is 10 ml though 25 ml aliquots are sometimes taken. The successive withdrawals cause a lowering of the surface of the suspension which introduces a slight error into the determination. A constant depth of 10 cm from surface is employed, however, for each withdrawal. It is usual to employ a rack with stops and a graduated scale to ensure accurate control and lowering of the surface of the pipette to the appropriate depth after each time interval.

It has been shown that particles enter the pipette from a spherical volume of suspension centred on the tip of the pipette (KOHN, 1928). As particles from above and below the theoretical 10 cm plane are withdrawn there is a compensation for error which is considered to be small due to this cause. If a dispersing agent such as sodium hexametaphosphate has been added it should be remembered that it is present in the dried residues. The percentage weight of material in each of the fractions is obtained by calculation and the corresponding particle size deduced by use of Stokes' law. The samples extracted after increasing time intervals contain progressively finer size fractions of the soil. The results are plotted as a cumulative percentage curve. In the curves shown in Fig. 11.6 the size subdivisions follow ones suggested at the Massachusetts Institute of Technology.

In the hydrometer method of particle-size analysis the sample is pretreated in the same manner as for the pipette analysis. The dispersed sample is placed in the 500 or 1,000 ml cylinder and allowed to come to temperature equilibrium. It is then thoroughly agitated and a stop-clock started the procedure being similar to that employed for pipette analysis. The calibrated hydrometer is carefully lowered into the suspension and readings taken after periods of 1/2, 1 and 2 and 4 minute intervals. The hydrometer is then withdrawn and cleaned. The procedure is repeated after increasing time intervals though the hydrometer is usually withdrawn after each successive reading for the longer time intervals. The change in density of the suspension with time obtained by reading the calibrated hydrometer can be converted into the change in equivalent particle size by use of formulae or nomographic charts derived from Stokes' law. The principles underlying the hydrometer method of particle-size analysis have been discussed by DAY (1953), who also compared it with the pipette method of analysis and found that close agreement in results

could be obtained by the two techniques. A standard procedure for hydrometer analysis is described by the BRITISH STANDARDS INSTITUTION (1975).

A modification to the hydrometer method employed divers which are streamline glass vessels of a known density which is slightly greater than that of the sedimentation liquid. The diver is completely immersed and sinks to a depth where it is in equilibrium with the density of the dispersion. It then moves downwards as sedimentation takes place. A set of divers of different density is required in order to obtain the particle-size distribution. The technique is claimed to have certain advantages over the hydrometer method such as avoidance of surface tension and depositional effects (JARRETT and HEYWOOD, 1954; BERG, 1959).

A particle with an equivalent spherical diameter of $2 \mu\text{m}$ takes approximately 8 hours to fall through a 10 cm column of water at room temperature. For particles smaller than about $1 \mu\text{m}$ sedimentation times become unduly long under a gravitational attraction of 1 g. Therefore other methods are normally employed when the particle-size distribution within the clay-grade fraction (less than $2 \mu\text{m}$) is required. When techniques which involve a relative motion between fluid and particles are adhered to the force on the particles may be increased by use of a centrifuge. Hence the sedimentation time may be shortened at will by varying the centrifugal force by control of the speed of rotation. Sedimentation times may be calculated directly or obtained from nomographs which have been set up for certain types of commercially available centrifuges (TANNER and JACKSON, 1947). An alternative system involves varying the velocity of a suspension by passing it through openings of different sizes in the form of a jet. Some arrangement is made for collecting particles the size collected being dependent on the velocity of the jet (GILLESPIE, 1955, GILLESPIE and RIDEAL, 1955; ORR and DALLAVALLE, 1959).

Particle-size distribution in the less than $1 \mu\text{m}$ range may also be obtained by measurement of particles observed or photographed with the electron microscope. Results may sometimes be more accurate than those obtained by sedimentation methods. For example OLIVIER and SENNETT (1973) found by measurement of micrographs that kaolinite particles were significantly larger than indicated by settling. Observation showed that the coarser particles were quite porous so that the density and thus the settling rate were effectively reduced. Hence the true size of the particles was larger than that found by the sedimentation method. When micrographic methods are used the statistics involved in counting require consideration as well as other uncertainties arising from instrumentation and technique in evaluating the precision of such measurements. When photographs taken on the scanning electron microscope are used it is advisable to measure only those particles

which are within the area of the picture lying no more than about 80% from its centre because of image distortion near the edges. The stub should be oriented at 0° or if tilted a correction should be applied for distortion in the vertical direction (KING and BANHOLZER, 1978). Sizing may be carried out by image analyzing computers such as the Quantimet (PERRIE and PEACH, 1973).

Mean crystallite size may be obtained from measurement of the width of X-ray diffraction powder lines (KLUG and ALEXANDER, 1954). A limitation is that line broadening may result from imperfections in the crystals as well as from small crystallite size. The procedures for separating the two contributions to line broadening are too involved to be performed on a routine basis.

Particle size may be measured electrically by means of the Coulter Counter. The change in resistance of an electrolyte is measured across a narrow opening on passage of a stream of small particles. As the change in resistance of the electrolyte is proportional to the volume displaced by the passage of each particle the size distribution may be obtained by use of electronic counting circuitry (KUBITSCHER, 1960). In a comparative study of the Coulter counter and pipette techniques SHIDELER (1976) obtained significantly coarser grain-size distributions with the Coulter Counter than by pipette. This difference was attributed to three major factors. These were a) coincidence error in the electronic analyses, b) the assumption of a spherical particle shape in the pipette analyses and c) the truncated size distribution at the lower analytical limit produced by the electronic technique. He concluded that the electronic and pipette methods are equally precise. More care is required however to maintain a high level of accuracy using electronic means but it is a much more rapid technique, making it more laboratory efficient. SWIFT et al. (1972) compared four methods of particle size analysis and pointed out that while the Coulter Counter method may be the most versatile it yields a volume distribution which cannot be directly related to settling velocity.

Fine particle size analysis has also been carried out by several other methods. JORDAN et al (1971), TILLY (1977) and JORDAN (1977) describe the use of a hydrometer which measures the amount of light transmitted through a suspension of silt-and clay-size particles. Electrically induced birefringence was used by OAKLEY and JENNINGS (1982) to size clay particles. GENRICH and BRENNER (1974) used a combination of sieving, centrifugation and filtration. Problems sometimes associated with the particle size distribution curve where the section found by sieving meets the section found by hydrometer analysis have been discussed by TODRES and CLAUSS (1971). They suggested that when significant amounts of montmorillonite are present in a soil ethylene glycol may be a suitable medium for hydrometer analysis of particle size distribution.

SURFACE AREA

Surface area is usually expressed as specific surface, which is surface area per unit weight or volume of sample. For colloids it is commonly given in units of m^2 of surface per g of solid. Many of the properties of clays and other fine-grained solids depend on the high specific surface. The shrink-swell potential of soils for example may be closely related to the specific surface area (ROSS, 1978). There are a variety of means by which surface area may be determined but the most reliable method is gas or vapour-phase adsorption. Its chief drawback is that a complete determination is often time consuming and a high vacuum apparatus is required. These factors have restricted the use of the method in soil-engineering laboratories. There are simplifications to the basic procedure which may be incorporated when the method is used in process control. The adsorption technique commonly used involves determination of an adsorption isotherm. A great many types of apparatus have been used for this purpose and many of these are described and reviewed by JOY (1953). The procedure involves measurement of the quantity of gas adsorbed by a known amount of solid at a constant temperature. The powder is placed in a high vacuum apparatus and thoroughly de-gassed. Small measured amounts of gas or vapour are admitted by increments to the sample and the pressure is determined. As gas is adsorbed by the solid the pressure is lower than predicted by the gas laws. The determination is carried out under isothermal conditions. A gravimetric technique is in general simpler than volumetric methods. The gain in weight of the de-gassed sample may be plotted against change in relative vapour pressure (Fig. 11.8).

The data obtained by gas or vapour-phase adsorption may be interpreted in several ways. Basically, however, the procedure involves determination of the number of molecules of gas required to form a monolayer on the surface of the solid. Since the area occupied by each molecule is known from other evidence, the area of the solid may be evaluated. A commonly employed procedure is based on the theory of BRUNAUER et al. (1938), and BRUNAUER (1943). This is known as the B.E.T. (Brunauer, Emmett and Teller) method though there are also other methods.

Nitrogen at the temperature of liquid nitrogen is commonly used as the adsorbate though other gases and vapours are also employed. When N_2 is used as adsorbate on a swelling clay mineral the calculated surface area is often considerably smaller than when a polar substance such as H_2O is used. This has been interpreted as indicating that only the external surface is accessible to N_2 whereas both internal and external surfaces are covered by H_2O . On this interpretation the difference between the two sets of measurements gives the internal surface area alone and so an estimate may be made of the contribution of the two types of surface to the total. The internal surface area is

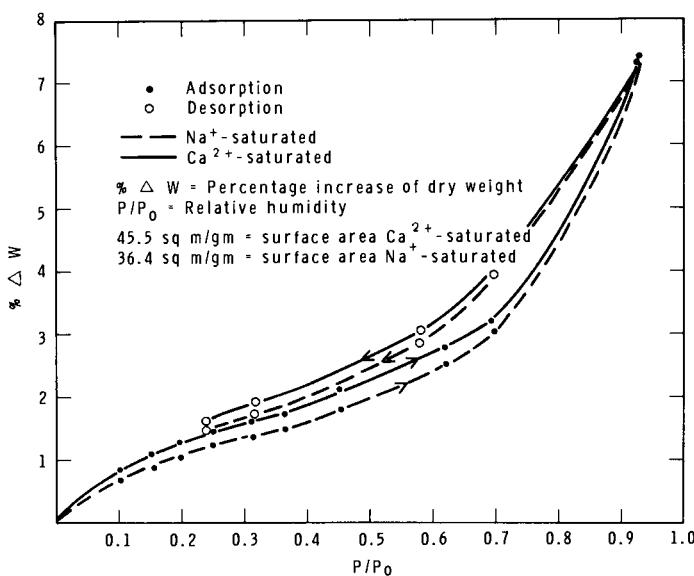


Fig. 11.8. H_2O adsorption isotherm of clay composed dominantly of illite.

commonly larger than the external surface. From the ratio of the surface areas determined by the water-vapour and nitrogen methods the number of unit layers per clay crystal in the dry state may be approximately calculated, the small edge surface area being neglected. As the N_2 and H_2O molecules are not very different in size it seems unlikely that access to different sorts of surface is the main factor which accounts for the different sets of results. Other explanations have been proposed in which the nature of the sites at which the molecule is adsorbed, the nature of the bonds and of the molecules themselves and the mechanism of the adsorption process are considered.

Surface area of clays may also be determined by measurement of ethylene glycol or glycerol retention (DIAMOND and KINTER, 1958; KINTER AND DIAMOND, 1958). In this technique an air dried sample of about 0.2 g of clay is wetted with a 2% solution of glycerol in water. The sample is heated at 100°C in an oven containing a source of free glycerol until a constant weight is attained. Under these conditions a monolayer of glycerol is formed on the clay-mineral surfaces. When a swelling clay such as montmorillonite is present measurement of the basal spacing by X-ray diffraction may be employed to confirm that a stable monolayer of glycerol has formed. The percentage weight of glycerol retained is calculated by difference from the original oven dry weight of the clay. The volume occupied by unit weight of glycerol was derived by Kinter

and Diamond from the density and a value of 4.5A^0 was adopted for the thickness of a monolayer from X-ray diffraction data. By combining these quantities they calculated a value of $1,765\text{m}^2$ for the area occupied by 1 g of glycerol in the form of a monolayer. A 1% retention of a monolayer of glycerol is equivalent to an external surface area of $17.65\text{ m}^2/\text{g}$ and an internal surface area of $35.3\text{ m}^2/\text{g}$.

If montmorillonite is present a separate determination is required to evaluate the contribution of the internal and external surfaces to the total surface area. Montmorillonite which has been pre-heated to a temperature of 600°C generally loses its capacity for the uptake of polar molecules on the internal surfaces between the unit layers. Hence glycerol is only adsorbed on external crystal surfaces by such preheated material. A measurement of the basal spacing by means of X-ray diffraction makes it possible to confirm that no inter-layer glycerol penetration takes place. The difference between the quantity of glycerol retained by the sample heated to 600°C and the sample dried at 110°C gives values from which the external and internal surface areas may be evaluated.

Various assumptions are involved in the glycerol retention method of surface-area determination. For example the density of a monolayer of glycerol may be different from that of the bulk liquid. The monolayer formed on the external surfaces is also assumed to be similar to that on the internal surfaces. However, the glycerol retention method generally gives estimates of surface area which are in reasonable agreement with those obtained by other methods.

The ethylene glycol method was modified by CARTER et al. (1965) who introduced the use of ethylene glycol monoethyl ether (EGME) for surface area determination. The technique is similar to but more rapid than the ethylene glycol method. DAVIS et al. (1971) used this technique to show that for some West Indian soils, as well as for some reference clays, the surface area of the Ca-saturated species was greater than the surface area of the Mg-saturated species, supporting earlier work by others.

Another technique for measurement of surface areas involves the use of methylene blue. HANG and BRINDLEY (1970) claim that the method has advantages over the BET procedure since it is applicable to a wide range of areas and may be used when minerals are under aqueous conditions. In addition they point out that the method is rapid, simple and economical and may also be used to determine exchange capacities. The clay, in the form of a very dilute suspension (.5 mg/200 ml water), is treated with a known concentration of methylene blue and the mixture is stirred occasionally and left overnight to ensure absorption equilibrium. After the clay has been centrifuged the

concentration of the supernatant liquid, containing the remaining methylene blue, is measured using a spectrophotometer. From the amount of methylene blue retained in solution, the quantity adsorbed by the clay and thus the surface area is determined. LOCAT et al. (1984) have modified the technique by use of chromatographic paper instead of a spectrophotometer.

The surface area may be derived by techniques which do not depend upon adsorption such as permeametry, computation from particle-size data, and absorption of radiation (OBER and FREDERICK, 1959; ORR and DALLAVALLE, 1959). Automatic systems are available for rapid determination of surface area.

POROSITY

Porosity is generally defined as the ratio of the volume of voids to the total volume of a material including voids, expressed as a percentage. Porosity is sometimes subdivided into primary porosity and secondary porosity. Primary porosity developed at the time of deposition and depends on whether a sediment was deposited with an open or close-packed fabric. Secondary porosity developed later due to authigenic growth of minerals, solution, formation of fractures, joints, cleavages and other partings. Other significant variables are the voids ratio, which is the ratio of the volume of voids to the volume of solids, and the pore size distribution. Pore size distribution data has been presented in the form of the cumulative pore diameter distribution curve which is similar to that used to represent particle size data (DIAMOND, 1970) and the differential distribution curve (GARCIA-BENGOCHEA et al., 1979). The pore size distribution has been used in the calculation of permeability which in general has been found to be most affected by the larger pores (GARCIA-BENGOCHEA et al., 1979).

When void spaces are interconnected the term effective porosity is often used. The distribution, type and degree of interconnection between void spaces affects fluid flow and liquid retention characteristics of soils, sediments and other porous materials. Two sorts of porosity may be present: a porosity which is internal to individual particles or mineral agglomerations and a porosity between such units (Fig. 6.3). This factor is known to affect the agreement obtained between observed and calculated permeability.

A clay soil is a non-rigid system and the porosity can be drastically altered by disturbance or drying. Evaporation causes drying shrinkage with a decrease in pore size and shift in pore size distribution. Hence it is inappropriate to determine this data from the commonly used relationship between water content and suction since the technique affects the parameters being determined. If the pore water in the soil is replaced by an organic liquid of lower surface tension drying shrinkage is reduced. Pore size

distribution may be similarly obtained from the desorption isotherm of the new liquid phase. Commonly the pore water is replaced by immersing the soil in a series of solutions of successively increasing concentration with respect to the organic liquid. Pore water may be removed from soils by freeze drying or critical point drying and the porosity determined by N_2 (or other gas or vapour) sorption and by mercury porosimetry.

Voids may be observed microscopically. The optical microscope may be used for pores at least as small as $10 \mu\text{m}$ and the electron microscope for finer pores. A mechanical stage is employed routinely in the quantitative study of air-entrained concrete (AMERICAN SOCIETY FOR TESTING and MATERIALS, 1982b) and a similar technique could probably be used for carbowax-impregnated samples of clay soils. Soils impregnated with a fluorescent polyester resin have been analyzed with a Flying Spot Particle Analyzer by WILKINS et al. (1977). They used the information to calculate means and variances of soil aggregate size, soil pore size and apparent soil porosity. Microscopical techniques are the only ones which permit direct observation of shape so in this respect they have an advantage over other methods. X-ray techniques and the analysis of flow data may also be used for the estimation of pore size distribution.

Comparisons of the different techniques have been made by a number of workers (DIAMOND, 1970; SILLS et al., 1973; LAWRENCE, 1977; De KIMPE, 1984). The general conclusions are that pores greater than 10^5 nm ($100 \mu\text{m}$) are best measured by microscopic techniques; mercury intrusion porosimetry is the most convenient and rapid method for the measurement of pores between 10^5 and 10 nm (100 \AA); and the BET procedure is most satisfactory for pores in the less than 10 nm size range. Changes in pore characteristics caused by moisture removal or replacement are probably the greatest cause of uncertainty in the interpretation of results.

DETERMINATION OF DENSITY AND SPECIFIC GRAVITY

Density is defined as the mass per unit volume and is expressed in units of kg/m^3 in the SI system and in g/cm^3 or lb/ft^3 in older literature. It varies with the temperature of the material. Relative density (specific gravity) is the ratio of the mass of a given volume of a material to the mass of an equal volume of a standard material such as water at a given temperature. In most scientific work the reference temperature is 4°C . As relative density is a ratio it is a dimensionless quantity and its numerical value is the same in all systems of units. When porous solids are considered the bulk density is determined and the value derived depends upon the degree to which a fluid penetrates void spaces when the volume is determined by displacement. For example some of the voids may be sealed and inaccessible.

The bulk density of a soil may be determined from a core or bulk sample in which the natural structure has not been disturbed. Special samplers are available by which "undisturbed" soil samples may be obtained (VEIHMEYER, 1929; LUTZ, 1947). The volume of the sample may be obtained by calculation if it is of regular shape or by mercury displacement. A procedure which combines the use of a top-loading balance with the mercury immersion method is described by CLEMENCY (1972). The sample may also be coated with a film of paraffin wax and the volume determined by displacement of a liquid such as kerosene. Allowance has to be made for the paraffin wax skin. If the void ratio, the degree of saturation and the grain density are known the bulk density of a soil may be calculated.

Relative density may be obtained by use of a pycnometer. In soils work a volumetric bottle of up to 500 ml capacity is often employed. The use of the large capacity bottle has the advantage that a more representative sample of soil, which is commonly inhomogeneous, may be employed and a less sensitive balance may be used for weighing. Sometimes the relative density of soil particles is determined relative to that of kerosene while the relative density of the kerosene relative to water is determined separately.

Nuclear methods have been employed for the *in situ* determination of soil density in the field. Such methods have been reviewed by the AMERICAN SOCIETY FOR TESTING AND MATERIALS (1960). It is sometimes difficult to get good resolution in three dimensions using these methods, however, and errors can occur in gamma-ray densitometry due to sample inhomogeneity and non-linear fluctuations in density. A device, referred to as the x-ray transmission computed tomography scanner, used in diagnostic radiology of the human body has been evaluated by PETROVIC et al (1982). He concluded that the device is a potentially promising tool which can be used to determine bulk soil density with good three-dimensional resolution.

An objective of the determination of relatively simple physical properties of soils such as bulk density is the prediction of engineering behaviour using various semi-empirical methods of calculation. More sophisticated field and laboratory test procedures are more costly and time consuming - considerations which become particularly important when studies of large areas and large numbers of samples are involved. An example of this approach has been described by ARYA and PARIS (1981). They used a model to predict the relationship between soil water pressure and soil water content (the soil water characteristic) based on particle density, bulk density and particle size distribution. Parameters such as bulk density are also used in soils engineering in connection with such problems as bearing capacity and settlement, compaction and slope stability analysis.

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Chapter 12

ENGINEERING ANALYSIS OF SOILS

Engineering analysis of soils is carried out in soil-mechanics laboratories and in the field during on-site investigations. There are several texts in which the analytical equipment and techniques are described in detail (LAMBE and WHITMAN, 1969; AKROYD, 1957; HER MAJESTY'S STATIONERY OFFICE, 1952; SCHMERTMANN, 1975; WILUN and STARZEWSKI, 1975). In addition recommended testing procedures are published by organizations such as the BRITISH STANDARDS INSTITUTION (1975), and the AMERICAN SOCIETY FOR TESTING AND MATERIALS (1983). Site investigations involve procedures such as bore hole logging, penetration tests, field vane tests and pressuremeter tests (GIBSON and ANDERSON, 1961; FLETCHER, 1965; EDEN and LAW, 1980).

The comparison of soils of similar type is facilitated by classification which is carried out at an early stage of a soils investigation. A good system of classification makes it possible to make more reliable predictions of behaviour at a new site from known behaviour elsewhere. Disturbed samples may be employed for the necessary tests as well as for mineralogical and chemical analyses. Strength and compressibility tests are carried out in order to assess such properties as slope stability, bearing capacity and settlement. When estimates of these properties are to be made on the basis of results obtained in laboratory tests undisturbed samples are required. These may be obtained from cohesive soils by pushing a thin walled sampling tube with sharpened edge into the soil. This is carefully extracted and sealed at the site of collection. Block samples sealed in wax may also be employed. Specific tests are used to assess such factors as the volume-change characteristics of the soil on wetting or drying, the conditions required to obtain optimum density on compaction and to determine unusual chemical properties of the soil which may lead to attack upon materials used in construction of foundations.

It is commonly found that there are difficulties in extrapolating the results of laboratory tests to observed field performance. This arises from the inhomogeneous and multiphase nature of the soil, and from the problem of obtaining representative samples which also retain the same properties as are possessed by the soil in the natural condition. It is also difficult, if not impossible, to devise tests which exactly reproduce service conditions. Mass properties are significantly affected by discontinuities such as fissures, joints, slickensides and bedding planes. Strength, stability and compressibility characteristics depend in turn on the nature of the minerals in the soil, the degree of preferred orientation of clays, the proportion of

cemented junctions, amount of overconsolidation, water content, etc. Long continued application of stress accompanied by creep may lead to strength decrease. When properly interpreted, however, engineering analyses are of great practical value and recent work indicates that the problem of correlating field performance with laboratory results is not insoluble even in difficult cases (CRAWFORD and EDEN, 1965).

Knowledge of the local geology of an area is of great help in extrapolating the information obtained by engineering tests on soil samples to their probable service performance and in estimating the detail required in sampling. Such deductions are based on knowledge of the pattern of stratification and upon the geological history of the area. This in turn is reflected in the physical and engineering properties of the sediments which are determined by laboratory and field tests.

MEASUREMENT OF SOIL MOISTURE AND MOISTURE MOVEMENT

There are two aspects to the measurement of soil moisture. One concerns determination of the total quantity of water in the soil and the other the estimation of the force with which the moisture is held. The latter may be correlated with the free energy of the air-water interface. The force of retention affects the permeability which is defined as "the relative ease of fluid flow under unequal pressure". Effective permeability is "the ability of a rock to conduct one fluid e.g. gas, in the presence of other fluids, e.g. oil or water" (BATES and JACKSON, 1980). The permeability of the matrix is sometimes termed primary permeability to distinguish it from that due to partings which is termed secondary permeability. Primary permeability is a property of a rock or soil considered as a material whereas secondary permeability is a bulk property of the rock or soil in mass.

Measurement of Moisture Content

The water content of the soil is defined as the ratio expressed as a percentage, of the weight of water to the weight of dry soil in the given mass. It may be determined by a gravimetric method. The soil sample is weighed before, and after drying to constant weight at $110^\circ \pm 5^\circ\text{C}$. This drying temperature is to an extent arbitrary as water is retained by many materials to much higher temperatures. If the result is to give the moisture content of the soil in the field care has to be taken to ensure that the sample is representative and that its moisture content does not change after collection and prior to analysis. Drying and weighing to determine water content has the disadvantage that it is time consuming and destructive since the sample is changed by the measurement. Drying can be speeded up by use of

an infrared heat source and commercial equipment is available in which a balance is built into the drying unit.

The disadvantages of drying and weighing to determine water content have led to many studies and to many devices for indirect measurement of soil water content. For example, moisture content may be determined by extraction with alcohol (BONAR, 1949) and by use of calcium carbide (CRONEY and JACOBS, 1951). Electrical resistance and capacitance and thermal conductivity measurements made directly on the soil have also been used. The neutron-moisture meter is an instrument which incorporates a radioactive source and which may be used to measure the moisture content of undisturbed soil in the field. Another indirect method, used largely in the laboratory, is gamma-ray attenuation (MEIGH and SKIPP, 1960). The tensiometric method for measurement of soil-moisture suction may be calibrated to give the soil-moisture content; as there is a hysteresis effect on wetting and drying this factor has to be considered in such a determination. There are various limitations which have to be taken into account in the use of these techniques. A review and comprehensive bibliography of methods of measuring soil-moisture content have been given by the HIGHWAY RESEARCH BOARD (1952), SHAW and ARBLE (1959), JOHNSON (1962), YONG and WARKENTIN, 1975.

Measurement of Permeability and Suction

The permeability of soil and also the pore-water pressure can be measured by field as well as by laboratory tests. Soils often show the greatest permeability in the horizontal direction owing to the influence of interbedded permeable layers. This however, is by no means invariably the case as joints and other partings are often approximately vertical. The rate at which fluid flows through a porous soil may be determined by Darcy's law. This states that flow velocity is directly proportional to the pressure or hydraulic gradient. The constant of proportionality, k , is known as the coefficient of permeability or hydraulic conductivity, which is a measure of the flow resistance of the medium and in the S.I. system is measured in ms^{-1} . The value of k varies from less than 10^{-9} for clays, to about 10^{-7} for silts and to about 10^{-2} for sands and sandstones; the value depends not only on the material but also on the nature of the permeating fluid and mechanism of permeation.

There is a variety of laboratory tests by which the primary permeability of cylindrical or conical samples may be measured and secondary permeability may be estimated by field tests and by calculations. When it is not possible to obtain suitable specimens the permeability may be estimated from the porosity, median pore diameter or specific surface area by use of the Kozeny-Carman equation. A factor to allow for variation of pore shape and a tortuosity

factor are introduced in the equation but in materials such as certain clay soils the calculated permeability may be in error. This is thought due in part to non-uniform pore sizes because of the presence of aggregations; inter-aggregate and intra-aggregate pore systems are commonly very different (Fig. 6.3). It is probable that fabric exerts more influence on permeability than any other property of soils and rocks.

When suitable samples are available the coefficient of saturated permeability may be obtained in the laboratory by measurement of the quantity of water which in unit time flows through a saturated soil sample of known dimensions under a known hydraulic head. In the constant head permeameter

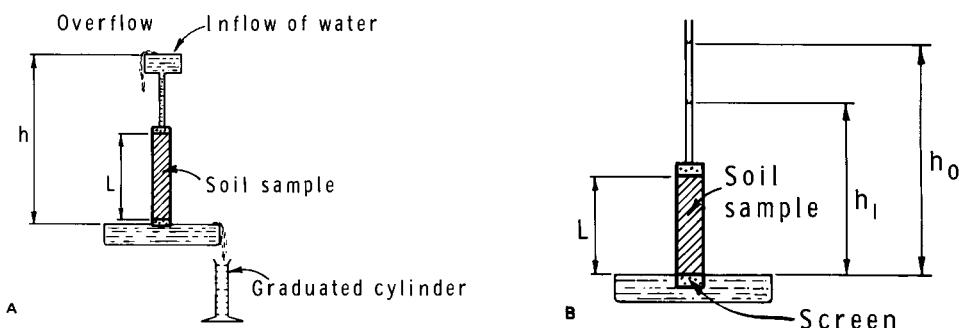


Fig. 12.1A. A. Constant head permeameter. Q =quantity of water flowing through in unit time; $k = \frac{Q}{A} \frac{L}{h}$ cm/sec.

B. Variable head permeameter. L =sample length; h_0 =initial head at time t_0 ; h_1 =head after time t_1 ; a =cross-section of standpipe; A =cross-section of sample; k =coefficient of saturated permeability; $k = \frac{2.303 a L}{A(t_1 - t_0)} \log_{10} \frac{h_0}{h_1}$ cm/sec

(Fig. 12.1A) the hydraulic head is kept constant by an inflow of water while the rate at which water flows through the sample is measured. This method is of most use for permeable soils. Variable head permeameters (Fig. 12.1B) may be used for soils of a wide range of permeability. The time is recorded for the height of water to change by a known amount in a narrow bore tube connected to the soil sample and through which the water is allowed to drain. For impervious clay soils the coefficient of permeability is better derived indirectly from data obtained during the consolidation test.

The use of consolidation theory to derive the soil permeability and coefficient of consolidation from the relationship between flow-rate and time obtained by an in situ constant head permeability test has been discussed in a number of papers (GIBSON, 1963, 1966, 1970; WILKINSON, 1968). The theory was originally developed for a soil which behaves as a porous, perfectly elastic

medium. In later work modifications were introduced to allow for the anelastic behaviour of real soils and non-linear permeability and compressibility relationships. Major sources of error result from head losses in the tip and leads, air in the piezometer pocket and soil smear adjacent to the piezometer.

In engineering, field methods are often employed since the observations are made under conditions which are most likely to be encountered in practice. In one method the data are collected during a pumping test. The water in a well or bore hole is pumped out causing a lowering of the water table; the localized depression assumes the shape of an inverted cone with asymptotic apex at the well. The permeability is calculated from the rate at which the water rises in the well when pumping is stopped. There are numerical and approximate graphical methods for carrying out the necessary computations which are reviewed in engineering texts. Both field and laboratory techniques of measurement have been described by REEVE and LUTHIN (1957).

The understanding of flow becomes more difficult in unsaturated strata and in clays where surface forces become important. In partly saturated soils moisture movements also take place by a diffusion mechanism in response to a gradient which results from differences in vapour pressure, due to differences in relative humidity, solution concentration or temperature. Relative differences in saturation between different parts of the system are probably the most common cause of movements of this sort. The quantity of fluid which migrates by this mechanism is proportional to the gradient and is given by Fick's law which is similar in form to Darcy's law. A physical picture of fluid migration through a porous system indicates that the relative contribution of vapour phase diffusion increases with decrease in relative humidity (ROSE, 1965).

The height above the phreatic surface at which water is held depends in part upon capillarity. Such water can exert a suction pressure or tension of several tens of MPa (thousands of p.s.i.) (Fig. 6.2). It is capable of migration from regions of low suction to regions of higher suction. A variety of methods is available for the measurement of soil-moisture suction. An instrument known as a tensiometer may be used. It consists of a porous pot which is filled with water and connected by a water-filled tube to a mercury manometer. When the porous pot is placed in contact with unsaturated soil, water is drawn out through the pores of the pot until equilibrium is attained. The soil-moisture suction may be read directly from the difference in level of the mercury in the manometer (Fig. 12.2).

Other methods of measurement include the direct suction method, the suction-plate method, the centrifuge method, electrical resistance and

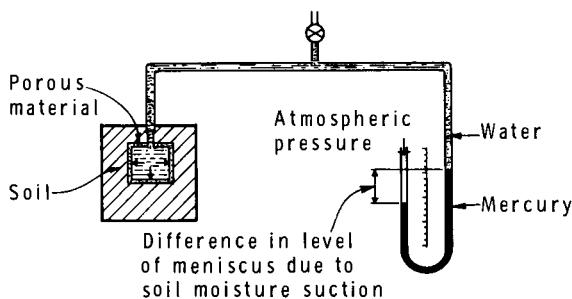


Fig. 12.2. Principles of method of measurement of soil-moisture suction by tensiometer.

capacitance methods, thermal conductivity methods and determination of relative humidity in situ. In the electrical methods the electrodes are embedded in a material of fixed porosity instead of being in direct contact with the soil as in electrical methods for measurement of moisture content. At high relative humidities changes in percentage moisture content are large for small changes in relative humidity. Hence any technique based on measurement of relative humidity requires considerable sensitivity in this range. At any value of the soil-moisture suction the actual moisture content of the soil is always greater on drying than on wetting owing to a hysteresis effect. This factor requires consideration when measurements are interpreted. Not all methods are equally applicable over the entire range of soil-moisture suction. Tensiometers and the porous plate method may be used for suction pressures from about 0.1 to 1 atm., centrifugal methods for measurement of suction up to several thousand kPa (several hundred p.s.i.) and vapour-pressure methods for suctions of several tens of MPa (several thousand p.s.i.) (Fig. 6.2). A number of the available methods have been reviewed by CRONEY et al. (1952). Good results from in situ tests with the thermocouple psychrometer are reported by WIEBE et al (1971) and WILLIAMS and PIDGEON (1983).

INDEX TESTS

The index properties of a soil are defined by the liquid limit, the plastic limit and the shrinkage limit. The plasticity index and the liquidity index are derived by calculation as is the activity.

The liquid limit is determined with the aid of the liquid limit device (Fig. 12.3). This is a brass cup with a cranking arrangement by means of which the cup can be lifted and dropped under standardized conditions. The intimately mixed soil and water sample is placed in the cup and a groove is made in the soil sample with a grooving tool and the number of bumps counted

which are required to cause the soil sample to flow together and close the groove over a distance of 12 in. (12.7 mm). The procedure is repeated after re-mixing the sample until a consistent value is obtained for the number of bumps required. The water content of the soil sample is then determined. The test is repeated several times with different amounts of water mixed with the soil to give a consistency such that the number of bumps required will be above and below 25. The results of several determinations are plotted

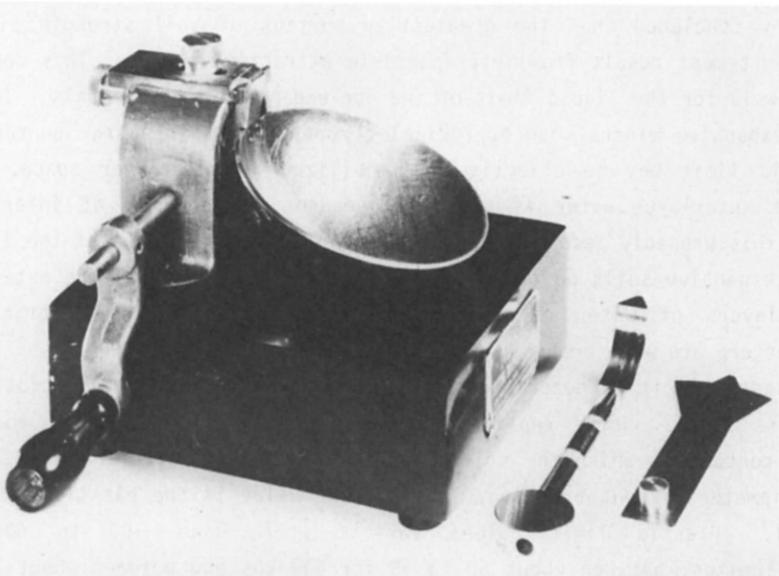


Fig. 12.3. Liquid limit device. (Photograph: Division of Building Research, National Research Council, Canada. Reproduced by permission.)

graphically with the number of bumps recorded as ordinates on a logarithmic scale versus the water content on an arithmetic scale. The corresponding points should be on an approximate straight line from which the water content corresponding to 25 bumps can be read off, assuming the appropriate range has been covered. An alternative procedure known as the one-point method by which the liquid limit may be calculated from an algebraic expression using the water content and number of bumps found in a single determination may also be used (AMERICAN SOCIETY FOR TESTING AND MATERIALS, 1983). Liquid limit values vary between about 900 to 150 for montmorillonites, between about 100 to 60 for illites and between about 90 to 30 for kaolinites. In general, minerals of high specific surface area and high exchange capacity show the largest range of values due to the increased influence of type of exchange ion and

effect of surface forces. Results obtained with different makes of liquid limit machine are not always consistent and causes for this have been reviewed by NORMAN (1958). Recommendations concerning standardisation of the design have been made by CASAGRANDE (1958).

The liquid limit is a moisture content which corresponds to a remoulded shear strength found under dynamic conditions. At the liquid limit the shear strength of soil has been reported to be between 2.0 and 2.5 kNm^{-2} (CASAGRANDE, 1932; NORMAN, 1958) and the pore water tension to be about 0.4 kNm^{-2} (CRONEY and COLEMAN, 1954). SEED et al. (1964) deduced from the corresponding effective stress and an assumed angle of friction of 30° that the shear strength due to internal friction would be only about 0.25 kNm^{-2} . Hence they concluded that the greatest proportion of soil strength at the liquid limit must result from inter-particle attractive forces. This concept accounts well for the liquid limit of the non-expansive clay minerals. In the case of expansive minerals an appreciable proportion of the water content at the liquid limit may be effectively immobilized in interlayer space. The amount of interlayer water is greatly dependent on the type of interlayer cation. This probably accounts in part for the great dependence of the liquid limit of expansive soils on cation type. Other factors such as the extent of ordered layers of water molecules associated with surfaces, fabric and microstructure are also probably involved (see Ch.7).

The plastic limit is determined by rolling out a thread of the moist soil on a glass plate. Three replicate determinations are made of the minimum moisture content at which the soil may be rolled into a thread 1/8 in. (3.2 mm) in diameter without breaking. The average value is the plastic limit of the soil. Plastic limit values vary between about 100 to 60 for montmorillonites, between about 50 to 35 for illites and between about 35 to 25 for kaolinites. At water contents below the plastic limit soils lose their plastic properties and this has been taken to indicate that the remaining water has physical properties which depart from those of water in bulk to an ever increasing extent (TERZAGHI, 1926). Others regard the plastic limit as the water content at which there is sufficient lubrication to allow interparticle sliding under load but which is insufficient to prevent maintenance of shape by interparticle cohesion (YONG and WARKENTIN, 1975). If the clay minerals comprise more than about 1/3 of the total soil the volume of the clay-water fraction is great enough to fill the voids between the particles of primary minerals. SEED et al. (1964) concluded that under these conditions the limit values of an inorganic soil are dominated by the properties of the clay fraction. This assumes that the water is associated almost entirely with the clay minerals. When the volume of the clay, at a water content equal to its limit, is too small to fill the voids the limit

value of the soil is generally independent of the clay content but if clay coats the surfaces of the primary minerals it may still have a significant effect on properties. Because of the major influence of the clay fraction on soil properties the activity (the ratio of the plasticity index to the clay fraction, p. 224) is often used to give an indication of the proportions and types of clay minerals present in the soil.

The shrinkage limit is the moisture content of a soil below which no further appreciable soil shrinkage takes place on continued drying. When saturated clay is dried there is a decrease in volume which at first is equal to the volume of water lost. As drying continues the decrease in volume becomes proportionately less and there is a gradual transition to a state in which further drying produces little volume decrease. The shrinkage limit is generally deduced by extrapolation from a graphical plot of soil volume against moisture content. The soil volume may be obtained from the volume of mercury displaced on immersion of the soil sample. Apparatuses of varying complexity have been employed for this purpose. MITCHELL (1976) gives shrinkage limit values of 8.5 to 15 for montmorillonite, 15 to 17 for illite and 25 to 29 for kaolinite.

Distilled water should be employed in the tests to minimize the possibility of ion exchange which may affect properties. For example, the exchange of Na-ions for Ca-ions on a montmorillonite has been reported to decrease the liquid limit of the sample from 700 to 124 and the plastic limit from 97 to 72 (GRIM, 1948, p.10). The soil should not be dried prior to test as some clay minerals and soil organic matter are affected irreversibly in their response to moisture. Index values are readily determined by careful technical personnel using simple apparatus and following a procedure such as recommended by the AMERICAN SOCIETY FOR TESTING AND MATERIALS (1983, D423-66, pp. 126-129; D424-59, pp. 130-131; D427-61, pp. 136-138) or the BRITISH STANDARDS INSTITUTION (1975).

Despite the use of standardized apparatus and procedures significant variability has been reported in results obtained by different laboratories (BURMISTER, 1967). It has been suggested that this is due in part to differences in sample pre-treatment and to shortcomings of the Casagrande method. These include difficulties of cutting a groove, particularly in sandy soils, the tendency of low plastic soils to slide in the cup rather than to flow plastically and the tendency of soils of low plasticity to liquefy with shock rather than to flow plastically. Because of these problems alternative procedures have been considered such as the use of a cone penetrometer. SHERWOOD and RYLEY (1970) tested a method developed in France which apart from the cone employs equipment routinely used in testing bitumen. Their data indicated that the cone test gave much more reproducible results than obtained

with the Casagrande method. They recommended that the liquid limit be re-defined as the water content at which a cone of weight 0.78 N (80 gf) and an apex angle of 30° will penetrate 20 mm in 5s into a soil when dropped from a position at which the point just touches the soil surface. This value would agree numerically with the Casagrande liquid limit up to values of 50 per cent and even at 100 per cent the difference would only be about 5 per cent. Following this work it was recommended in BRITISH STANDARDS (1975) that a cone penetrometer be used to measure the liquid limit in preference to the Casagrande apparatus.

In the Soviet Union similar studies by VASILEV (1942) based on the principle of the Swedish cone test led to the adoption of a cone test as standard (GOST 5184-49). SKOPEK and TER-STEPANIAN (1975) conclude that the shear strength at the liquid limit is about 8.5 kNm^{-2} when this test is used whereas it ranges between 1 and 3 kNm^{-2} in the Casagrande test. The liquid limit is therefore lower in the Soviet test. These authors also suggested a conversion relationship between both liquid limit values. WROTH and WOOD (1978) suggest that the plastic limit should also be measured by the cone test. Attempts to make better use of correlations between index properties, shear strength and compression index led them to propose that the plastic limit be redefined as the water content at which the strength is 100 times that of the liquid limit.

DETERMINATION OF SHEAR STRENGTH

The principal objectives of shear tests are to determine the maximum shearing resistance, the creep behaviour, the residual strength and the stress-strain and volume change characteristics resulting from shearing stresses (HVORSLEV, 1939; BISHOP et al., 1971). There are four chief categories of test used to obtain an estimate of the shear strength of a soil. These are the direct shear test, the triaxial compression test, the torsional shear test and the vane shear test. Less direct estimates of soil behaviour are obtained by bearing tests and penetration tests; modelling experiments using centrifugal methods have given valuable information concerning modes of failure resulting from consolidation, yielding, rupture and fracture (SCHOFIELD, 1978; 1980). The engineering significance of the results obtained in any of these tests depends on how closely field performance can be predicted from the experimental data.

Mohr's hypothesis is much used in soil mechanics in the analysis of shear strength of soils. Mohr introduced a diagrammatic method for the derivation of shear and normal stress on a plane which is at right angles to one principal plane. In general the principal plane chosen is that which contains the major and minor principal stresses, σ_1 and σ_3 , respectively. The plane

itself, on which the stresses are required, then makes an angle, α , with the minor principal stress and its normal makes the same angle, α , with the major principal stress. In the Mohr diagram shearing stresses are plotted in the direction of the ordinate versus normal stresses in the direction of the abscissa. Shear stresses are zero on the principal planes so values which correspond to σ_1 , and σ_3 the major and minor principal stresses, are plotted along the abscissa from the origin. Through these points a circle is constructed of radius $\frac{1}{2}(\sigma_1 - \sigma_3)$ with centre on the abscissa at a distance from the origin of $\frac{1}{2}(\sigma_1 + \sigma_3)$ (Fig. 12.4A). The difference between the major and minor principal stresses, $(\sigma_1 - \sigma_3)$, is called the deviator stress or stress difference. If the magnitude and direction of σ_1 and σ_3 are known the normal and shear stresses on an inclined plane may be read directly from the diagram. If the normal to such a plane is inclined at angle α to the major principal stress and represented by AB in Fig. 12.4A the value of the normal stress on this plane is given by the magnitude of OC and the value of the shear stress is given by measurement of BC. So the radius of the Mohr circle gives the value of the maximum shear stress. In Mohr's hypothesis the failure of the material is assumed not to be influenced by the intermediate principal stress.

Data from a series of strength tests may be represented on the diagram. In the direct shear test for example a series of tests of the same sort on similar samples may be performed in which different values of the vertical compressive force are employed. Similarly in the triaxial test different values of the lateral confining pressure, σ_3 , may be used on a series of samples. In this way a series of values is obtained for the maximum principal stress, σ_1 , at which failure occurs. From the series of values for σ_1 and σ_3 obtained in the separate tests a series of Mohr circles is constructed and plotted together on the same diagram. A line which is approximately straight may be drawn as tangent to the circles and is known as Mohr's envelope (Fig. 12.4B). Its exact shape and position depends upon the material and in practice may be curved. The equation of the line is given by Coulomb's Law $\tau_f = c' + \sigma' \tan \phi'$. Mohr's circle is a graphical representation of the applied stress and Mohr's envelope similarly represents the properties of the material under the conditions of test. The Mohr-Coulomb theory predicts that a material is in imminent danger of failure if Mohr's envelope is tangential to Mohr's circle. In other words if the greatest stress circle just touches the Mohr envelope the material is at the point of failure under the given set of stress conditions. If the circle does not touch the envelope failure is unlikely at those conditions of stress. According to theory at failure the angle α between the shear plane and the horizontal should equal $(45 + \phi/2)$ but in practice α is often larger than the value measured on Mohr's construction. The apparent cohesion may be read directly from the value of the ordinate at

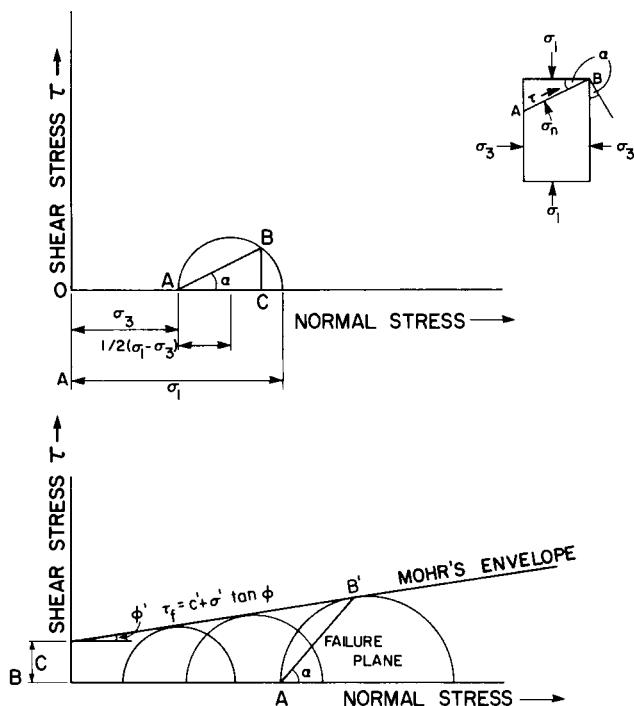


Fig. 12.4. Mohr's diagram.

A. Mohr's stress circle, σ_1 =major principal stress; σ_3 =minor principal stress; OC=normal stress on plane AB= σ_n ; BC=shear stress on plane AB= τ ; α =inclination of plane AB to horizontal.

B. Mohr's envelope for triaxial test at failure. τ_f =shear strength; c' =effective cohesion intercept; ϕ' =effective angle of shearing resistance or friction; α =predicted angle between shear plane and horizontal; σ' =normal effective stress.

the point at which it is intercepted by Mohr's envelope. The angle between Mohr's envelope and the horizontal axis is ϕ , the angle of internal friction. Data from strength tests may be interpreted by calculation rather than by the graphical procedure of Mohr. Such techniques are discussed in soil mechanics texts.

A series of Mohr circles plotted together may give a single diagram a complex appearance. This drawback may be overcome by use of a p-q diagram. In this representation state of stress in a given test is represented by a single point. The coordinates of the point are p,q and are given by taking $p=\frac{1}{2}(\sigma_1+\sigma_3)$ and $q=\pm\frac{1}{2}(\sigma_1-\sigma_3)$ so that in effect a single point on a Mohr circle is plotted. When several points from different tests are joined together the resulting trajectory is referred to as the stress path and represents successive states of stress.

In order to obtain a proper estimate of soil strength the effective stress has to be evaluated; it is the difference between the total stress and the pore pressure of the liquid phase. In laboratory tests the pore pressure may be measured by a device which is in hydraulic continuity with the soil-pore fluid via the porous plates which are in contact with the soil sample in the testing machine. Electrical transducers and null systems which balance pore pressure against a known pressure have been used. Alternatively pore pressure may be measured by a probe inserted into the soil sample. As another alternative the experiment may be carried out under such conditions that changes in the pore pressure are known. The measurement of pore pressure has been described by BISHOP et al. (1961) and GIBBS et al. (1961).

In laboratory shear tests pore-pressure control is achieved by adopting three drainage conditions. There are two varieties of test in which no drainage is allowed during shear and a third variety in which the sample is fully drained during shear (SKEMPTON and BISHOP, 1950, pp.93-94). In the undrained (quick) test the soil is sheared at a more rapid rate than that at which changes in soil moisture can occur and drainage is prevented. In the consolidated-undrained or consolidated-quick test the soil is consolidated under load and then sheared rapidly so that no moisture movement into or out of the soil can take place. In the drained or slow test the sample is allowed to consolidate or swell and then slowly sheared so that no excess pressure develops in the pore space.

The vane shear test is generally carried out in the field but can also be performed on laboratory samples if a small vane is used. In bearing tests the soil is loaded over an area of the order of several square feet. Penetration tests are performed in the field or laboratory with a loading area of a few square inches. Bearing tests mainly measure elastic strain and irreversible compressibility whereas the penetration test measures mainly shear deformation due to plastic flow. Recent discussions of cone penetration testing have been given by ALPERSTEIN and LEIFER (1976), BALIGH et al. (1980) and ROY et al. (1980).

Direct Shear Test

In the direct shear test a split container is employed (Fig. 12.5). The soil sample is stressed to failure by moving one part of the container relative to the other. The apparatus consists of a rectangular box or ring-type container which can be separated into two halves in the horizontal plane. The soil sample is made to fit snugly into the box and is loaded vertically by a constant compressive force. In the horizontal plane one half of the box is sheared relative to the other. Two procedures have been

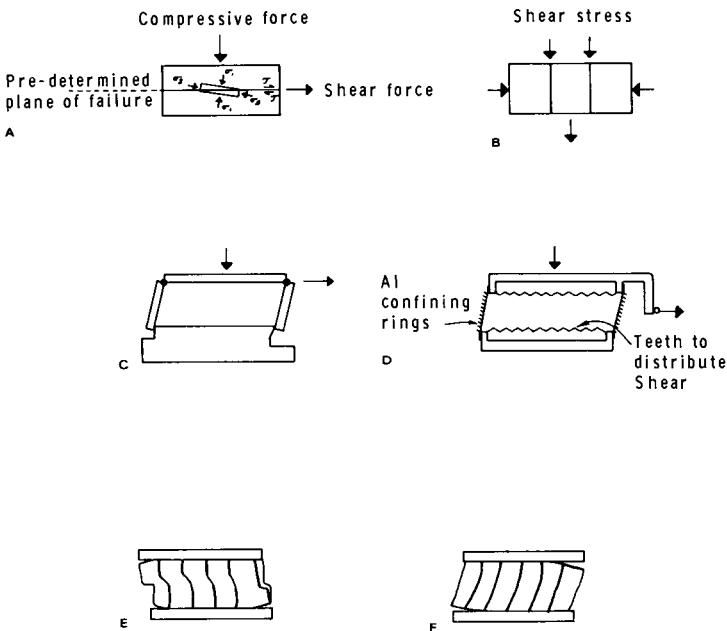


Fig. 12.5. Principle of plain shear-strain apparatuses.

- A. Direct shear test.
- B. Double direct shear.
- C. More uniform simple shear. (After ROSCOE, 1953, p.187. Reproduced by permission of the author.)
- D. More uniform simple shear. (After KJELLMAN, 1951, p.226. Reprinted from Geotechnique by permission of the Institution of Civil Engineers.)
- E. Shear strains non-uniformly distributed. (After ROSCOE, 1953, p.189. Reproduced by permission of the author.)
- F. Shear strains more uniformly distributed. (After ROSCOE, 1953, p.189. Reproduced by permission of the author.)

followed. In one the shear force is increased at a given rate and the resulting strain is measured. This type of shear-test machine is termed stress controlled. In the alternative system the separated parts of the container are moved relative to one another at a given rate and the force is measured. This type of machine is termed strain controlled. The force is transmitted through the soil and is measured on the other half of the box which is connected to a measuring device such as proving ring. (A proving ring consists of a high carbon steel ring containing an extensometer mounted so as to record radial deflections.) Some form of dial gauge extensometer is incorporated by means of which dimensional changes in the vertical direction can also be recorded. From this measurement an approximate value for change in volume is deduced. The top and bottom surfaces of the soil are often placed in contact

with a toothed grid to improve transmission of shear. Porous stones can be fitted for tests in which drainage of pore water is allowed (AMERICAN SOCIETY FOR TESTING AND MATERIALS, 1983).

Many modifications and attempted improvements to the simple apparatus have been made. A double direct shear apparatus (Fig. 12.5B) is described by HOUSEL (1964, pp.357-360). A more uniform distribution of shear strain has been achieved by encasing the sample in a rubber sleeve surrounded by a series of aluminium rings (Fig. 12.5D) (KJELLMAN, 1951). A shear box with hinged end pieces which tilt during shear has been employed by ROSCOE (1953, 1965) (Fig. 12.5C). Direct shear tests have been used for the determination of residual strength - the post-peak shearing resistance of soils at large displacements. Modifications to the standard shear box generally provide for the automatic reversal of the direction of shear movement (KENNEY, 1967; CULLEN and DONALD, 1971).

Testing is carried out on either undisturbed or remoulded samples depending on the information required and the engineering application. The type of test is often selected with the object of approximately duplicating conditions in the field. A series of samples, as near identical as possible, are tested using different values of radial pressure on each sample.

The direct shear test is simple experimentally and in elementary theory; however, it suffers from certain disadvantages. For example, the plane of shear failure is pre-determined by the nature of the test and this plane is unlikely to be the weakest in the sample as a whole. Different results are obtained when the drainage conditions are altered. The distribution of shearing strains within the soil (Fig. 12.5 E,F) (ROSCOE, 1953) and the stress distribution on the plane of failure are non-uniform and failure takes place progressively.

Triaxial Test

In the triaxial test the apparatus (Fig. 12.6, 12.7) is designed so that stress may be applied in both the vertical and horizontal directions. In the normal type of triaxial apparatus a 3-3½ inch long cylindrical sample with length to diameter ratio of about 1½-3 is subjected to a constant confining pressure in the horizontal or radial direction and an increasing axial or vertical stress until the sample fails in shear. The axial pressure represents the major principal stress. The pressure in the horizontal plane which represents the other two principal stresses is equal in all directions as it is applied hydraulically through water, oil, or air. The axial stress is applied through end plates one of which may be free to tilt to allow for non-uniform deformation. As with the direct shear devices the triaxial apparatus may be either stress controlled or strain controlled. The sample is

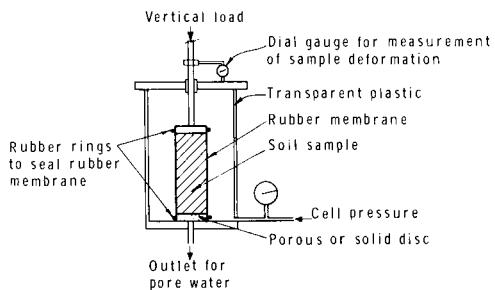


Fig. 12.6. Schematic of triaxial compression chamber.

sealed in a fluid-proof sleeve, generally a rubber membrane, and contained in the cylindrical pressure cell which is usually made of transparent plastic so that the sample can be kept under observation during test. The fluid pressure is measured by a pressure gauge or manometer and the axial stress is measured by a proving ring or similar device in a strain controlled apparatus. Known weights may be employed if the apparatus is of the controlled stress type. Porous stones may be used as end plates for the cylindrical sample. Connections can be made to a suitable measuring device such as a burette so that volume changes in the sample during test can be recorded by measurement of the volume of pore water expelled from the sample (assumed saturated). Lateral distortion of the sample can be calculated from this data if the axial deformation is known. Alternatively strain gauges may be connected to the sides of the sample or the deformation may be estimated optically. The pressure in the pore fluid can also be measured. A series of samples, as near identical as possible, are tested using different values of radial pressure on each sample.

In the undrained or quick test the sample is sealed in an impermeable membrane and the end plates are non-porous to prevent drainage. The sample is sheared to failure by slow application of the vertical load. A rate of strain of the order of $\frac{1}{2}\%$ per minute is often employed. In the consolidated-quick or consolidated-undrained triaxial test the sample is first allowed to come to equilibrium with respect to pore water content by being consolidated at a fixed lateral pressure. When no further water is expelled the drainage channels are closed and the sample is sheared to failure as in the undrained test. Measurement of the pore-water pressure may also be made. In the slow or drained test the sample is consolidated under constant pressure. An increasing axial load is then applied sufficiently slowly for pore pressure to be approximately maintained at equilibrium by drainage from the pores into the



Fig. 12.7. Triaxial test apparatus. (Photograph: Division of Building Research, National Research Council, Canada. Reproduced by permission.)

porous plates. Volume changes in the sample are measured and the sample is sheared to failure.

There are variations to the manner in which the sample is loaded to failure. Instead of increasing the axial pressure as in the more usual test this may be decreased while the lateral pressure is held constant. Alternatively the axial load may be held constant while the lateral pressure is increased. The axial pressure becomes the minor principal stress in such a test. In a modification to the triaxial test described by WU et al. (1963) the intermediate principal stress may be varied. Clays are often plastic so may suffer a large amount of strain before failure. The cylindrical sample

often distorts to a non-uniform barrel-shape during test. More brittle samples show less strain during loading and fail on more clearly defined rupture surfaces.

Disadvantages of the conventional triaxial test include the equalization of the intermediate and minor principal stresses, the fact that no allowance is made for the effects of creep, problems associated with the rubber membrane and the non-uniform development of pore pressures, stress and deformation. Various attempts have been made to develop apparatus which allows truly triaxial tests to be carried out. For example KO and SCOTT (1967) described a cubical test box in which any combination of the three principal stresses may be applied to the sample. Significant differences in behaviour were found between samples tested in the new apparatus and those tested in conventional triaxial apparatus. These differences led to discussions concerning the significance of the results obtained in the two sorts of apparatus (READES and GREEN, 1974; LADE and DUNCAN, 1975).

The rubber membrane, commonly used in triaxial tests, may affect strength results and when being fitted it may disturb the sample particularly in the case of soft and sensitive soils. Various methods to allow for the restraint and to correct errors in the measured stresses have been proposed (HENKEL and GILBERT, 1952; La ROCHELLE, 1967; PACHAKIS, 1976). Use of a fluid such as liquid paraffin, immiscible with the pore fluid in the sample, was suggested by IVERSEN and MOUM (1974) as another possible solution to the problem.

Except at very small strains distortion of the sample often leads to development of a barrel-shape with localized zones of dilation and the premature formation of a predominant failure surface. These problems are attributed largely to end restraint due to friction between the sample and end platens. Various attempts have been made to reduce or eliminate end restraint by use of specially made end fittings or lubricated platens (ROWE and BARDEN, 1964). Short samples with the ratio of length to diameter of about $1\frac{1}{2}$ to $2\frac{1}{2}$ diameters have been reported to yield the best results. BISHOP and WESLEY (1975) developed a form of hydraulically loaded triaxial cell in which both stress controlled and strain controlled tests may be carried out. Unlike a conventional triaxial cell vertical load in a compression test is applied from below and so no corrections are required for loading ram weight. Extension tests are also possible and no loading frame is required in this type of apparatus. More recently DUSSEAUT (1981) described a hollow cylinder triaxial test device.

Major advantages of the triaxial test include the control of drainage conditions and the possibility of measuring pore water pressures (BISHOP and HENKEL, 1974). The triaxial test is more involved than the direct shear test but the apparatus is more versatile and adaptable. Also the plane of failure

is not predetermined, the conditions of test are more controllable and the state of stress can be ascertained throughout the test. The distribution of strain and stress in the sample although non-uniform (SHOCKLEY, 1961) is more so than in the direct shear test and failure is a less progressive process. The test has played a major role in basic research on shear-strength and pore pressure characteristics and is also often used in practice.

Unconfined Compression Test

The unconfined compression test is in a sense a special form of triaxial test in which there is no horizontal pressure so the minor and intermediate principal stresses are zero. It is widely used in practice both in the field and for routine laboratory soil testing. It is used only on cohesive soils as such material does not require lateral support. Various forms of apparatus have been devised. In the test most commonly employed a cylindrical sample is confined between end plates and loaded to failure by increase in axial pressure. Load has been applied by various means such as spring and hydraulic systems.

As in the triaxial test and unlike the direct shear test the failure surface is not pre-determined. Failure may therefore occur in the weakest portion of the clay cylinder. The mid-portion of the sample is, however, subject to the greatest strain as the end portions are restrained laterally by the end plates. If the sample fails in a brittle manner a definite maximum load before failure is recorded. When plastic failure takes place no maximum load is reached and the strength at some arbitrarily defined strain such as 20% is taken in place of the peak.

Torsion Tests

The torsion test is most commonly carried out in a ring shear apparatus in which a cylindrical or hollow cylindrical sample is subjected to both normal loading and torsion. The method was pioneered by HVORSLEV (1936) and modifications have been subsequently developed by others (HAYTHORNTHWAITE, 1961, pp. 990; BISHOP et al., 1971; TOWNSEND and GILBERT, 1973). The test has been most used in research particularly in the measurement of residual strength. It has certain advantages over other tests in that the sample may be subjected to large displacements without reversal of direction and the cross-section of the sample remains more nearly constant during shear. On the other hand the torsional shear displacement of the specimen varies with the radius, there are high local stress concentrations and variation during test in the orientation of the principal stresses. Also the test is not simple to carry out nor the apparatus easy to construct.

The Vane Shear Test

The vane shear test was proposed as a convenient method for measurement of the undrained shear strength of soft clays in situ. The vane consists of four blades at right angles to one another (Fig. 12.8). This is inserted into the soil to be tested and the torque is measured which is required to cause shear failure on the cylindrical surface within which the vane rotates. Certain advantages have been claimed for the method. For example: stress release generated by removal of samples for laboratory testing is avoided because soils are tested in situ; with proper care sample disturbance caused by insertion of the vane is probably less than the corresponding effects caused by sample removal; the test is relatively inexpensive. On the other hand the failure surface is imposed and this is unlikely to be the plane of greatest weakness. While early workers felt that reasonably satisfactory results can be obtained more recent publications have suggested that the test overestimates the shear strength of highly plastic clays. Studies of peat by LANDVA (1980) led him to conclude that, for this material at least, the vane shear test is of little engineering use.

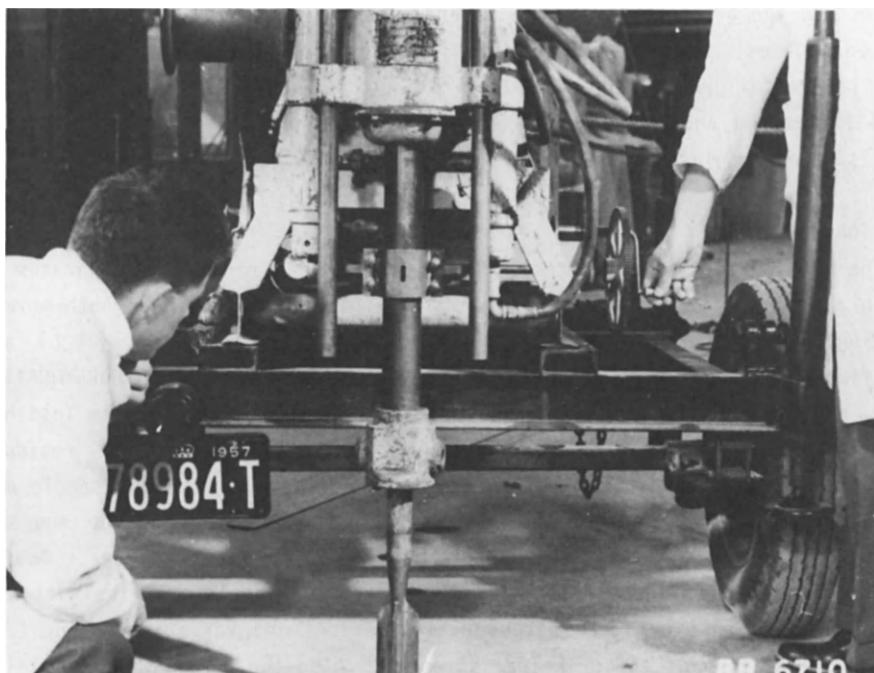


Fig. 12.8. Vane shear apparatus. (Photograph: Division of Building Research, National Research Council, Canada. Reproduced by permission.)

CONSOLIDATION

Consolidation tests are designed to give data which, when interpreted in terms of consolidation theory, allow reasonable predictions to be made of foundation settlement. When a load is applied to a saturated soil it is initially carried by the pore solution which is less readily compressed than the soil structure. This causes a pressure to develop in the pore fluid termed the "hydrostatic excess pressure". This may be measured in the field by the use of piezometer tubes. The excess pressure in the pore water dissipates at a rate which depends upon the permeability and the load is transferred to the soil structure. The change in volume during consolidation is equal to the volume of pore solution which is expelled and corresponds to the change in void fraction of the soil. In clay soils the permeability is low and settlement may continue for years following loading, therefore knowledge of the rate of volume change is just as important as is its total amount. Both parameters are estimated from laboratory tests and the results extrapolated by application of theory to field use.

The consolidation test is carried out on undisturbed samples (remoulded samples are also tested) by means of an oedometer (consolidation press) (Fig. 12.9, 12.10). This consists of a circular metal container sometimes called the consolidation ring in which the sample is placed. This is contained between two porous stones through which the sample is loaded. A dial gauge micrometer is employed to record changes in thickness of the sample. On application of load the sample consolidates as water is expelled via the porous stones. As the test is rather slow these are kept continuously wet to prevent evaporation. In some types of apparatus a ring used for obtaining an undisturbed soil sample is used in the consolidation apparatus so eliminating

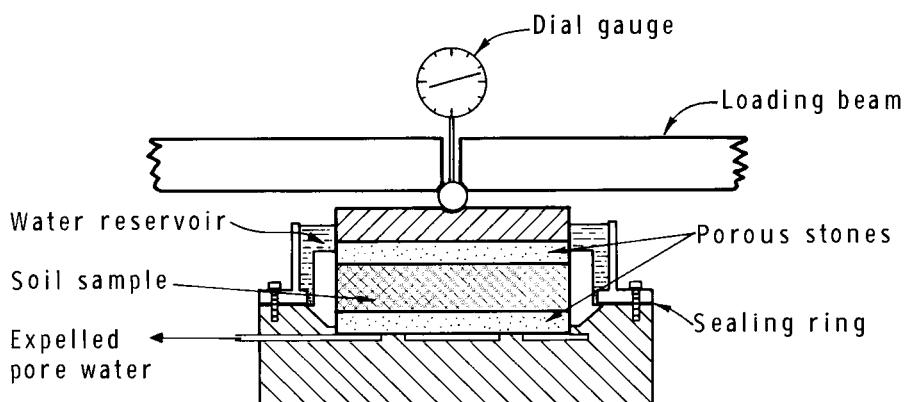


Fig. 12.9. Schematic of cross-section of fixed ring consolidometer.

the need for sample transference. A sample is commonly 3 inches (7.62 cm) in diameter and 0.79 inches (2 cm) in thickness though other sample sizes are also employed. In general larger samples are needed for less homogeneous soils, but the 3 inch sample is common from normal boreholes.

Load is applied in successive increments. Readings of the vertical compression of the sample are taken after increasing time intervals following application of the load until the soil attains equilibrium. This is generally after a time of about 24 hours for a sample 2 cm thick. At this stage the sample has attained a definite void ratio and water content at which it is in equilibrium under conditions of lateral restraint and the applied vertical

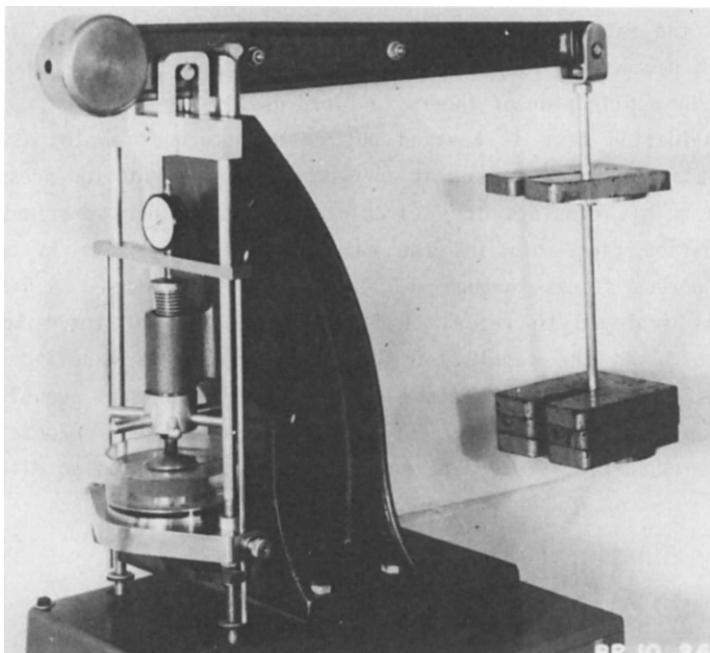


Fig. 12.10. Consolidation apparatus. (Photograph: Division of Building Research, National Research Council, Canada. Reproduced by permission.)

load. The load on the soil is then increased and the procedure repeated. Successive loads are applied which are generally double the preceding one and a commonly employed loading sequence is 0.5, 1.0, 2.0, 4.0, 8.0 tons/sq.ft. (approximately kg/cm^2). For soft clays a smaller initial and final load may be employed such as 0.1, 0.3, 0.5, 1.0, 2.0 and 4.0 tons/ft².

Load increment ratios are thought to have an important bearing on the effects of compression. When loads are applied in small increments fabric elements have the greatest chance of readjusting to new equilibrium positions.

Under these conditions compression, distortion and pore pressure generation are minimized. When load is applied in larger increments shear distortion and compression are expected to be greater. On completion of the loading cycle the sample's capacity for moisture uptake or swelling may be determined by removing the load and recording the vertical movement on the dial gauge. A test method designed to give data from which heave may be predicted and in which two consolidometers are employed simultaneously has been described by JENNINGS and KNIGHT (1957).

The conventional oedometer using a mechanical loading system has certain drawbacks. Control of drainage and the measurement of initial pore pressure have been considered inadequate and side friction has been cited as a possible source of errors in the estimation of applied stress. Hydraulic consolidometers overcome some of these disadvantages since back pressure may be used to facilitate saturation of the specimen and the starting time of the test is known more precisely because of better drainage control. Other advantages are that they facilitate tests run under conditions of controlled gradient, constant rate of strain and constant rate of stress (GORMAN et al., 1978). Also load may be applied to a number of cells by means of a common water pressure system.

In a hydraulic oedometer described by ROWE and BARDET (1966) water pressure is applied to the sample through a jack made from 0.07 inch thick rubber. In using this type of apparatus SHIELDS (1976) found that the force exerted by the bellows may differ from that calculated from the hydraulic pressure and the cross-sectional area of the oedometer. Investigation showed that the problem arose because the diaphragm was not sufficiently flexible to cover the entire surface of the platen through which pressure is transmitted to the soil sample via the porous disc. He concluded that all types of hydraulic oedometer need to be calibrated and more flexible material used for the diaphragm in some cases.

Data from the consolidation test is commonly plotted graphically with void ratio as ordinate versus logarithm of pressure as abscissa. The curve (Fig. 12.11) commonly has a straight line portion, the equation of which is:

$$e = - C_c \log_{10} p + C$$

where e = void ratio, p = pressure, C_c = compression index, and C = constant. An undisturbed sediment gives a different curve from that of the same material remoulded at the same moisture content. The magnitude of the change is greater for extra-sensitive cohesive sediments than for sediments of low sensitivity (Fig. 12.12).

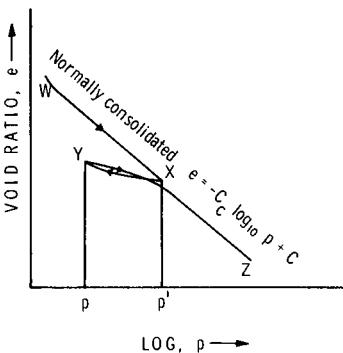


Fig. 12.11. Changes in void ratio on compression of normally consolidated and overconsolidated clay. C_c =compression index; XY=rebound on unloading; p' =pre-consolidation or precompression load; Y=sample overconsolidated; on reloading overconsolidated sample follows curve YZ.

The laboratory data are used for the determination of several important coefficients. Some of the most important of these coefficients are the compression index, C_c , the coefficient of consolidation, c_v , the coefficient of volume change, m_v , and the coefficient of permeability, k .

The compression index is a measure of the compressibility of the sample. The compressibility is defined as the "property of a soil or rock pertaining to its susceptibility to decrease in volume when subjected to load" (AMERICAN SOCIETY FOR TESTING AND MATERIALS, 1983, p. 175). The compression index, C_c , is obtained from the slope of the linear portion of the curve on the graph of void ratio as ordinate versus logarithm of pressure as abscissa. The relationship is expressed as:

$$C_c = \frac{-\Delta e}{\Delta \log_{10} \sigma'}$$

where e is void ratio and σ' is the normal effective stress. It has values of the order of 0.15 for sandy clays and more than 1.0 for highly colloidal bentonitic clays (TERZAGHI, 1955, p.568). The compression index increases in value with the clay content and liquid limit of the sample.

The coefficient of consolidation, c_v , relates to the rate of volume change or settlement. Its value depends upon the permeability and the thickness of the sediment. It is given by the following relationship:

$$c_v = \frac{k(1+e)}{a_v \gamma_w}$$

k =coefficient of permeability, a_v =coefficient of compressibility, and γ_w =unit weight of water. The coefficient of consolidation decreases for normally

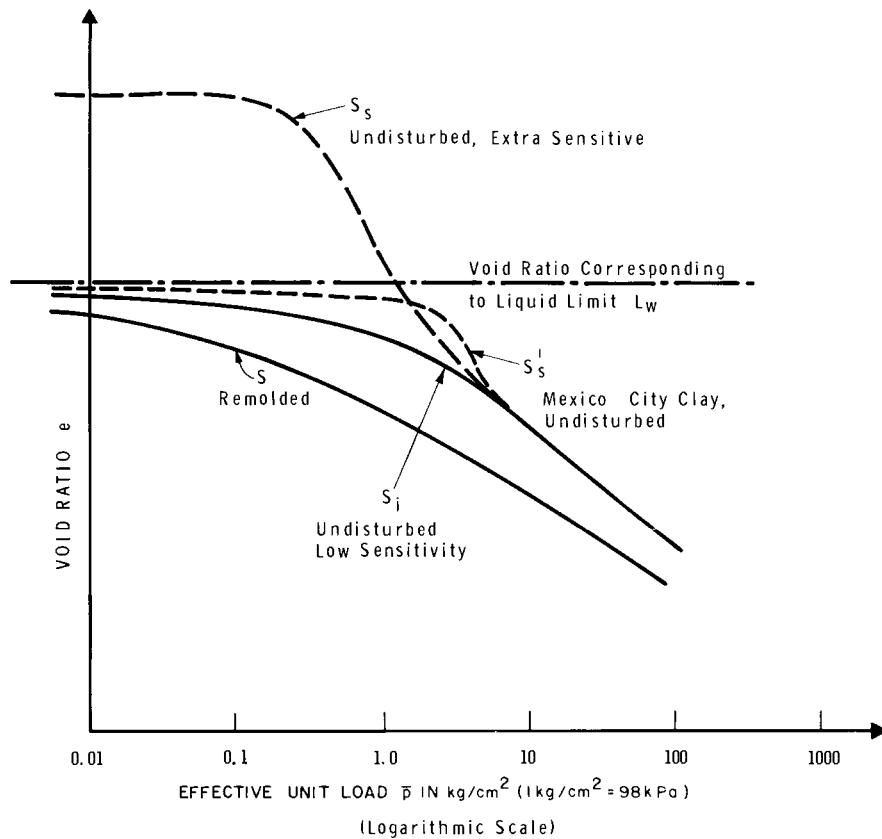


Fig. 12.12. Principal types of relationships between unit load and void ratio for cohesive sediments. (After TERZAGHI, 1955, p.568).

consolidated clays from about $1^{-10} \text{ cm}^2/\text{sec}$ for lean clays to about $10^{-6} \text{ cm}^2/\text{sec}$ for very colloidal clays (TERZAGHI, 1955, pp.574-575). The degree of consolidation of a sediment at any given time can be computed from the theory of consolidation if c_v is known.

The coefficient of compressibility (compression), $\alpha_v(L^2 F^{-1})$, is "the secant slope, for a given pressure increment, of the pressure-void ratio curve" (AMERICAN SOCIETY FOR TESTING AND MATERIALS, 1983, p.174); the coefficient of volume compressibility, m_v , is given by the relationship $\alpha_v/(1+e)$. The coefficient of permeability can be derived from the following relationship:

$$k = \frac{c_v m_v \gamma_w}{(1+e)} \text{ cm/sec}$$

where γ_w = unit weight of water (g/cm^3).

The value of the preconsolidation load can be estimated from the graph of void ratio versus log pressure. The preconsolidation load is given by a point on the pressure axis close to the value which corresponds to the maximum curvature of the graph. In the method recommended by LAMBE (1951, p.83) a horizontal line and tangent are drawn to the point of maximum curvature. The horizontal line and tangent are bisected and the bisector is produced to meet a line drawn backwards from the straight line section of the high pressure portion of the curve. The intersection of this line and the bisector corresponds to the approximate value of the preconsolidation load (Fig. 12.13). The original procedure was devised by CASAGRANDE (1936) and other techniques have been described by SCHMERTMANN (1955). The preconsolidation load is generally a safe bearing pressure for clay. The value of the preconsolidation pressure derived from laboratory tests has, however, been shown to vary with the loading procedure (CRAWFORD, 1964).

An indication that a soil has been preconsolidated may be given by relatively high values (2-3) of the lateral stress ratio, K_0 . This quantity, also sometimes termed the coefficient of lateral stress, is the value of the ratio of horizontal to vertical stress, σ_h/σ_v . (The subscript zero, attached to the K, is used when there is no indication of any unusual increase in lateral stress). Under normal conditions of sedimentation consolidation takes place due to the increase in thickness of the layers of sediment. Vertical stress therefore tends to increase more rapidly than horizontal stress, and the value of K_0 is typically less than unity. If the vertical load is reduced by erosion, or other causes, the value of K_0 may exceed unity because the horizontal stress does not decrease as much as the vertical stress.

The degree of consolidation of a sample is represented as the ratio between the change in void ratio after a given time and the change in void ratio when consolidation is complete. The percentage consolidation may be represented as ordinate versus time or logarithm of time as abscissa. Use has been made of many other graphical methods to represent the time dependent deformation of cohesive soils under constant load. Plots of stress versus time under constant strain may show stress decrease with time due to stress relaxation. A strain versus time curve may show a primary, secondary and tertiary stage analogous to that which describes the creep behaviour of other materials. In the primary stage rate of strain decreases with time, in the secondary stage rate of strain remains essentially constant for a period. This linear part of the curve may be followed by a concave upward, tertiary section, in which rate of strain accelerates with time and leads to failure.

The laboratory tests give data on the relationship between void ratio and load and on the relationship between time and percentage of total consolidation for the load. In order to calculate the amount and rate of

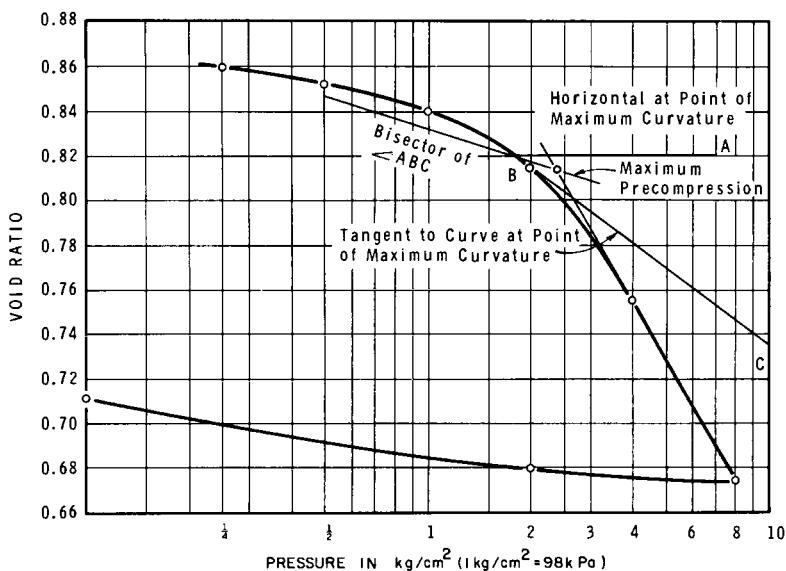


Fig. 12.13. Graphical deduction of preconsolidation load. (After LAMBE, 1951, p.87).

settlement of a foundation the nature and thickness of the soil strata at the construction site and the stress distribution in the soil following construction are also needed. The nature of the soil is obtained from knowledge of the local geology and test borings. Soil composition sometimes has an effect. For example FOOT and LADD (1981) found that soils with high organic content showed increased initial settlement and significant undrained creep deformation. An interesting experimental approach to the study of consolidation of loose subaqueously deposited sediments was taken by BEEN and SILLS (1981). They used a non-destructive x-ray technique to measure the density change which accompanied self-weight consolidation. Results compared well with those predicted by a theoretical model and were also in good agreement with data from estuarine suspensions.

Difficulties are often encountered in predicting the actual amount of consolidation in the field from results of laboratory experiments. It is likely that one major cause of this difficulty is the great difference between rates of loading in the field and laboratory. Loads imposed by engineering structures may cause consolidation which continues for years or even centuries; on the other hand vehicular traffic imposes transient loads the duration of which is measured in milliseconds. Another shortcoming of the laboratory test procedure is that drainage and compression are both

one-dimensional. This can lead to large errors in the estimation of the rate of consolidation in certain types of sediments such as varved clays. The silty layers in such a deposit can have quite a high permeability in the horizontal direction. Permeability in the vertical direction, however, is low due to the intervening claybands.

Tabulated solutions to the problem of stress distribution for common cases of loading have been published by JURGENSON (1934) and TERZAGHI (1943). In recent work more general equations have been derived governing one dimensional consolidation of saturated clays by use of non-linear finite strain theory (GIBSON et al., 1967, 1981). One important implication the authors draw from their work is that settlement maybe faster than predicted by conventional theory whereas the dissipation of excess pore pressure may be slower. If correct this could lead to overestimation of the excess pore water pressure, if an effective stress analysis were used, and to potentially unsafe design. In other recent work the relationships between permeability and void ratio and between the coefficient of consolidation and effective stress have been discussed (SAMARASINGHE et al., 1982). One dimensional consolidation theory of unsaturated soils has been considered by FREDLUND and HASAN (1979) and LLORET and ALONSO (1980).

Consolidation is thought to be accompanied not only by hydrodynamic lag due to movements of pore fluids but also by secondary effects due to changes in the type and number of bonds per unit volume and to re-orientation of the fabric elements of which the soil skeleton is composed; such changes may continue after excess pore pressures have dissipated. Rate process theory was applied to creep phenomena by MITCHELL et al (1968) and more recent discussions taking account of thermal activation, electrical double layer theory and other factors have been given by HANRAHAN (1979), KAVAZANJIAN and MITCHELL (1980), PUSCH and FELTHAM (1981), SRIDHARAN and JAYADEVA (1982) and SRIDHARAN and RAO (1982).

COMPACTATION

The compaction test is intended to determine the optimum moisture content at which the void fraction of a soil may be reduced to a minimum by mechanical compaction. Compaction is measured in terms of the dry bulk density and the value which can be attained ranges from about 140 lb/ft^3 (2249.52 kg/m^3) for a well graded gravel to about 90 lb/ft^3 (1441.66 kg/m^3) for a clay. State of compaction may be determined experimentally by both field and laboratory techniques. There are a number of laboratory methods in use and the soil sample may be compacted by either dynamic or static means. Many of the tests in which dynamic compaction is employed are similar except for differences in the size of mould and sample and in the amount of energy used in compaction.

In the U.S.A. a commonly employed procedure is termed the Proctor test (PROCTOR, 1933), and a similar one termed the standard compaction test is employed in Britain. Modifications to the original Proctor test have been made.

The soil sample is broken up and sieved and intimately mixed with a few percent of water. If the soil is initially saturated it has to be dried prior to test. The soil sample is placed in the mould in three layers of equal thickness. Each layer is compacted before the next over-lying layer is placed in the mould. In the method for determining moisture-density relations recommended by the AMERICAN SOCIETY FOR TESTING AND MATERIALS (1983, D698-78) the mould internal diameter may be 4 in. (101.6 mm) or 6 in. (152.4 mm). The rammer may have a weight of 5.5 lb (2.49 kg) when it is dropped from a height of 12 in. (305 mm); the rammer is dropped 25 times in the case of the 4 in. (101.6 mm) mold and 56 times in the case of the 6 in. (152.4 mm) mold. The weight of soil in the mould and its water content are determined. From the weights and known volume of the mould and sample the dry density of the soil is calculated. The test is repeated on a series of at least four specimens the water contents of each of which increase by increments of about 1.5 percent. Results are plotted graphically with dry density as ordinate versus percent water content as abscissa. A curve is obtained which shows a maximum at a density corresponding to the optimum water content (Fig. 8.1). If much coarse material is removed when the soil is sieved a correction is included in the calculation of the density. It is good practice to allow the soil to remain in contact with the mixing water overnight prior to compaction.

A hydraulic press may be employed to compact the soil sample in the mould and this is employed in one variant of the static compaction test. In field estimations of compaction the dry density of the soil in situ is obtained. The moisture content and weight of a known volume of soil are determined and the dry density calculated. The maximum density and optimum moisture content depend on the type and amount of compaction and it is for this reason that there is sometimes difficulty in relating laboratory results to those obtained by use of field equipment. Despite this limitation compaction tests are useful as they indicate the density which can be attained at the optimum moisture content and show whether a particular soil will compact to a low or high maximum density. Hence they can be used as a control on results obtained with field equipment. Specifications commonly call for a compacted density of 100% Proctor or 95% of modified Proctor density.

Engineers often judge the probable behaviour of a compacted soil by reference to the relative compaction. This is defined as "The dry density of the soil in situ divided by the maximum dry density of the soil as determined by the Proctor compaction test or other standard test. It is generally

expressed as a percentage" (SCOTT, 1965, p.249). Relative compaction has been most often used for cohesive soils. Granular and non-cohesive soils and fills have often been evaluated in terms of the relative density or degree of compaction. This is defined as, "The ratio of the difference between the void ratio of a cohesionless soil in the loosest state and any given void ratio to the difference between its void ratios in the loosest and in the densest states" (BATES and JACKSON, 1980, p.528). Relative density has been used to compare such engineering properties of soils as the shear strength, compressibility and sensitivity to earthquakes. Because of the similarity between relative compaction and relative density LEE and SINGH (1971) proposed a conversion relation between the two quantities. A statistical study led TAVENAS and LA ROCHELLE (1972) to conclude that there is a significant scatter in results between replicate determinations in presently used laboratory and field methods of measurement so results should be used with caution.

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INDEX TO AUTHORS CITED IN TEXT¹

- ABDEL-KADER, F.H., 336
 ABE, N., 246
 ABRAMS, M.S., 264
 ADAMS, J.M., 351
 ADAMS, T.D., 67
 AHMAD, N., 394
 AITCHISON, G.D., 184
 AJAZ, A., 222
 AKKY, M.R., 262, 263
 AKROYD, T.N.W., 401
 ALAM, M.M., 190
 ALEKSINA, I.A., 67
 ALEXANDER, L.E., 327, 379
 ALEXIADES, C.A., 108, 150
 ALLAM, M.M., 238
 ALLEN, H., 18
 ALONSO, E.E., 198, 290, 428
 ALPAN, I., 244, 430
 ALPERSTEIN, R., 413
 ALTSCHAFFL, A.G., 73, 83, 198, 212,
 216, 394
 ALVISET, L., 310
 AMERICAN ASSOCIATION OF STATE HIGHWAY
 AND TRANSPORTATION OFFICIALS, 2
 AMERICAN CHEMICAL SOCIETY, 261, 265
 AMERICAN GEOLOGICAL INSTITUTE, 114
 AMERICAN SOCIETY FOR TESTING & MATERIALS,
 14, 53, 56, 185, 200, 252, 260, 262,
 273, 300, 302, 374, 391, 392, 401,
 407, 409, 415, 424, 425, 429
 AMIS, E.S., 170
 AMOS, D.F., 215
 AMPIAN, S.G., 285, 288, 289, 292, 297
 ANALYTICAL CHEMISTRY, 379, 380
 ANDERSON, A.B.C., 172, 187
 ANDERSON, D.M., 236
 ANDERSON, J.G.C., 36
 ANDERSON, J.U., 330
 ANDERSON, T.F., 369
 ANDERSON, W.F., 401
 ANDRESEN, A., 430
 ANDREW, R.W., 335
 ANGLO-AMERICAN CLAYS CORP., 232, 291
 ANONYMOUS, 268, 289
 ANSAL, A.M., 243
 ANSEAU, M.R., 316
 AOMINE, S., 114, 171
 APOSTOLOPOULOS, C., 275
 APPELO, C.A.J., 80
 ARBLE, W.C., 403
 ARNOLD, R.W., 18
 ARULANANDAN, K., 212
 ARYA, L.M., 392
 ASPHALT INSTITUTE, 254, 258
 ASSARSON, K.G., 268
 ASTBURY, N.F., 225, 229, 230
 ATTERBERG, A., 12
 AUSTIN, G.S., 335
 AXARIS, G.S., 134
 AYLMORE, L.A.G., 115, 398
 AZBE, V.J., 268
 BAGNOLD, R.A., 36
 BAILEY, S.W., 98, 103, 104, 105, 110,
 111, 112, 297
 BAJWA, I., 332
 BAKER, W.H., 232
 BALDWIN, T., 80
 BALGORD, W.D., 44
 BALIGH, M.M., 413
 BALLIVY, G., 397
 BALMER, G.G., 262
 BANDYOPADHYAY, S.S., 183
 BANERJEE, S., 201
 BANHOLZER, G.S., 367, 376, 386
 BARBER, D.J., 372
 BARDEN, L., 70, 192, 198, 418, 423
 BARKAN, D.D., 250
 BARKER, J.A., 68
 BARNES, H.F., 278
 BARNHISEL, R.I., 336
 BARRETT, R.B., 351
 BARSHAD, I., 56
 BASSIN, H.J., 364
 BATES, R.L., 29, 30, 182, 402
 BATES, T.F., 36, 50, 68, 77, 103,
 343, 379, 430
 BAUDRAN, A., 229
 BAVER, L.D., 171, 174
 BAYLISS, P., 65, 106, 112, 342
 BAZANT, Z.P., 229
 BEATHARD, R.M., 36
 BECHTOLD, B.C., 295
 BECK, P.A., 397
 BEEN, K., 427
 BEETEM, W.A., 154
 BELL, F.G., 263
 BELL, A.L., 245
 BELL, G.M., 169
 BELOV, N.V., 98, 99
 BENNET, P.H., 119, 120
 BENNETT, R.H., 372
 BENSON, L.V., 62, 64, 89
 BENTLEY, S.P., 234, 242, 243
 BERG, R.L., 213
 BERG, S., 385
 BERNAL, J.D., 169
 BERNER, R.A., 68
 BERUBE, M-A., 246
 BESKOW, G., 204
 BETTER ROADS, 275
 BEUTELSPACHER, H., 348, 376

¹ Page references to authors covered by "et al" in text are in reference lists at end of chapters.

- BEVAN, J.C., 135
 BICKLEY, F., 85
 BIDDLE, P.G., 200
 BIDDULPH, R.B., 315
 BILLINGS, G.K., 353
 BIRCH, F., 223
 BISCAYE, P.E., 67, 336
 BISHOP, A.W., 184, 231, 232, 410, 413,
 418, 419
 BJERRUM, J., 72
 BLACK, C.A., 154, 351
 BLACKMORE, A.V., 189
 BLANKS, R.F., 263
 BLATT, H., 77
 BLEIFUSS, R.L., 294
 BLIGHT, G.E., 184, 244, 254, 430
 BLOCH, J.M., 159
 BLOOR, E.C., 221, 223
 BOCHKO, R., 120
 BOGUE, R.H., 277, 299
 BOHOR, B.F., 364
 BOLES, J.R., 77
 BOLLAND, M.D.A., 161
 BOLT, G.H., 71, 150, 217
 BOMAN, P., 268
 BONAR, A.J., 402
 BOON, J.A., 65
 BORIE, B.S., 374
 BORST, R.L., 376
 BOSWELL, P.G.H., 75, 234, 236
 BOYOUCOS, G.J., 206
 BOWDEN, J.W., 157
 BOWEN, N.L., 49
 BOWLES, J.E., 12, 254
 BOYDE, A., 367, 368
 BOYLE, J.R., 61
 BOZOZUK, M., 177, 253
 BRADLEY, W.F., 348
 BRADY, J.G., 296
 BRAGG, R.H., 327
 BRANNOCK, W.W., 351
 BRASHER, B.R., 212
 BREKKE, T.L., 34
 BRENNER, J.M., 386
 BRESLER, E., 215
 BREWSTER, G.R., 332
 BRICKER, O.P., 85
 BRIDGE, P.M., 431
 BRINDLEY, G.W., 104, 109, 110, 135,
 140, 154, 296, 304, 305, 306, 307,
 334, 336, 347, 373, 389
 BRITISH STANDARDS INSTITUTION, 14, 262,
 303, 382, 385, 401, 409, 410
 BROISE, Y., 252
 BROMS, B.B., 268
 BROOK, R.J., 316
 BROOKS, N.H., 37
 BROTSCHI, J., 313
 BROWN, B.E., 112
 BROWN, G., 114, 164, 334, 338, 339
 BROWN, J.D., 430
 BROWN, J.E., 201
 BROWN, J.L., 138, 371
 BROWN, K.M., 135
 BROWN, R.W., 435
 BROWN, S.D., 309
 BROWNELL, W.E., 311
 BRUNAUER, S., 387
 BRUNS, D.W., 262
 BRUUUN, P., 37
 BRYANT, W.P., 135
 BRYDON, J.E., 112, 336
 BUCHELE, W.F., 399
 BUCKINGHAM, E., 171
 BUCKLEY, H.A., 110, 111
 BUERGER, M.J., 306, 332
 BUESSEM, W.R., 236
 BULENS, M., 304, 305, 318
 BUNGENBERG DE JÖNG, H.G., 147
 BUOL, S.W., 18
 BUREAU OF MINES, WASHINGTON, D.C.,
 293, 294, 298, 300
 BUREAU OF RECLAMATION AND THE CORPS
 OF ENGINEERS, 12
 BURLAND, J.B., 184, 201, 232
 BURMISTER, D.M., 409
 BURN, K.N., 34, 177
 BURST, J.F., 66, 74, 75, 79, 111
 BUSECK, P.R., 58
 BUTTERWORTH, B., 310, 311
 BUTTON, D.D., 155
 CABRERA, J.G., 120
 CAISERMAN, A., 179
 CALLE, C., 109, 141
 CAMPANELLA, R.G., 433
 CAMPBELL, G.S., 435
 CANADA DEPT. AGRICULTURE, 15
 CAN. GEOTECH. J., 30
 CANADIAN MINERALOGIST, 103, 106
 CARDER, K.L., 394
 CAREY, K.L., 213
 CARGILL, K.W., 432
 CARMAN, P.C., 179
 CARRIGY, M.A., 77
 CARROLL, D., 29, 155, 157
 CARTER, D.L., 389
 CARTER, G., 372
 CARTHÉW, A.R., 343
 CARY, J.W., 435
 CASAGRANDE, A., 12, 13, 115, 119,
 204, 228, 237, 408, 426
 CASTRO, A., 246
 CATTON, M.D., 262
 CEBULA, D.J., 187
 CELAUBO, B., 282
 CHAGNON, J-Y., 246
 CHAKRABORTY, A.K., 304
 CHAMP, D.R., 26
 CHAN, C.K., 190, 252
 CHAPMAN, D.L., 148, 150, 351
 CHARBONELLE, J., 161
 CHAUSSIDON, J., 354
 CHEN, W.F., 225, 231, 245

- CHENG, H.H., 165
 CHERNOCK, W.P., 397
 CHHABRA, R., 351
 CHILINGARIAN, G.V., 69, 79
 CHORLEY, R.J., 23
 CHRIST, C.L., 57
 CHRISTENSEN, R.H., 229
 CHRISTIAN, J.T., 184
 CHU, T.Y., 279, 280
 CLAASSEN, H.C., 89
 CLARE, K.E., 264, 265, 269, 271
 CLARK, D.R., 100
 CLARK, J.I., 174, 191
 CLARK, J.S., 135, 353
 CLARK, N.J., 243
 CLARKE, F.W., 26, 50, 51, 52, 54
 CLAUSS, K.A., 386
 CLEMENCE, S.P., 198
 CLEMENCY, C.V., 392
 CLEMENTZ, D.M., 160
 CLEWS, F.H., 310
 CLEWS, F.J., 319
 CLOOS, P., 153
 COBLE, R.L., 309, 310
 CODY, R.D., 332, 340, 341
 COFFIN, D.E., 330
 COFFMAN, C.B., 154
 COLE, W.F., 311
 COLEMAN, J.D., 408, 431
 COLLIGON, J.S., 372
 COLLINS, K., 209
 COLLINS, L.E., 41, 120
 CONFERENCE ON IN-SITU MEASUREMENT OF
 SOIL PROPERTIES, 200
 COPELAND, L.E., 327
 COREY, R.B., 164
 CORRENS, C.W., 58
 CORTE, A.E., 125
 COSSLETT, V.E., 369
 COTTRELL, A.H., 308
 COULTER, H.W., 34
 COVENY, R.M., 125
 CRAIG, M.J.K., 229
 CRAIG, W. ROSS, 248
 CRAWFORD, C.B., 34, 35, 241, 402, 426
 CREMERS, A., 353
 CROFT, J.B., 262, 263
 CRONEY, D., 204, 275, 403, 406, 408
 CROOKS, J.H.A., 245
 CRUCHLEY, A.E., 269, 271
 CRUZ, M., 105
 CUBITT, J.M., 341
 CULLITY, B.D., 374
 CUMMINGS, A.E., 12
 CUMMINS, W.A., 12, 77
 CURTIS, C.D., 55, 75, 78, 125
 CUTLER, J.F., 292, 295, 311
 CYTRYN, S., 251
 CZARNECKA, E., 125, 160, 348
 DALLAVALLE, J.M., 385, 390
 DANELIYA, R.G., 39
 DAS, B.M., 231
 DAVEY, N., 285
 DAVID, D., 185
 DAVIDSON, D.T., 262, 271, 272, 279,
 280
 DAVIDSON, H.L., 245
 DAVIS, C.E., 389
 DAVIS, W.M., 22
 DAVISON, E.H., 292
 DAY, P.R., 384
 DE BAKKER, H., 18
 DEBBRECHT, J.D., 83
 DE BRUYN, C.M.A., 254
 DELEN, R.C., 432
 DEER, W.A., 97
 DEFALIAS, Y.F., 229
 DE JONG, E., 27
 DE KIMPE, C.R., 391
 DELMON, B., 315
 DELAGE, P., 240
 DELMON, B., 305, 318
 DEMIREL, T., 359
 DEMORTIER, G., 351
 DEMPSEY, B.J., 208
 DEMPSTER, P.B., 144
 DENISOV, N.J., 234
 DENT, D., 18
 DESAI, C.S., 184
 DE SOUZA-SANTOS, H., 352
 DE SOUZA-SANTOS, P., 352
 DEPT. OF ENVIRONMENT, LONDON, 252
 DESHPANDE, T.L., 329
 DEVINE, S.B., 341
 DE VRIES, J.L., 327
 DE WET, J.A., 254
 DE WOLFF, P.M., 327
 DIAMOND, S., 251, 313, 332, 334, 388,
 391
 Di RUPO, E., 307
 DIXON, J.B., 105, 330, 338
 DOHERTY, P.E., 370
 DOMTAR CONSTRUCTION MATERIALS LTD.,
 ONT., CANADA, 290
 DONALD, I.B., 244, 430
 DONALDSON, G.W., 182, 201
 DONNAN, F.G., 148
 DONOVAN, J.J., 242
 DOUILLET, Ph., 105
 DOWNING, R.A., 45
 DOYLE, L.J., 382
 DRISCOLL, R., 200
 DRNEVICH, V.P., 432, 434
 DUBERNAT, J., 136
 DU BOYS, P., 37
 DUDLEY, J.H., 192, 198
 DUMBLETON, M.J., 271
 DUNCAN, J.F., 319

- DUNCAN, J.M., 229, 418
 DUNN, J.R., 311
 DUSSEAUXT, M.B., 198, 238, 418
 DUTZ, H., 348
- EADES, J.L., 137, 266, 269, 272
 EBERL, D.B., 66
 ECKEL, E.B., 33
 EDEN, W.J., 34, 35, 125, 137, 139,
 401, 402
 EDIL, T.B., 341
 EDLEFSON, N.E., 172
 EDWARDS, D.G., 157
 EGASHIRA, K., 171
 EGELSTAFF, P.A., 170
 EGGLETON, R.A., 58
 EHRENREICH, T., 278
 EHRLICH, R., 376
 EISENBERG, D., 170
 EISMA, D., 355
 ELDERFIELD, H., 67
 ELDIN, G., 232
 ELEK, S., 355
 ELIASON, J.R., 157
 EL-SHEEMY, H.M., 156
 EMBLETON, C., 42
 EMMETT, P.H., 387, 394
 ENDELL, K., 205
 ENDERBY, J.E., 170, 216
 ENGINEERING GEOLOGY, 207
 ENGLAND, G.L., 432
 ESLINGER, E., 77, 83
 EUGSTER, H.P., 110, 305, 339
 EVANS, E.G., 310
 EVANS, I., 119
 EVANS, S., 351
 EXLEY, C.S., 64
 EXPANSIVE SOILS, PROC. INTL.
 CONF., 181
 EYRING, H., 225
- FAHNESTOCK, R.K., 39
 FAIRBRIDGE, R.W., 1
 FANG, H.Y., 225
 FANNING, C.D., 154
 FARMER, V.C., 135, 348, 355
 FAROUQ, A., 125
 FARROW, R., 334
 FEBRES-CORDERO, E., 246
 FEDERAL AVIATION ADMINISTRATION FOR
 DESIGN OF AIRPORT PAVEMENTS, 12
 FEININGER, T., 40
 FELDMAN, R.F., 281
 FELT, E.J., 264
 FELTHAM, P., 428
 FERNANDEZ-MARCOS, M.L., 58
 FERNANDO, J., 183
 FERRELL, R.E., JNR., 353
 FERTL, W.H., 79
 FIÈRENS, P., 300
- FILIPPOV, M.N., 140
 FINBARR, A.O., 198
 FINKL, C.W., JNR., 1
 FISCHER, E.D., 295
 FISCHER, W.R., 66
 FITZMAURICE, R., 251
 FLANK, W.H., 305
 FLEET, M.E.L., 67
 FLEMING, R.H., 32, 46
 FLETCHER, GORDON, F.A., 401
 FLETCHER, N.H., 170
 FLINN, D., 374
 FLINT, R.S., 24, 25
 FLUGGE, W., 229
 FOOKES, P.J., 53
 FOORD, E., 357
 FOOTT, R., 427
 FORMAN, S.A., 111
 FOSCOLÓS, A.E., 78, 86
 FOSTER, M.D., 119, 331
 FOSTER, P.K., 319
 FOUNDATION FRANCAISE D'ÉTUDES
 NORDIQUES, 207
 FOWLER, R.H., 169
 FRAGASZY, R.J., 249
 FRANCIS, C.W., 154
 FRANKEL, L., 57
 FRANKS, F., 170, 368
 FRANKS, S.G., 77
 FRANSHAM, P.B., 34
 FRANZMEIER, D.P., 185, 212
 FRASER, A.R., 137, 354
 FREDERICK, K.J., 390
 FREDERICKSON, A.F., 67
 FREDRICKSON, A.G., 226, 227
 FREDLUND, D.G., 184, 428
 FRENKEL, H., 181
 FRIEDMAN, M., 30, 395
 FRINK, C.R., 337
 FRIPIAT, J.J., 136, 162, 171, 348
 FRONDEL, C., 114
 FRYER, G.E., 396
 FRYMAN, S., 274
 FUGGE, W., 229
 FULLER, W.B., 252
 FULRATH, R.M., 309
 FUNK, J.E., 285
 FUNK AND WAGNALLS, 219, 285
- GADD, N.R., 34
 GAIDA, K.H., 79
 GALLAN, E., 56
 GARCIA, A., 19
 GARCIA-BENGOCHEA, I., 180, 390
 GARDNER, W.H., 435
 GARGA, V.K., 430
 GARRELS, R.M., 28, 29, 57, 85
 GAUDETTE, H.E., 111
 GEBHART, J.E., 395
 GELINAS, P., 246

- GENRICH, D.A., 386
 GERBORN, B., 262
 GHOSH, D.K., 304
 GIBB, J.G., 144
 GIBBS, R.J., 67, 340, 413
 GIBSON, R.E., 290, 401, 404, 428
 GIESE, R.F., 105, 109, 110, 155, 187
 GIFFORD, P., 275
 GILBERT, C.M., 86
 GILBERT, J.D., 418
 GILBERT, P.A., 419
 GILKES, R.J., 61
 GILLESPIE, T., 385
 GILLOTT, J.E., 3, 65, 78, 119, 125,
 139, 160, 174, 191, 240, 242, 266,
 269, 275, 312, 313, 317, 330, 348,
 362, 364, 367, 369
 GIPSON, M., 329
 GIUFFRE, O., 282
 GLAESER, R., 108
 GLASS, H.D., 67
 GLASSER, F.P., 300
 GLASSTONE, S., 143
 GLAZNER, A.F., 324
 GLOVER, R.E., 39
 GOLDBERG, E.D., 83
 GOLDICH, S.S., 58
 GOLDSCHMIDT, H., 115
 GOLDSTEIN, M., 234
 GOLLEY, C.R.L., 397
 GOMERSALL, A., 253
 GONZALEZ, C.L., 394
 GOODHEW, P.J., 371
 GOODMAN, B.A., 107
 GORHAM, E., 26
 GORING, G., 165
 GORMAN, C.T., 423
 GOUY, G., 148, 150
 GRABOWSKA-OLSZEWSKA, B., 4, 87, 119,
 140, 248, 398
 GRADUSOV, B.P., 62
 GRAF, W.L., 24
 GRAHAM, J., 237
 GRANHOLM, S., 277
 GRANT WHITEHOUSE, U., 66, 67
 GRANQUIST, W.T., 348
 GRATTON-BELLEW, P.E., 125
 GRAY, M.N., 273
 GREEN, G.E., 418, 430
 GREEN, K.T., 319
 GREENE, R.S.B., 376
 GREENE-KELLY, R., 362, 369
 GREENLAND, D.J., 52, 353, 376
 GRESKOVICH, C., 307
 GRIFFIN, G.M., 67
 GRIFFIN, J.J., 67
 GRIFFITH, A.A., 308
 GRIGAL, D.F., 154
 GRIM, R.E., 66, 102, 137, 161, 225,
 234, 235, 266, 269, 271, 278, 285,
 293, 305, 409
 GRIMSHAW, R.W., 144, 146
 GROMKO, G.J., 201
 GROSSMANN, L.N., 309
 GROSSMANN, R.B., 185
 GROVES, A.W., 348
 GUDE, A.J., 62
 GUGGENHEIM, E.A., 54
 GUITIAN-OJEA, F., 82
 GULENS, J., 42
 GUNTHARD, H.H., 348
 GUNTHER, P.R., 86
 GUTSCHICK, K.A., 267
 GUVEN, N., 294
 HABER, F., 143
 HABERCOM, G.E.J., 254
 HACK, J.T., 24
 HADEN, W.L., 297
 HAENNI, P.P., 105
 HAGGIS, G.H., 372
 HAINES, W.B., 199
 HAJEK, B.F., 343
 HALL, P.L., 170
 HALLETT, B., 41
 HAMILTON, E.L., 72, 182, 184
 HAND, J.H., 80
 HANDY, R.L., 253, 263, 266, 279, 280
 HANG, P.T., 389
 HANNA, R.M., 358
 HANRAMAN, E.T., 428
 HANSBO, S., 178
 HANSON, R.F., 64
 HARDESTY, J.M., 311
 HARDY, W.B., 151
 HARMS, J.C., 39
 HARRIS, G.B., 374
 HARRISON, W., 67, 68, 73
 HART, L., 12
 HARWARD, M.E., 63, 109, 332, 334
 HASAN, J.V., 428
 HASHIGUCHI, K., 231
 HASHIMOTO, I., 330
 HASLAM, R.T., 268
 HATHAWAY, J.C., 332
 HAUG, R.M., 154
 HAUSHILD, W.L., 39, 46
 HAWKINS, R.K., 170
 HAYES, M.H.B., 52, 212
 HAYNES, J.R., 80
 HAYTHORNTHWAITE, R.M., 419
 HAYWOOD, H., 385
 HEAKAL, M.S., 329
 HEILMAN, M.D., 394
 HELFERICH, F., 153
 HELLER-KALLAI, L., 78, 106, 108, 348
 HELMHOLTZ, 148
 HEMMEN, E.H., 396
 HENDRICKS, S.B., 157, 187
 HENKEL, D.J., 418
 HENMI, T., 376
 HENRY, N.F.M., 325

- HERBILLON, A.J., 329
 HER MAJESTY'S STATIONARY OFFICE,
 221, 222, 252, 253, 401
 HERMANN, E.C., 268
 HEROLD, D., 19
 HERRIN, M., 279
 HERRMANN, L.R., 244
 HERZOG, A., 266
 HIDALGO, A., 358
 HIGGINS, J.D., 249
 HIGGS, D.V., 374
 HIGHWAY AND TRANSPORTATION OFFICIALS
 FOR HIGHWAY CONSTRUCTION, 12
 HIGHWAY RESEARCH BOARD, 203, 252, 261,
 266, 273, 274, 275, 312, 403
 HILF, J.W., 431
 HILLIER, J., 399
 HILT, G.H., 271
 HINCKLEY, D.N., 292
 HINER, M.L., 18
 HINGSTON, F.J., 158
 HINTEN, J.F., 170
 HIPP, B.W., 157
 HIRSCH, B., 144
 HLAVAY, J., 348
 HODGSON, J.F., 157
 HOFFELT-FONTAINE, G., 351
 HOFFMAN, R.W., 348
 HOGENTOGLER, C.A., 199, 254
 HOLDREN, G.R., 80
 HOLDRIDGE, D.A., 306, 311
 HOLE, F.D., 19
 HOLLAND, H.D., 29
 HOLMES, A., 36
 HOLMES, C.D., 24, 36, 41
 HOLTZ, W.G., 181, 431
 HOOD, D.W., 28
 HOOVER, J.M., 253, 261
 HOPE, E.W., 103
 HOPKINS, T.C., 432
 HOPSTOCK, D.M., 289
 HORNE, R.H., 170
 HOULSBY, G.T., 229
 HOUSEL, W.S., 415
 HOUWINK, R., 236
 HOWE, R.A., 216
 HOWER, J., 66, 77, 111, 334
 HOWER, M.E., 77
 HSIEN-MING WAN, 336
 HUANG, P.M., 156
 HUANG, R.J., 229
 HUANG, Y.H., 434
 HUFF, W.D., 397
 HUGHES, R.E., 364
 HUGO, F., 217, 283
 HULBERT, M.H., 372
 HUMPHESON, C., 89
 HUMPHREY, E.E., 303
 HUNTER, R.J., 150
 HURLESS, A.C., 280
 HUSSEY, M.J.L., 432
 HUTCHINSON, J.N., 33, 34
 HVORSLEV, M.J., 228, 232, 410, 419
 IANNICELLI, J., 289
 IBERG, R., 296
 IIYAMA, J.T., 141, 163
 ILER, R.K., 143, 145, 148
 ILYCHEV, V.A., 250
 INCZEDY, J., 355
 INESON, J., 25
 INGLES, O.G., 253
 INGRAM, R.L., 75
 INTERNATIONAL TABLES, 374
 ISHIBASHI, I., 216
 ITO, T., 246
 IVERSON, K., 418
 IWAI, S.I., 305
 JACKSON, J.A., 402, 430
 JACKSON, M.L., 29, 30, 36, 50, 56,
 58, 61, 62, 63, 68, 77, 88, 91,
 108, 138, 154, 164, 182, 330, 338,
 351, 352, 379, 385
 JACKSON, R.E., 42
 JACOBS, D.J., 156, 157, 275
 JACOBS, H., 136
 JACOBS, J.C., 403
 JAMES, R.W., 170
 JANZER, V.J., 161
 JARRETT, B.A., 385
 JARUSOV, S.S., 156
 JARVIS, R.S., 24
 JAWED, I., 299
 JAYADEVA, M.S., 428
 JEFFERSON, M.E., 187
 JEFFREY, L.M., 83
 JENKINS, R., 327, 332
 JENNINGS, B.R., 386
 JENNINGS, J.E.B., 184, 198, 232, 423
 JENNY, H., 56, 158
 JERNIGAN, D.L., 376
 JETTER, L.K., 374
 JOHN, B.S., 42
 JOHNS, W.D., 66, 135
 JOHNSON, A.J., 403
 JOHNSON, A.W., 254
 JOHNSON, J.C., 297
 JOHNSON, L.D., 216
 JOHNSON, L.R., 135, 332
 JOHNSON, M.W., 32, 46
 JOHNSON, T.C., 184, 204
 JOHNSTON, G.H., 201, 309
 JONAS, E.C., 154
 JONAS, K., 355
 JONES, R.L., 394
 JOPLING, A.V., 4
 JORDaan, I.J., 314, 316
 JORDAN, C.F., 295, 386
 JOSHI, R.C., 273
 JOURDREY, J.W., 295
 JOURNAL OF MICROSCOPY, 121, 122, 123
 JOURNAL OF SEDIMENTARY PETROLOGY, 2
 JOY, A.S., 387
 JURGENSON, L., 428

- KAARSBERG, E.A., 361
 KAFIG, E., 368
 KAPLAR, C.W., 213
 KATTI, R.K., 261
 KATZ, D.L., 83
 KAUZMANN, W., 170
 KAVAZANJIAN, E., 428
 KAWAMURA, M., 251
 KAYSER, F., 161
 KELL, T.R., 120
 KELLER, G.H., 135
 KELLER, W.D., 14, 26, 64, 66, 67, 105,
 306, 336, 364, 376
 KEMPER, W.D., 129
 KENNEDY, G.C., 332
 KENNEDY, H.L., 263
 KENNEY, T.C., 74, 222
 KEREN, R., 68
 KERR, P.F., 65
 KERRICH, J.E., 184
 KESLER, T.L., 292
 KEZDI, A., 251, 261, 263, 267
 KIERSCH, G.A., 36
 KING, C.A.M., 42
 KING, D.T., 367, 386
 KING, L.C., 23
 KINGERY, W.D., 309, 310
 KINNIBURGH, W., 301
 KINTER, E.B., 332, 334, 388
 KIRKMAN, J.H., 105
 KISHK, F.M., 156
 KITTRICK, J.A., 103, 327, 330
 KJELLMAN, W., 415
 KLAUSNER, Y., 229
 KLEIJN, W.B., 189
 KLIEGER, P., 263
 KLUG, H.P., 327, 379
 KNIGHT, K., 198, 423
 KNODEL, P.C., 198
 KO, HON-YIN, 418
 KODAMA, H., 135, 136, 141, 157,
 336, 347
 KOHLER, E.E., 266
 KOHNKE, H., 173
 KOLOMENSKI, Y.N., 20, 140
 KOMAMURA, F., 229
 KOMAR, P.D., 382
 KOMARNENI, S., 65
 KOMORNICK, A., 185
 KONRAD, J.M., 207
 KOP, A.R., 263
 KOREXENIDES, N.A., 134
 KOZENY, J., 179
 KRAMER, J.R., 29
 KRANCK, K., 67
 KRANER, H.M., 309
 KRISHNA, P., 95
 KRISTMANNSDOTTIR, H., 65
 KRIZEK, R.J., 30, 232, 238, 243, 290,
 341
 KROMER, H., 309
 KRUMBEIN, W.C., 28
 KRUYT, H.R., 143
 KRYUKOV, P.A., 79
 KUBITSCHEK, H.E., 386
 KUENEN, P.H., 25, 30
 KULBICKI, G., 305
 KURTOSSY, S.S., 373
 KURTZ, H.F., 295
 KWAK, J.C.T., 332
 LACKEY, J.B., 37
 LADD, C.C., 271, 427, 430
 LADE, P.V., 418
 LAGALY, G., 147
 LAGUROS, J.G., 269
 LA IGLESIA, A., 55, 56, 62
 LAJOIE, G., 242
 LAM, D., 273
 LAMBE, T.W., 115, 120, 180, 188, 205,
 252, 263, 265, 273, 275, 276, 280,
 401, 426, 427
 LAMKIN, G., 376
 LANCASTER-JONES, P.F.F., 253, 258
 LANDVA, A.O., 420
 LANE, E.W., 36
 LANGBEIN, W.B., 24
 LANGDON, T.G., 310
 LANGEPLIER, W.F., 29
 LANGEVELD, A.D., 330
 LANGMUIR, I., 143, 187, 189
 LAROCHELLE, P., 249, 418, 430, 434
 LAW, F.M., 45
 LAW, K.T., 253, 401
 LAWRENCE, G.P., 391
 LAWRENCE, W.G., 155
 LAWVER, J.E., 289
 LEA, F.M., 263
 LEADABRAND, J.A., 263
 LEDOUX, R.L., 105, 348
 LEE, C., 179
 LEE, G.B., 352
 LEE, K.L., 430
 LEE, S.Y., 105
 LEFEBVRE, G., 240, 397
 LEGGET, R.F., 1, 3, 303
 LEHMANN, H., 348
 LEIFER, S.A., 413
 LEININGER, R.K., 335
 LE MAITRE, J., 304, 305
 LEOMBRUNO, R.R., 370
 LEONARD, A.J., 304, 315, 318
 LEONARDS, G.A., 232, 233, 234, 275
 LEOPOLD, L.B., 24, 36
 LERMAN, A., 29, 67
 LEVIN, E.M., 306
 LEVINSON, A.A., 65, 339
 LEWIS, R.W., 89
 LIEBHAFSKY, H.A., 351
 LIGER, C., 310
 LILLY, A.A., 262
 LIM, B.S., 311

- LIN, C.S., 180
 LINDEN-ALIMAK, A.B., 277
 LIPSHIE, S.R., 82
 LIPSON, H., 355
 LISITZIN, P., 67
 LITVAN, G.G., 368
 LITZ, P.E., 397
 LIVINGSTONE, D.A., 27
 LLORET, A., 198, 428
 LOCAT, J., 242, 243, 390
 LOCH, J.P.G., 215
 LOEWENSTEIN, W., 100
 LOH, A.K., 435
 LOHNES, R.A., 359
 LOOV, R.E., 316, 317
 LOUGHNAN, F.C., 14, 55, 75, 135
 LOVELL, C.W., 212, 216, 394
 LOVELY, W.G., 399
 LOVERING, T.S., 57
 LOW, P.F., 180, 187, 188, 236
 LOWE, D.R., 74
 LOWITZSCH, K., 327
 LUNDGREN, R., 434
 LUNDIN, S.T., 309
 LUPINI, J.F., 237
 LUTHIN, J.N., 405
 LUTZ, J.A., 157
 LUTZ, J.F., 392
 LYNCH, M.P., 83
 LYON, R.J.P., 347
 LYONS, J.M., 274
 LYTTON, R.L., 201
 MACEWAN, D.M.C., 112, 154, 161, 334, 335
 MACEY, H.H., 225, 235, 298
 MACKAY, J.R., 203
 MACIAS, F., 82
 MACKENZIE, F.T., 67, 104
 MACKENZIE, R.C., 29, 186, 330, 341, 342, 355
 MALVERN, L.E., 435
 MANCINI, F.P., 274
 MARTIN, I., 137
 MARKER, V., 258
 MARONEY, D.M., 306, 315
 MARSHALL, C.E., 145, 155, 158, 178
 MARTIN, R.T., 135, 205, 362, 373
 MARTIN-RUBI, J.A., 159, 336
 MASON, B., 26, 28, 51
 MASSACHUSETTS INSTITUTE, 261
 MAST, W.E., 330
 MATEOS, M., 278
 MATHERS, F.C., 268
 MATHIESON, A., 109
 MATSUI, T., 237
 MATTYASOVSKY-ZSOLNAY, L., 309
 MAXWELL, J.A., 136
 MAZDIYASNI, K.S., 316
 MCATEE, J.L., 376
 MCBRIDE, M.B., 155
 MCCURNEY, J.W., 310
 MCCARTER, R.S., 66
 MCCOOL, M.M., 206
 MCCORMICK, G., 202
 MCCRACKEN, R.J., 19
 MCDONALD, B.C., 4
 MCDOWELL, C., 269, 270
 MCEWAN, D.M.C., 334
 MCGOWN, A., 120, 209
 MCGRAW-HILL BOOK CO., 102
 MCINTYRE, D.B., 324
 MCIVER, R.D., 74
 MCKEAND, E., 253, 258
 MCKEE, T.R., 105, 371
 MCKESSON, C.L., 258
 MCKINLAY, D.J., 180
 MCKYES, E., 242
 MCLENNAN, S.M., 51
 MCMURDIE, H.F., 306, 318
 MEADE, R.H., 71, 75
 MEDHIN, B.W., 216
 MEHRA, O.P., 330
 MEHTA, P.K., 313
 MEIGH, A.C., 403
 MEINZER, O.E., 25
 MELDAU, R.F., 125
 MELON, G.B., 77
 MENARD, L., 252
 MERING, J., 137, 186
 MERMENTHALER, TH., 296
 MERRITT, F.S., 12
 MERYMAN, H.T., 368
 MÈSRI, G., 229
 METCALF, J.B., 266, 267
 MEUNIER, A., 56
 MEYER, C., 63, 65
 MEZUMAN, U., 68
 MICHAELS, A.S., 180, 274, 280
 MIDDLETON, G.F., 36, 251
 MIDDLETON, S., 211
 MIELENZ, R.C., 312, 313
 MIGGLIACCIO, R.R., 34
 MIGLIORINI, C.J., 30
 MIKLUCHIN, J., 292
 MILER, R.H., 88
 MILLER, R.D., 189, 206, 217
 MILLER, W.D., 336
 MILLHOLLEN, G.L., 304
 MILLOT, G., 77
 MILNE, I.H., 335
 MINATO, I., 317
 MINKOV, M., 198
 MIRTSKHULAVA, T.Y., 39
 MITCHELL, B.D., 330, 342, 355
 MITCHELL, J.K., 201, 246, 266, 292, 362, 409, 428
 MITCHELL, W.A., 32, 115
 MOH, Z.C., 263, 280

- MOHAN, K., 300
 MOHR, E.C.J., 91
 MOHR, O., 230, 231
 MONORITI, E.J., 279
 MOODIE, C.D., 165
 MOON, C.F., 240
 MORAN, S., 211
 MORGAN, J., 169
 MORGESTERN, N.R., 184, 207, 238, 364
 MORIKAWA, H., 317
 MORTLAND, M.M., 159, 161
 MORTON, G.A., 399
 MOTTE, C.J.B., 158
 MOUAT, H.A., 315
 MOUM, J., 418
 MUAN, A., 301
 MUELLER, M.H., 374
 MUMPTON, F.A., 107
 MURAD, E., 66
 MURAYAMA, S., 229, 230
 MURPHY, P.J., 395
 MURRAY, H.H., 67, 291, 292, 296, 297,
 367, 369
 NADAI, A., 220, 231
 NAGASAWA, K., 156
 NAGY, B., 236
 NAKAHARA, M., 304
 NATIONAL BUILDING RES. INST.
 C.S.I.R., 313
 NATIONAL BUREAU OF STANDARDS, 310
 NATIONAL LIME ASSOCIATION, WASHINGTON,
 D.C., 272
 NATIONAL RESEARCH COUNCIL, CANADA,
 202, 208
 NEAL, C., 66
 NEILSON, G.W., 216
 NELSON, B.W., 106, 112, 344
 NERETINA, A.Ya., 282
 NEUMANN, B.S., 376
 NEWMAN, A.C.D., 164
 NEWNHAM, R.E., 306
 NICHOLLS, G.D., 351
 NICHOLS, F.P., 278
 NICOLAS, J., 105
 NIKOLAEVA, S.K., 247
 NISHITA, H., 154
 NIXON, W.C., 397
 NOBLE, W., 298, 315, 376
 NOKKO, 310
 NORDIN, C.F., 46
 NORLING, L.T., 280
 NORMAN, L.E.J., 408
 NORRISH, K., 61, 103
 NORTHEY, R.D., 73, 74, 232
 NORION, F.H., 235, 298
 NYE, J.F., 41
 OAKLEY, D.M., 386
 OATLEY, C.W., 366
 O'BANNON, C.E., 274
 OBENSHAIN, S.S., 336, 338
 OBER, S.S., 390
 OBERLANDER, T.F., 23
 O'BRIEN, N.R., 120
 ODIN, C.S., 111
 ODOM, J.W., 188
 OERTEL, G., 82
 O'FLAHERTY, C.A., 273
 OINUMA, K., 347
 OJAKANGAS, R.W., 66
 OKADA, K., 317
 OLEJNIK, S., 160
 OLIVIER, J.P., 364, 385
 OLSEN, H.W., 120, 180
 O'NEILL, M.W., 182
 OOSTERBAAN, M.D., 275, 281
 OOSTERWYCK-GASTUCHE, M.C. van, 62
 ORMSBY, W.C., 348
 ORR, C., 385, 390
 OSBORN, E.F., 301, 303
 OSBORNE, V., 135, 353
 OSIPOV, V.I., 4, 87, 120, 121, 122,
 123, 140, 235, 240, 248, 364, 398
 OSTER, J.D., 189
 OTTEWILL, R.H., 211
 OVERBREEK, J.TH.G., 150, 187, 189,
 190
 PACHAKIS, M.D., 418
 PACKARD, R.G., 262
 PADOSLOVICH, E.W., 141
 PARCHE, J.V., 272
 PARHAM, R.F., 330
 PARIZEK, E.J., 125
 PARKER, J.C., 189
 PARKER, R.L., 52
 PARRISH, W., 327, 354
 PARRY, R.H.G., 222
 PASK, J.A., 307, 316
 PATRICK, D.M., 216
 PATTERSON, S.H., 296, 297, 376
 PAUL, A., 27
 PAULING, L., 95
 PAUS, K., 268, 277
 PEACH, P.A., 376, 386
 PEARSON, M.J., 82, 341, 351
 PEASE, R.F.W., 397
 PENCK, W., 23
 PENNER, E., 34, 125, 137, 174, 205,
 206, 207, 242, 275, 361
 PERCIVAL, H.J., 304
 PERRIE, L.A., 376, 386
 PERRY, C., 65, 125
 PERRY, E.A., 83
 PETERS, T., 296
 PETERSON, N.P., 65
 PETTIJOHN, F.J., 51, 58, 59, 74, 271
 PETROV, V.P., 282
 PETROVIC, A.M., 392

- PEZERAT, H., 136, 141
 PFEIFFER, H.G., 356
 PHILIP, J.R., 172
 PHILLIPS, F.C., 114, 344
 PHILIPSON, W.R., 18
 PHIPPS, T.B., 372
 PICQUET, P., 300
 PIDGEON, J.T., 200, 201, 406
 PITTMAN, E.D., 78, 125
 PLANCON, A., 334
 PLEYSIER, J., 353
 PLUNKETT, J.J., 279
 POLYZOPOULOS, N.A., 134
 PONCELET, A., 162
 PONCELET, G., 162
 POORMOAYED, N., 182
 POPPE, L.J., 332
 POSNER, A.M., 161, 163, 164, 395
 POST TENSIONING INSTITUTE, 201
 POTTER, P.E., 74
 POWELL, T.G., 77, 82
 POWERS, T.C., 263
 PRAKASH, S., 250
 PROCTOR, R.R., 252, 429
 PROST, R., 56, 141, 187
 PROTZ, R., 61, 153
 PROUST, D., 61
 PRYOR, W.A., 6/
 PUSH, R., 226, 428
- QUAKERAAT, J., 332
 QUICK, G.L., 86
 QUIGLEY, R.M., 3, 125, 336, 373
 QUIRK, J.P., 83, 115, 157, 161, 163,
 164, 353, 367, 369, 395, 398
- RADFORD, K.C., 309
 RADOSLOVICH, E.W., 103, 110, 358
 RAITBURD, Ts. M., 115
 RAMACHANDRAN, V.S., 269
 RAMBERG, E.G., 399
 RAMON, K.V., 159
 RANDOLPH, K.B., 281
 RANGE, X.J., 321
 RANKAMA, K., 28
 RAO, A.S., 428
 RAU, E.I., 140
 RAUSEL-COLOM, J.A., 164
 RAUTUREAU, M., 98
 RAVINA, I., 187, 278
 RAWLINS, S.L., 435
 RAY, K.W., 268
 RAZZAGHE-KARIMI, M., 56
 READES, D.W., 418
 REE, T., 225
 REED, M.A., 205
 REESMAN, A.L., 26, 44
 REEVE, R.C., 405
 REICH, T., 261
 REICHE, P., 54
- REIMERS, C.E., 382
 REINER, M., 221, 226, 228
 REINSON, G.E., 82
 REITEMEIER, R.F., 157
 RELTOV, B.F., 234
 RENDULIC, L., 232
 RENGARTEN, E.V., 85
 REYNOLDS, R.C., 67, 108, 334
 RHOADES, J.D., 181
 RHOTON, F.E., 65
 RICH, C.I., 157, 332, 336, 338
 RICHARDS, A.F., 242
 RICHARDS, B.G., 178
 RICHARDSON, E.V., 46
 RICHART, F.E., JNR., 222, 250
 RIDEAL, E., 385
 RIEKE, H.H., 69
 RIEKE, P.E., 398
 RILEY, C.M., 301
 RITCHIE, P.D., 144, 162
 RITCHIE, T., 299
 RITTER, W., 165
 ROBBINS, C.R., 318
 ROBBINS, E.G., 262
 ROBERT, J.L., 163
 ROBERT, M., 56
 ROBIN, G.de Q., 41
 ROBNETT, Q.L., 268
 RODDA, J.C., 26
 RODMAN, R.W., 281
 ROMINGER, J.F., 73
 ROSCOE, K.H., 182, 415
 ROSE, D.A., 25, 405
 ROSENBAUM, M.S., 79
 ROSENFARB, J., 245
 ROSENQUIST, I. TH., 115, 235, 236,
 242, 292, 348
 ROSENTHAL, G., 225
 ROSNER, J.C., 273
 ROSOLOWSKI, J.H., 307
 ROSS, C.S., 107
 ROSS, D.K., 212
 ROSS, G.J., 163
 ROSS, M., 135
 ROSS, S.J., JR., 185, 293, 387
 ROUSSEAU, J.M., 348
 ROWE, P.W., 418, 423
 ROY, D.H., 348
 ROY, M., 413
 ROY, R., 65, 106, 107, 112, 304, 336,
 344, 348
 RUBEY, W.W., 37
 RUFF, O., 144
 RUSSELL, E.W., 271
 RUSSELL, J.D., 100, 137, 354
 RUSSOW, J., 321
 RUTKA, A., 18
 RUTLEDGE, P.C., 73
 RYELEY, M.D., 409

- SABRY, M.M., 272
 SADEK, H., 169
 SAFIULLAH, A.M.M., 180
 SAHAMA, TH. G., 28
 SALEEB, A.F., 231
 SALES, R., 63, 65
 SALT, D.W., 169
 SALT INSTITUTE, 254
 SAMARASINGHE, A.M., 428
 SAMSON, H.R., 148, 271
 SAND, L.B., 343, 348
 SANDER, B., 361
 SANDERS, J.E., 30
 SANGREY, D.A., 18
 SANTOS, H. DE S., 140
 SANTOS, P. DE S., 105,
 SAUNDERS, M.K., 53
 SAWHNEY, B.L., 81, 153, 154, 157, 336
 SCHAFER, H., 165
 SCHEIDEGGER, A.E., 33
 SCHIELTZ, N.C., 319
 SCHIFFMAN, R.L., 290, 432
 SCHIROTZU, H., 112
 SCHMERTMANN, J.H., 401, 426
 SCHNEIDER, W., 275
 SCHOEN, R., 341
 SCHOFIELD, A.N., 216, 410
 SCHOFIELD, R.K., 148, 173, 187, 189,
 205, 271
 SCHRAMM, L.L., 332
 SCHWIBEL, J.R., 399
 SCHULLER, K.H., 309
 SCHULTZ, L.G., 108, 296
 SCHULZE, H., 151, 330
 SCHUMM, S.A., 36
 SCHUSTER, R.L., 30
 SCOTT-BLAIR, G.W., 221
 SCOTT DENATALE, J., 244
 SCOTT, J.D., 211
 SCOTT, J.S., 430
 SCOTT, R.F., 229, 418
 SEARLE, A.B., 144, 146
 SEED, H.B., 190, 252, 408
 SELA, J., 367
 SELLARS, B., 77
 SELMER-OLSON, R., 34
 SELSING, J., 309
 SENGUPTA, S., 67
 SENNETT, P., 364, 385
 SEREDA, P.J., 266, 281
 SERGEYEV, Y.M., 4, 64, 119, 120,
 240, 376
 SERRATOSA, J.M., 164, 348
 SETHI, A.J., 246, 249
 SHAINBERG, I., 179
 SHANNON, E.V., 293
 SHAPIRO, L., 348
 SHARPE, C.F., 31
 SHARPE, J.W., 162
 SHAW, M.D., 403
 SHEARIN, A.E., 358
 SHEELER, J.B., 254, 280
 SHELDON, R.W., 399
 SHEN, C.K., 262, 263
 SHEPARD, R.E., 278
 SHEPPARD, R.A., 62, 78
 SHERIDAN, R.E., 74, 80
 SHERIF, M.A., 183
 SHERMAN, G.D., 58, 62
 SHERWOOD, P.T., 263, 264, 265, 409
 SHIBATA, T., 229, 230
 SHIDELER, G.L., 386
 SHIELDS, D.H., 423
 SHIELDS, D.R., 246
 SHOCKLEY, W.G., 419
 SHORT, A., 301
 SHRIVE, N.G., 316, 317
 SIDDIQUI, HASNUDDIN, M.K., 148
 SIEBERT, J.E., 398
 SILLS, G.C., 427
 SILLS, I.D., 391
 SIMONS, D.B., 37, 38, 39
 SINGH, A., 32, 430, 433
 SKALNY, J., 299
 SKEMPTON, A.W., 32, 33, 34, 71, 73,
 74, 222, 224, 232, 233, 234, 413
 SKINNER, A.E., 246
 SKINNER, B.J., 25
 SKIPP, B.O., 403
 SKOPEK, J., 410
 SLADE, P.G., 141, 358
 SLATE, F.O., 254
 SLAUGHTER, M., 306, 358
 SLEYTR, U.B., 372
 SLOANE, R.L., 120
 SLOCOMBE, B.C., 252
 SMALLEY, I.J., 34, 40, 120, 243
 SMART, P., 119, 120
 SMECK, N.E., 86
 SMITH, A., L., 346, 348
 SMITH, A.N., 310
 SMITH, D.K., 301
 SMITH, J.V., 110, 339
 SMITH, R., 212
 SMYKATZ-KLOS, W., 342
 SNETHEN, D.R., 183
 SNOWDON, L.R., 86
 SOCIETY FOR ANALYTICAL CHEMISTRY,
 379, 380
 SODERBLOM, R., 27, 234, 242
 SOKOLOV, V.N., 4, 87, 120, 121, 122,
 123, 140, 247, 248, 364, 398
 SOLOMON, D.H., 159
 SOMASIRI, S., 156
 SOPER, A.K., 170
 SORBY, H.C., 69
 SPIVAK, G.V., 140
 SRIDHARAN, A., 190, 232, 238, 428

- STANDARD, J.C., 135
 STARKEY, J., 29, 374
 STARZEWSKI, K., 401
 STATENS JARNVARGARS GEOTEKNIKA
 KOMMISSION, 33
 SIEILA, D., 18
 STEPHEN, I., 112, 335
 STERN, O., 148, 150
 STEWARD, R.G., 394
 STEYN, A.P., 217, 283
 STONE, W. E. E., 171
 STRAHLER, A.N., 24, 33
 STUBICAN, V., 348
 STUDER, H.P., 149
 SUGDEN, D.E., 42
 SUKLJE, L., 229
 SULLWOLD, H.H., JR., 74, 75, 76
 SUMNER, G.G., 348
 SUQUET, H., 108, 109, 136
 SVERDRUP, H.V., 46
 SWALLOW, H.T.S., 296
 SWENSON, E.G., 312, 313
 SWIFT, D.P.J., 386
 SYERS, J.K., 88

 TABER, S., 204, 206
 TAIT, J.M., 63
 TAMURA, T., 157, 336, 338
 TAN, K.H., 343
 TAN, T.K., 229, 230
 TANNER, C.B., 385
 TARZI, J.G., 61, 153
 TAIVENAS, F., 430, 434
 TAYLOR, A., 374
 TAYLOR, D.W., 33, 70
 TAYLOR, J.M., 354
 TAYLOR, T., 229, 232
 TCHALENKO, J.S., 364
 TCHOUBAR, C., 334
 TEAGUE, L.S., 62, 64
 TEHOUBAP, C., 98
 TELLER, E., 387, 394
 TELLERIA, M.I., 104, 338
 TER-STEFPHANIAN, G., 229, 234, 410
 TERWILLIGER, G.R., 309
 TERZAGHI, K., 13, 34, 68, 69, 70, 115,
 189, 232, 237, 408, 424, 425, 428
 TESORIERE, G., 267
 THENG, B.K.G., 161, 293
 THIELEPAPE, W., 165
 THIESEN, A.A., 332
 THIESSEN, P.A., 148
 THOMAS, J.B., 125, 157
 THOMAS, R.K., 211
 THOMPSON, C.D., 111, 208, 373
 THOMPSON, G.L., 332, 340, 341
 THOMPSON, M.R., 208, 268
 THOMSON, G.H., 253
 THORN, C.E., 25
 THORNES, J.B., 24

 TILLER, K.G., 157
 TILLY, C.R., 386
 TITKOV, N.I., 274
 TODRES, N.A., 386
 TOMPKINS, R.E., 78, 364
 TOOLEY, F.V., 311
 TORRANCE, J.K., 234
 TOTH, S.J., 157
 TOUILLAUX, R., 354
 TOURTELOT, H.A., 362
 TOVEY, N.K., 119, 367
 TOWE, K.M., 66
 TOWNSEND, F.C., 419
 TRANSPORTATION RESEARCH CIRCULAR,
 267
 TRAXLER, R.N., 257, 261
 TRIGG, C.F., 36
 TREMBLAY, M., 434
 TRUNZ, 327
 TSONG, I.S.T., 372
 TUCK, J.J., 212
 TUDDENHAM, W.M., 347
 TUNCER, E.R., 351
 TURNER, F.J., 220, 373, 374
 TWIDALE, C.R., 24
 TYRELL, G.W., 1
 TYUTYUNOV, I.A., 205

 UDAGAWA, S., 306, 315
 UENO, M., 231
 UNIFIED SOIL CLASSIFICATION
 SYSTEM, 5
 U.S. ARMY CORPS OF ENGINEERS,
 33, 204
 U.S. ARMY ENGINEER WATERWAYS
 EXPERIMENT STATION, 12
 U.S. BUREAU OF PUBLIC ROADS, 2
 U.S. DEPT. AGRICULTURE, 15, 17,
 18, 40, 134
 U.S. WATERWAYS EXPERIMENT STATION,
 274

 VAN AARDT, J.H.P., 313
 VAN BAREN, F.A., 91
 VANCE, A.W., 399
 VAN DER GAAST, S.J., 355
 VAN DER MAREL, H.W., 348, 376
 VAN DER MERWE, D.H., 182, 183,
 201, 254
 VAN OLPHEN, H., 119, 148, 150, 152,
 158, 161, 235
 VAN OOSTERWYCK-GASTUCHE, M.C., 55
 VAN VLACK, L.H., 299
 VARNES, D.J., 31, 32
 VASILEV, A.M., 410
 VAUGHAN, P.R., 246
 VEIHMEYER, F.J., 392
 VELDE, B., 56, 61, 65, 110, 111
 VENKATAPPA, RAO, G., 232
 VERINA, V.K., 83

- VERMA, A.R., 95
 VERSTAPPEN, H. TH., 22
 VERWEY, E.J.W., 150, 187, 189, 190
 VINAS, J.M., 358
 VIOLANTE, P., 63
 VISSER, S., 313
 VIVATRAT, V., 430
 VOGAN, R.W., 125
 VOGELER, P.E., 263
 VOIGT, G.K., 81
 VON ENGELHARDT, W., 79
 WADA, K., 63, 157, 158, 335, 336, 352, 376
 WAGNALLS, (AND FUNK), 219
 WAGNER, A.A., 12
 WAGNER, D., 357
 WAHLBERG, J.S., 161
 WALDORF, D.M., 65
 WALKER, C.T., 80
 WALKER, F.C., 64, 109, 431
 WALKER, G.F., 334, 335
 WALL, G.J., 66
 WALSH, P.F., 201
 WALTON, T., 206, 207
 WANG, F., 311
 WARKENTIN, B.B., 120, 189, 403, 408
 WARNE, S., 342
 WARREN, B.E., 169
 WARSHAW, C.M., 335, 336
 WASHBURN, A.L., 125
 WASHINGTON, H.S., 50
 WATANABE, T., 317
 WEAVER, C.E., 55, 66, 77, 78, 113, 334
 WEAVER, R.M., 52
 WEBER, J.N., 304
 WEBSTER'S THIRD INTERNATIONAL
 DICTIONARY, (1961), 22, 310
 WEERTMAN, J., 41
 WEINERT, H.H., 53
 WEISS, A., 147, 160, 161, 304
 WEISS, L.E., 220, 348, 373, 374
 WENDLANDT, W.W., 341
 WESLEY, L.D., 418
 WEST, J.M., 252
 WESTFALL, D.G., 157
 WEYL, D., 309
 WEYL, W.A., 143, 145
 WHITAKER, H., 225
 WHITE, A.F., 62
 WHITE, J.L., 105, 303, 347, 348
 WHITE, J.W., 211
 WHITE, W.A., 75
 WHITE, W.B., 65
 WHITMAN, P.V., 401
 WHITTACKER, E.J.W., 64, 106
 WHITTON, J.S., 248
 WICKHAM, C.S., 351
 WICKS, F.J., 64
 WIEBE, H.H., 406
 WIECKOWSKI, T., 105
 WIEGNER, G., 155
 WIEWIORA, O., 105
 WIKLANDER, L., 158
 WILCOX, P.D., 315
 WILDING, L.P., 86, 88
 WILLIAMS, A.A.B., 182, 200, 201,
 205, 406
 WILLIAMS, A.N., 319
 WILLIAMS, P.M., 281
 WILLIAMSON, W.D., 235, 236
 WILLIAMSON, W.O., 75, 298
 WILKINS, D.E., 391
 WILKINSON, W.B., 404
 WILSON, M.D., 78, 125
 WILUN, Z., 401
 WINCHELL, A.N., 97
 WINDLE, W., 397
 WINDOM, H., 83
 WINKELMOLEN, A.M., 361
 WINSLOW, E.H., 356
 WINTERKORN, H.F., 251, 261
 WITTKE, W., 243
 WONG, BOON, 307
 WONG, Y.K., 119, 367
 WOOD, A., 33
 WOOD, C., 393
 WOOD, D.M., 410
 WOOD, L.E., 216
 WOODBINE CORPORATION, 267
 WOODBURN, J.A., 201
 WOODHAMS, F.W.D., 137
 WOODWARD, R.J., 434
 WOOSTER, W.A., 355
 WRIGHT, A.F., 307
 WRIGHT, H.J.L., 150
 WRIGHT, P.J., 268
 WROTH, C.P., 201, 216, 229, 410
 WU, T.H., 417
 YAMANOUCHI, T., 254
 YARIV, S., 106
 YATSU, E., 23
 YODER, H.S., 79, 110, 305, 339
 YONG, R.N., 120, 242, 246, 403, 408
 YOSHIDA, T., 364
 YOSHIMI, Y., 222
 YOSHINAGA, N., 114, 354
 YOUNG, F.D., 18, 275
 YOUNG, R.C., 83
 ZACHARIASEN, W.H., 113
 ZALAZNY, L.W., 215
 ZEMANY, P.D., 356
 ZHUCHKOVA, A.A., 85
 ZIENKIEWIZ, O.C., 70
 ZOELLNER, A., 309
 ZUIDBERG, H.M., 242
 ZUSSMAN, J., 106, 347
 ZWORYKIN, V.K., 365

SUBJECT INDEX

- Accessory minerals, 50
- Acid conditions and clay mineral formation, 56, 61, 105
- Active layer, 201
- Activity, classification of clays, 224
- , defined, 224
- , mentioned, 406, 274, 409
- Additives, frost heave control by, 275
- , soil stabilization and, 254-274
- Adsorbed water, detected by DTA, 343
- see also water
- Adsorption, 143, 154, 157, 171, 158, 160, 171
- , charge on colloidal particles and, 147
- , isotherm of illitic clay, 388
- , methods of surface area estimation, 387
- , negative, 157
- , on amorphous compounds, 145, 157
- , potential, 171
- Aerial photographs, 36
- , before and after slide, 35
- Affine strain, 220
- Ageing, in clay-water systems, 226, 235, 237, 240, 242
- , of soil cement, 263
- Agglomeration of colloidal suspension, 152
- Agglomerations, 174-176, 180, 238, 240, 374, 375, 382
- Aggregations, breakdown of, 329-331
- , in soil fabric, 115, 120, 124, 129, 180, 190, 243, 404
- , sorting and, 67
- A-horizon, 15
- Air-dry sample, X-ray analysis of, 332
- Alcohol, and flocculation of colloids, 152
- A-line, 13-14
- Alkali-aggregate reactions, 147, 312-313
- Alkali conditions, affect on lime soil stabilization, 272-273
- , clay mineral formation and, 56, 64
- Allogenic, 78
- Allophane, 62, 63, 114, 157, 158, 171, 348, 376,
- Alluvial channels, bed roughness in, 37
- Alumina,
 - , colloidal, 148
 - in refractories manufacture, 303
 - , in soil stabilization, 272
 - , production, 285, 295
 - , solubility, 55-56
- Aluminium, and boron sorption, 67
- , as coating in SEM work, 367
- , in plants, 57
- , in silicate structures, 95
- , production, 285, 295
- , to oxygen radius ratio, 100
- Aluminous compounds, removal prior to mineral analysis, 330
- Amesite, 106
- Amorphous constituents, 91, 242, 272, 346, 347, 348 - see also non-crystalline
- , aggregate reactions and, 313
- , exchange capacity and, 154, 157
- , hydrothermal association of, 63
- , identification, 323
- , moisture expansion and, 310
- , removal of, 329
- , surface of, 145
- , thermogravimetry and, 344
- , use of term, 113
- , X-ray analysis and, 328
- Amphiboles, 61, 64, 98
- Amphibolite, 50
- Amphoteric compounds, 160
- Analysis, arrangement and orientation, 361-374
- , engineering, 401-430
- , mineralogical, 323-351
- , particle size, 379-386
- , physical, 361-392
- , shape of minerals, 374-379
- , X-ray diffraction, 323-341
- Anauxite, 105
- Andalusite, 50
- Andesite, 50
- Angle of internal friction, 412
- shearing resistance, 231
- Anion exchange, 158
- Anions in ionic structures, 93, 94
- Anorthite, 311
- Antidunes, 38, 74
- Antigorite, 106, 344
- Antithixotropy, 226
- Apatite, 50
- Apparent cohesion, 231
- Aragonite, 95
- Archean rocks, 51-52
- Argillaceous, 1
- Argillites, 1, 79
- Arrangement and orientation in clays, analysis of, 361-374
- Asbestos, 98
- Asphalt, as soil stabilizer, 257-261
- Association of particles in clay suspension, 154
- Assyrians, 285
- Astigmatism, 363
- Atoms, in crystals, 92
- , vibration frequencies, 346-347
- Attapulgite, 290, 297
- , permeability and, 179
- , plasticity affected by, 224

- Atterberg limits, 12, 262, 263
Authigenesis, 58
Authigenic minerals, 61, 78, 126-128, 390
Auxiliary pre-treatments, 324, 329-339
Axes, crystallographic, 92-93
Azonal soils, 15
Azovskite, 114
- Babylon, 285
Background, on X-ray diffraction pattern, 324, 332
Bacteria, 125
Ball and pillow structures, 74
Ball clays, 14, 296-297
Basal reflections, 326, 327
--, enhancement of, 332
--, integral series of, 333, 334
--, non-integral orders, 333
--, variation in R.H. and, 333
- spacing, 93
--, in clay mineral classification, 103
--, in smectites, 107
--, of vermiculite, 109
- surfaces, and adsorption, 157
Basalt, 50, 62, 64, 66
Base exchange, in electron microscopic investigation, 371
--, of illites, 111
--, of kaolinite-serpentine group, 105
--, of smectites, 107
--, of vermiculites, 108 - see also cation exchange, exchange reactions
Base level, 22
Bauxite, 14
-, origin and uses, 295
-, refractory raw material, 303
Bearing capacity, 401
- tests, 413
Bed roughness in alluvial channels, 37
Beidellite, 61, 107
-, recognition, 334
Beneficiation of raw clay, 289
Benitoite, 98
Benthos, 75
Bentonites, 290, 293-295 - see also smectites, montmorillonite
-, compression index, 424
-, defined, 293
-, industrial uses, 294
Bernoulli's principle, 40
Beryl, 98
B.E.T. method, 387
B-horizon, 15
Bingham plastics, flow curve, 226
--, mechanical analogue, 228, 229
Biological agencies, 30, 32, 57, 66, 115, 125
Biotite, - see also mica, 51, 56, 57, 61, 110
- Birefringent behaviour and clay mineral orientation, 363
Bitumen, defined, 257
-, soil stabilizers, 257-258, 261
Bloating clays, 301, 307, 351
Boehmite, 295, 296
Boltzmann distribution, 150
Bonding, and ion exchange, 155
-, and structure, 93-95
-, brittle, 234
Boron, 67-68
Boulder beds, 51
-, clay, 2, 42, 49, 51, 379
Bragg, angle, 326
-, equation, 324, 325, 327
--, geometrical illustration, 325
Breaking strength, 221
Breccias, 51
Brick manufacture, winning and processing clay for, 292
Bricks, 298, 310, 311, 312
Britain, ceramic mixes to resist moisture expansion, 311
-, fullers earth, 297
-, kaolin deposits, 63, 288
-, lime stabilization in, 267
Brittle bonds, 234
- components, 243
- fracture, 308
- materials, 222
- micas, 103, 104, 111
Broken bonds and ion exchange, 155
Bronsted acids, clay minerals as, 159
Brownian movement, 150, 382
Brucite, in clays, 92
- like layers, 61, 66, 100
BT-cut quartz crystal, as sample mount, 332
Bulk density, 392
--, on compaction, 428
--, soil stabilization and, 252
- modulus, 223
--, and moisture expansion, 310
Burial of sediment, 69, 73
-, mineralogical change and, 77, 78
Calcined clay, 303, 313
Calcite, 92, 95
Calcitic lime, 268
Calcium, as exchange ion on montmorillonite, 107
-, in plants, 57
- chloride in stabilization, 254
- hydroxide, 264, 271, 273
- silicate hydrates, 272
Calgon, 159
Camera, X-ray, 326-328
Canada balsam, 363
-, control of frost heave in, 275
-, ground movement near elm tree, 177
-, quick clays in, 34, 35, 177, 199, 227, 242, 373

- Capillarity, and moisture level, 405 -
see also moisture
- Capillary potential, 171, 178
- water, 172 - see also moisture
- Carbonates in clays, 92
- , in brick clays, 296
- , removal prior to mineral analysis, 329
- Carbonation, in lime soil
stabilization, 271, 272
- Carboniferous, 75
- , seat earths or under clays, 296
- Carbowax 6000, 362, 391
- Cathode ray tube in scanning electron
microscope, 365, 366
- Cation, coordination, 100, 101
- fixation, 61
- , in interlayer positions, 104
- proxying in silicates, 100
- , role in ionic structures, 93, 94
- screening, 144
- exchange, 154-158 -- see also base
exchange, exchange reactions
- capacity of illites, 111
- , of smectites, 107
- , of vermiculites, 108
- , determination of, 154, 351
- , clay mineral transportation and,
65-66
- , in interlayer complexes, 337
- , rate of 155, 156
- Cement aggregate reaction, 313
- alkalis, 299
- compositions in lime-alumina-silica
system, 301
- in soil stabilization, 254, 261,-266
- manufacture, 290, 295, 351
- , oilwell, 300-301
- Cementitious agents, 75, 129, 190, 254
- , in consolidation, 71
- , removal of, 329-332
- mechanism in soil cement, 265
- of soil stabilization, 271-273
- Centrifuge, 385
- Ceramic classification, 14
- , articles used by archaeologists,
285
- classification of clays, 13, 14
- industry, forming methods, 298
- , major products, 297
- mixture for classical products, 297
- Cesium sorption, 65, 157
- Chamosite, 106
- Champlain sea sediments, 226
- Changes in composition and content of
pore solutions on burial, 78-79
- on firing clays, 304-307
- Characteristic radiation, 326
- Charge balance, 152
- density, 109, 147, 155
- on layers, 103, 104, 107, 110, 152
- on particles, 143, 147
- reversal on colloids, 147
- Chemical analysis, 348, 351
- composition of clay, shale, slate
and schist, 54
- potential and moisture interaction,
172
- processes at normal temperatures,
56-63
- at elevated temperatures, 63-65
- in clay mineral formation, 54-65
- reaction, rate of, 54
- China clay, 14, 292
- production in Cornwall, 291
- Chlorite, 59
- Chlorites, 50, 64, 67, 98, 103, 112,
382
- , and ammonium fixation, 156,
- and sepichlorites, compositional
relationships, 106
- , attacked by acids, 329
- , burial, affect on, 77
- , distinction between 7\AA and 14\AA -,
distinction from kaolinites, 335
- , DTA of, 344
- , formation, 66
- , infrared analysis of, 347
- , interlayer complexes with, 335-338
- , resemblance to vermiculites, 109,
112
- , swelling, 61, 112, 185, 335
- C-horizon, 15
- Chromatic aberration, 363
- Chrysotile, 106, 344
- Classification, of clay - see clay
classification
- of intermediate and fine-grained
sediments, 2
- of landslides, 31
- of materials - see rheological
classification of materials
- of phyllosilicates, 103, 100-112
- of silicates, 98-112
- of soil, pedological, 15-18
- Clay, classification of, 1-14, 224,
233
- , composition, 53, 91-142
- , conversion to shale, 72
- , definition of, 1
- , drying of, 367-369
- , durability of clay-containing
materials, 310-314
- , economic raw material, 290-297
- , firing of, 304-307
- , major uses in U.S.A., 398
- , marine, 66, 67, 115, 227, 242
- , membrane electrode, 155
- , mineralogical changes in after
deposition, 77, 78
- Clay minerals, authigenic, 49
- -, formation, 52-65

- , identification, 93, 324, 326, 328, 332, 335, 338, 343, 344
- , in sedimentary cycle, 65-68
- , reaction with lime, 271
- , some thermograms of, 345
- , X-ray reflections from, 336, 337
- , miscellaneous industrial uses, 285
- , organic complexes, 161
- , orientation in, 361-374
- , origin and evolution of, 49-89
- , parent material of, 49-52, 57, 59
- , particle size range, 1, 143
- , physical changes in, after deposition, 74-75
- , plasticity affected by, 224
- , porosity of, 390
- , post-depositional changes in, 68-69
- , processing, 289-290
- products, 297-303
- raw materials, 290-297
- , strength of materials made from, 308-310
- till, 2
- , winning and pre-treatment, 288-290
- Clays as materials, 285-321
- Claystones, 1
- Cleavage, 98
- Clintonite, 100, 111
- Close packing, in clay-water system, 235, 238
 - in crystals, 94, 95, 98, 110
 - in soil fabric, 115
 - of spheres, 94
- Cobalt sorption, 157
- Coefficient of compressibility, 424, 425
 - consolidation, 69, 200, 424, 428
 - internal friction, 231
 - lateral stress, k , 426
 - permeability, 69, 178, 403, 404, 424
 - , sorting, 381
- Cohesion, 231-232, 238, 267
- Co-ions, 150
- Colloidal clays and consolidation, 424
 - constituents in DTA, 343
 - dimensions, 143, 361
 - micelle, 148
 - particles, and ion exchange, 154
 - particles, balance of charge on, 153
 - particles, properties, 143-145
 - properties in raw clay beneficiation, 289
 - silicate, definition, 143
 - state, definition, 143
 - suspension, 55, 145-153
- Colloids, and ion exchange, 153-161
 - , mentioned, 57
 - , macromolecular, 147
 - , migration in soils, 125
- Coma, 363
- Combination bands, in infrared spectra, 347
- Compaction, 69-74, 75, 251, 253, 401, 428-430
 - , defined, 68
 - , degree of, 430
- density-moisture content relations of soils, 180-181, 252
- and change in composition of pore solutions, 79
- and lime stabilization, 270
- and soil stabilization, 252, 253, 266
- relative, 429-430
- structures, 93
- test, 428, 429
- Competence, 36
- Complexes formed by clays, 161
- Composition of clays, 53, 91-114
 - and fabric of clays, 91-142
 - of soils and argillaceous rocks, 91
- Compressibility, 223, 425
 - , defined, 424
 - tests, 401
- Compression index, 423
 - primary, 426
 - secondary, 426
 - unconfined, 252, 419
- Compressive forces, 219
- Concrete aggregates, 303, 311, 312
 - deterioration, 311
- Cone penetrometer, 409, 410
 - , penetration testing, 413
- Cones, in ceramic classification, 14
- Consistency, in soil stabilization, 254
 - , of ceramic mix, 298
- Consolidation, 69-74, 75, 191, 253, 404, 421-428
 - , and heave potential, 184-185
 - , and mineralogical changes, 77-78
 - apparatus, 422
 - , defined, 68
 - , model analogy, 70
 - press, 421
 - , primary, 426
 - , secondary, 426
 - tests, 421-428
 - , X-ray technique and, 427
- Consolidometer-schematic, 421
 - , hydraulic, 423
- Constant head permeameter, 404
- Contours of slab-on-ground movements, Regina, Sask., 184
- Coordination, 44, 100, 169, 170
- Cordierite, 50, 311
- Cornwall, England, china clay production, 291
 - , china clay deposits, 288
 - , china clay deposits origin, 292
- Corundum, 59, 305, 307

- Coulomb forces, 93
- Coulomb's law, 231, 238, 411
- Coulter counter, 386
- Counter ions, 148, 152, 153, 158
- Covalent bonding, 93
- Creep, 236, 238, 310, 402, 410, 418, 426, 427, 428
- Cristobalite, 114, 304, 306
- , $\alpha \rightarrow \beta$ transition, 306-307
- Critical point method, 369, 391
 - surface, 32
 - tractive force, 37
 - void ratio, 182
- Cronstedtite, 8
- Cross-sections of valley during geomorphic cycle, 22
- Crust, thickness, 50
- Cryoprotectants, 368
- Cryptocrystalline minerals, in aggregate reactions, 313
- Crystal chemistry and moisture uptake, 185
 - , investigated by infrared analysis, 348
 - of silicates, 98-100
 - faces and Miller indices, 93
 - size effect on X-ray diffraction pattern, 327
- Crystalline components, 91
 - , affected by burial, 77
- Crystallography, 92-93
- Cubic close packing, 94, 95
- Cumulative particle size analysis, 379, 381
- Currents, 29, 67
- Cut-back, 258
- Cycle of erosion, 22
- Cyclosilicates, 98
- Darcy's law, 69, 70, 178, 403, 405
- Debye-Scherrer photographs, 327, 339, 373
- Deflocculated system, 113, 235
- Deflocculating agents, 57, 276, 298, 329
- Deformation, modulus of, 223
- Degraded minerals, 65, 66, 156
- Degree days, 201
 - of consolidation, 426
- Dehydroxylation of clay minerals, 304
- Density determination, 391-392
 - currents, 30
 - of clay minerals, 381
 - optimum, 401
 - moisture relations, 252, 253, 429
- Denudation, 26
- Deposition, 65
- Depth, focus in microscopes, 363, 366
 - of burial estimation, 73
- Derivation slopes, 24
- Desiccated layers, 72, 73
- Deterioration, 310, 311
- Detrital clay minerals, boron content, 67
 - , orientation of, 75
- Deviator stress, 411
- Dewatering of clays, 289
- Diagenesis, 30, 49, 77, 120, 240, 266, 364
- Diaspore, 92, 295, 296
- Dickite, 105, 336, 376
- Dielectric constant and colloidal suspensions, 150, 151
- Differential intersalination, 335
 - , scanning calorimetry, 341, 342, 344
 - , settlement, 68, 167
 - , thermal analysis (DTA), 341, 344
 - , factors affecting, 342
 - , instrumentation, two arrangements for, 342
 - , mentioned, 323
 - , quantitative, 343
 - , sensitivity, 341
- Diffraction, defined, 323, 324
 - , intensity of, 339 - see also X-ray
 - , order of, 324
 - , of light, 363
- Diffractometer, 326, 328
 - , in fabric studies, 374
 - , reflection geometry, 327
- Diffuse double layer, 148, 152, 153, 187-191
- Dikes, 49
- Dilatant systems, 226, 235, 237, 238
- Dilation, 220
- Octahedral structure, 61, 105, 110, 112
 - , defined, 104
 - , recognition, 104, 339
- Dipole nature of water molecule, 93 - see also water
- Direct shear test, 410, 413-415
- Disaggregation and removal of cementitious matter, from clay soils, 329-332
- Discharge, defined, 36
- Discussion of strength and rheology, 234-243
- Dislocations, motion impeded by grain boundaries, 308
- Disperse phase, 145
- Dispersing agents, 56, 243, 276, 298, 311, 331, 375
- Dispersion for electron microscope study, 374, 376
 - medium, 145
 - , particle-size analysis and, 382
- Displacive phase transformations, 306
- Distortion, 220
- Divers, in particle-size analysis and, 385

- Dolomite, in aggregate reactions, 311, 312
- , in clay, 92
- , in soil stabilization, 268, 270, 271
- Donnan membrane theory, 79, 158, 187
- Double direct shear, 414, 415
- layer theory, 148, 152, 153, 187-191
- Draglines, 186, 188
- Drained triaxial test, 416
- Dried crusts and consolidation, 72, 73
- Drill-lime stabilization, 267
- Dry strength of ceramic articles, 299
- Ductile, 222, 223
- Durability of clay-containing materials, 310-314
- soil cement, 262, 263
- d-values, 208, 325-328, 333, 339
- , of dioctahedral and trioctahedral minerals, 339
- Earth, the, 21
- Edges of clay minerals, 144-145
- , positive charge on, 148, 149, 152
- Edge-to-edge arrangement, 115, 120, 240
- face arrangement, 115, 152, 240
- Effective stress, 69, 71, 232, 238, 413, 428
- Efflorescence, 296, 311
- Egypt, 285
- Elasticity, 223
- model, 227
- , plasticity and viscosity, 223-227
- Elastic limit, 221
- Elastico-viscous model, 228
- Electrical methods for measurement of soil moisture, 403
- , for measurement of soil suction, 405
- Electric charge on particles, 144, 147, - see also charge
- Electrochemical properties of clays, 155
- Elektrokinetics, stabilization by, 274
- Electrolytes, 67, 151, 152
- Electron, beam penetrating power, 369
- diffraction, 323
- micrographs, 116, 118, 149, 377, 378
- , granularity, decrease of, 371
- microscope, 148, 323, 361, 364-372, 374, 385
- transfer, 55
- Electro-osmosis, 145, 274, 289
- Electrophoresis, 145
- Electrostatic forces, 43, 154, 157
- Elemental composition, 323, 351
- Elutriation, 289
- Eluviation, 56
- Emulsion, 258
- Endothermic peaks on thermogram, 244, 341, 343, - see also differential thermal analysis
- Energy and moisture interaction, 171
- Engineering analysis of soils 401-434
- classification of soils, 5-14
- England, Cornish kaolin, 288
- , Fullers earth, 297 - see also Britain
- Enthalpy, 54, 342
- Eocene, 75
- Epipedon, 15
- Epitaxy, 49, 55, 266
- Epoxy resin, used in preparation of microscopic thin sections of clay, 363
- Equipment for winning clays, 286-288
- see also clay
- Equivalent spherical diameter, 381
- Eras, geological, 21
- Erosion, 22, 24, 65, 263
- and transportation, 29-42
- by ice, 40-42
- by mass movements, 30-36
- by wind, 39-40
- in channels, 36-39
- Ethylene glycol, 108, 328, 333
- Ettringite, 263
- Evansite, 113
- Evaporated gold, and dissipation of electric charge, 366
- Exchange, forces, 93
- reactions, 4, 65, 66, 79, 105, 107-111, 153-161, 186, 224, 261, 267, 271, 323, 331, 337, 351
- Exothermic peaks on thermogram, 341, 343, 344 - see also differential thermal analysis
- Expansive minerals, 61, 65, 66, 107, 108, 112, 185-191, 334-338
- soils, 182-185, 253-254, 274
- External surface of clay minerals, 387
- Extinction between crossed polarizers, 364
- Extrusive rocks, 49
- Fabric, axes, 361
- elements, 114, 125, 189, 236, 361
- , ceramic body and, 298
- , clays and, 71, 75, 114-134, 153, 371
- , compaction and, 252
- , hydrothermal action and, 64
- , kaolin deposits and, 64, 292
- , moisture interaction and, 174, 179, 404, 408
- , strength and rheology and, 235, 237, 238, 240, 242
- , swelling pressure and volume change and, 189, 190

- Face-to-face arrangement, 113, 120, 152
- Factors of safety, 33
 - soil formation, 56
- Failure, 219, 231
- Faults and slides, 34
- Feldspars, 50, 77, 98, 306
- Feldspathoids, 50
- Fick's law, 405
- Fire clay, 14, 296, 303
- Firing of clays, 304-307
- Fissility and burial, 75
- Fixation of ions, 156-157
- Flint clays, 14
- Flocculation, clay minerals and, 67, 267
 - colloidal suspension and, 145, 151, 152
 - fabric and, 75, 113
 - permeability and, 181
 - thixotropy and, 226
- Flow curve, 225, 226
 - laminar, 225, 234
 - properties of colloidal suspensions, 152
 - rate, 179-180, 191
 - regime, 37-39
 - slides, 31, 234, 241
 - turbulent, 225, 226
- Fluidity, 225
- Flume experiments, 37
- Fluorine proxying for oxygen, 100
- Flux, 297, 303, 306, 336
- Fly ash, 267, 273
- Formation of clay minerals, 52-65
 - see also clay
- Forsterite, 307, 344
- Foundations, heave of, 185 - see also heave
- , settlement of, 421
- Fourier method, shape analysis by, 376, 379
- Fourier transforms, 334
- Free oxides, 351
 - radical interaction, 55
- Freeze drying, 367-369, 391
 - thaw, 125, 129, 133
- Freeze-etch technique, 369
- Freezing index, 202, 275
 - , and moisture movements, 368
 - and soil improvement, 209
 - point depression, 206
- Freezing zone, 206
- Fresh-water deposits, fabric, 115 - see also fabric
- Freundlich adsorption isotherm, 158
- Friction, in strength and rheology, 238
 - , internal, 231, 412
- Frost action, 40, 53, 54, 167, 201-209
 - Frost action and overconsolidation, 203-204
 - heaving, modification of, 261, 274, 275
 - penetration, 201
 - , soil fabric and, 125
 - , susceptible soils, 204-205
 - Froth floatation, 289
 - Frozen soil, 91
 - Fuller's earth, 297
 - Fundamental absorption bands, in infra-red spectra, 346
- Garnet, 50, 98
- Gas hydrates, 74, 80
- Gehlenite, 311
- Gels, 61, 113, 145, 343
- Generalized Newtonian liquid, 226
- Geological classification of clays, 1-4
 - time, 21, 51
- Geomorphic cycle, valley cross sections, 22
- Geomorphology, 22-25
- Georgia kaolin, origin, 292
 - , production, 291
- Germany, use of lime stabilization in, 267
- Gibbs free energy, 54
- Gibbsite, in bauxite, 295
 - sheets in clay minerals, 61, 100
- Gilgai structure, 182
- Glacial till, 3
- Glaciers, valley, 29, 41
 - surges, 41
- Glass atomic configuration, 113
 - , fired product, 306, 307
 - , strength and, 308
- Glassy phase, aggregate reactions and, 313
 - , mechanical properties and, 309, 310
 - , moisture expansion and, 310
- Glaucite, 66, 111, 376
- Glycerol, 108, 109, 328, 333, 334, 336, 388, 389
- Gneiss, 50
- Geothite, 42
- Gold, colloidal on edges of kaolinite, 148
- Graded stream, 22
- Grading, use of term in geology and engineering, 379
- Grain shape, 70
 - size, clay, 1
 - , ice lens growth and, 204
- Granites, 50
- Granodiorites, 50
- Gravels, 51
- Gravimetric method, of measurement of soil moisture content, 402

- Gravitational forces and consolidation, 71
 -- and flocculation of colloids, 150, 151
 --, and pore water, 172
 - water, 172
 Gravity, as agent of transportation, 2
 -, slopes, 24
 Great soil groups, 15, 17
 Greenalite, 106
 Grinding equipment for clay, 289
 Ground movement near elm tree in Leda clay, Ottawa, Canada, 177
 - water, 25, 26, 34, 40
 Groups in classification of phyllosilicates, 104
 Gypsum, in clays, 56, 125, 131, 132, 311
 -, in Portland cement, 311
- Haematite, 92
 Halloysite, 56, 105-106, 243, 382
 -, identification, 336, 343, 344, 377
 -, permeability and, 179
 -, shape, 105, 376, 377
 -, water uptake and, 185
 Heat content, 54
 Heave, 125, 147, 182, 184, 200, 202, 423
 Hectorite, 107, 148, 295, 330
 Helicitic structures, 236
 Helmholtz free energy, 54
 Hexagonal close packing, 94, 95, 101, 110
 Hisingerite, 114
 Homogeneous strain, 220
 Honeycomb structure, 115, 119, 120, 121, 228
 Hooke body, 223, 227, 228
 Hooke's law, 221, 223
 Horizons, soil, 15, 56, 125 - see also soil
 Hormites, 98
 Hornblende, 51, 57
 Hornfels, 50
 Hydration, 56
 Hydraulic conductivity, 403
 -, lift, 37
 Hydrogen bond, 93, 101, 104, 105, 160, 186
 Hydrological cycle, 25-29
 Hydrometer method, of particle-size analysis, 382, 383, 384, 385
 Hydrophobic colloids, 147, 151, 152
 Hydrostatic pressure, 69, 171, 421
 Hydrothermal action, 54, 56, 63, 64, 105, 106, 120
 Hydrothermal alteration, of tholeiites, 64
 Hydrous compounds, 92
- Hydroxyl group, 100, 101, 155, 158
 - orientation, 155
 Hypabyssal rocks, 49
 Ice crystal growth, 205
 -, erosion and transportation by, 29, 40
 - glass, 368
 - lenses, 125, 203, 204-207, 275, 276
 - lens growth disrupting concrete, 201
 -, segregation in varved clay, 203
 Identification of principal groups of clay minerals by X-ray diffraction, 337
 Igneous rocks, 49, 50, 52, 59, 65, 98, 112
 Illite, 110-111
 -, adsorption isotherm of, 388
 -, ammonium fixation and, 156
 -, analysis, 338, 345, 378
 -, boron content and, 67
 -, dehydroxylation, 304
 -, formation on burial, 77
 -, in ball clays, 14
 -, in sedimentary cycle, 65, 67
 -, index properties, 13
 -, plasticity affected by, 224
 -, reaction with cement, 263
 -, reaction with lime, 269, 271, 272
 -, shape of, 376, 378
 -, water uptake and, 185
 Illuviation, 56
 Ilmenite, 50
 Image analyzing computers, sizing by, 386
 Imbibition of moisture, 147 - see also moisture
 Imogolite, 62, 114, 157, 158, 171, 347, 376
 Impregnation of clay, 362
 Incompressible material, 223
 Index properties, 12, 13, 68, 74, 200, 224, 242, 271, 407, 424
 - tests, 182, 406-410
 Indices, crystallographic, 93
 Infrared analysis, 346-348
 --, quantitative, 348
 - radiation, absorption, 323, 346, 347, 348
 --, nature, 346
 - spectra, characteristic, 346
 --, of phyllosilicates, 349-350
 Inner layer, 150
 Inosilicates, 98
 Insulators, 14
 Inter-axial angles, 93
 Inter-crystalline swelling, 185 - see also moisture
 Intergradient complexes, 61, 336-338
 Interlayer bonding, 107
 Intermicellar solution, 148, 157, 158

- Interparticle bonds, 236
- Internal friction, 233, 412
 - gradients, 167
 - standards, 340
 - stress, 102, 103, 310
 - surface area, 389
- Interstratified clay minerals, 112, 113
- Intra-crystalline swelling, 185 - see also moisture
- Intrusive rocks, 49
 - vein, mineralogical alteration adjacent to, 63
- Inverse pole figure technique, 374
- Ion exchange, 153 - see cation exchange, base exchange, exchange reaction
 - hydration, 170-171, 186
 - selectivity, 153
- Ionic bonding, 93
 - crystals, 308
 - structures, 94, 95
 - substitutions, 100, 102, 104, 107, 143
- Ions at surfaces, 144
 - in crystals, 93
 - solution, 168-171
- Iron, affect on X-ray diffraction pattern, 324
 - compounds, removal of, 330
 - in plants, 57
 - pyrites, 311
 - sulphide-sulphate equilibria, 242
- Isoelectric point, 158
- Isomorphous, 95, 100, 104
- Isopentane, in freeze drying, 367
- Jamaica, bauxite producer, 295
- Japan, fullers earth, 297
- Jarosite, 56, 125, 132
- Jarusov's rule, 156
- Jericho, 285
- Joints, 34, 74, 401, 403
- Kaolin, analysis, 338, 344
 - , anion adsorption, 148
 - , anion exchange, 158
 - , bonding of layers, 104
 - , boron content of sediments and, 67
 - , content affected by burial, 77-78
 - , Cornwall, England, deposits, 63, 289
 - , dehydroxylation, 305, 344
 - , disorder in, 342
 - , distinction from chlorite, 335, 347
 - , economic deposits, 289, 292
 - , edge charge illustrated by electron micrographs, 149
 - , exchange, 105, 155
 - , expansion of, 160
 - , firing, 306, 309
 - , formation, 56, 61-62, 64, 105
 - , Georgia, 291, 292
 - , high purity, 286
 - , identification, 335-336
 - , in china clays and ball clays, 14, 296
 - , index properties, 13
 - , industrial uses, 292, 295
 - , infrared spectra, 105
 - , in sedimentary cycle, 67
 - , pastes, 79
 - , plasticity affect on, 224
 - , production, 291
 - , reaction with cement, 263, 266
 - , reaction with lime, 269, 271, 272
 - , shape of, 105, 376, 377
 - , surface area, 144
 - , water mixtures, 236
- Kaolinite-serpentine group, 101, 105-106, 111
- Kelvin body, 228
- Kliachite, 114
- Kozeny-Carman equation, 179, 403
- Kyanite, 50, 303
- Lambert-Schmidt projection, 373, 374
- Laminar flow, 40
- Landforms, 22
- Landslide, 29
 - classification, 31
 - control, 237
 - deposit, 379
- Lateral stress ratio, K_s , 426
- Lateritic weathering, 295 - see also weathering
- Lattice, collapse of, 335, 336, 337
 - constants, 93
 - , internal stress and, 197, 103
 - , polytypes and, 95
 - parameters 93
 - spacings, Bragg equation and, 325
 - , changed by R.H., 334
 - , diagnostic changes in, 328
 - strain, 58
- Law of mass action, 153, 158
- Layer charge, 104, 107, 110 - see also charge
 - structures, 61, 98, 100-113, 144, 158
 - , illustrated, 60, 102
- Layers, defined, 104
- Lean clays, 425
- Leather hard, 285
- Leda clay, 177, 199, 241, 373
- Lepidolite, 110
- Leucite, 50
- Leucophyllite, 110
- Lewis acids, clay minerals as, 159
- Light-weight aggregates, 290, 297, 301

- Lime, chemical reactions involving, 268
 - , index properties affected by, 271, 272
 - , reaction with clay minerals, 265, 271
 - stabilization, 254, 267-273
 - , alkalinity effect, 272
 - , organics and, 271
 - , recommended amounts, 270
 - , strength of, 269
 - spreading, 257
- Limestone, 51, 52
- Limit tests, 12, 406-410
- Limonite, 114
- Liquidity index, 12, 406
- Liquid limit, 68, 74, 258, 262, 408, 410, 424
 - , defined, 12
 - , re-defined, 410
 - device, 406, 407
 - , estimation, 406, 407
 - , lime stabilization and, 271
 - , values, 407
- Liquids, 235
- Lithification, 72
- Lithogenesis, 240
- Lizardite, 106
- Load casts, 74
 - folds, 76
 - pockets, 74
 - void ratio relationships, 424
 - waves, 74
- Loading sequence in consolidation test, 422
- Locked sands, 238
- Loess, 4, 40, 122, 192-197
- Lutite, 1
- Macromolecular colloids, 147
- Mafic minerals, 50
- Magma, 49
- Magnesium, octahedrally coordinated, 95
- Magnetite, 50, 92
- Major uses of clays in U.S.A., 298
- Manganese, 57
- Marble, 50
- Margarite, 111
- Marine deposits, 66, 67, 68, 115, 227
 - , boron content, 67
 - , fabric, 115
- Marl, 285
- Mars, 21
- Mass absorption coefficient, 339
 - action law, 143
 - movements, 30-36
 - properties, 401
- Measurement of moisture content, 402
 - permeability and suction, 403-406
 - soil moisture and moisture movement, 402-406
- Mechanical analogues of rheology of clay, 230
 - damage, in clay mineral formation, 54
 - stabilization, 251-254
- Metakaolin, 304-305
- Metallic coating, removal of, 366-367
- Metamorphic, 69, 77
 - rocks, 49, 50, 59, 111
- Metamorphism, 77, 107
- Metasomatism, 111
- Meteoric water, 35, 171
- Mica, 50, 59, 61, 64, 77, 98, 103, 104, 107, 109-111, 306, 336
- Micellar solution, 148
- Microorganisms, 130
- Microscopic sections, 362, 363
- Microstructure, 114, 120, 309
- Migmatite, 50
- Migration of moisture, 177-181 - see also moisture
- Miller indices, 93
- Mineralizers, 305, 306
- Mineralogical alteration adjacent to intrusive vein, 63
 - analysis of clay, 323-359
 - changes and pressures, 77, 78, 79
 - composition of igneous rocks, 51
 - , and plasticity, 224
 - , from chemistry, 348, 351
- Minnesotaite, 107
- Mixed layer minerals, 61, 63, 66, 110, 113, 185, 333-334, 335
- Mixing plant, 254
- Models, rheological, 227-230
- Modelling experiments, 410
- Modification of frost heaving in soils, 274-276
- Modulus of deformation, 223
 - rigidity, 223
 - shear, 223
- Mohorovicic discontinuity, 21
- Mohr-Coulomb hypothesis, 230, 410, 411
 - diagram, 231, 410, 411, 412
 - envelope, 231, 411, 412
- Moisture content, 12, 172
 - , index properties and suction, 200
 - measurement, 402-403
 - , optimum for maximum density, 252-253
 - , optimum for soil cement, 262
 - , density relations on compaction, 429
 - gradients, 299
 - interaction with clays and clay minerals, 167-217
 - measurement, 402-406
 - migration, 177-181
 - , and volume change, 181-201
 - movement, 167, 177, 402

- regime of soil, 167, 177, 200
- retention, 171-177
- suction, 72, 172, 178, 199, 200, 232, 405, 406
- uptake, 147, 181, 252, 310, 311, 312, 423
- pressures, 185
- Molecules, 93
- Monoclinic, 77, 110
- Monolithic refractories, 303
- Montmorillonite, 62, 64, 66, 79, 108, 222, 274, 331 - see also bentonites, smectites
- adsorbed on kaolinite, 148
- ball clays and, 14
- boron content and, 67
- burial and, 77, 78
- dehydroxylation of, 304, 344
- detection, 334, 344
- economic importance, 293
- electron micrographs, 378
- index properties and, 409
- interlayer complexes with, 336-338
- pastes, 79
- permeability and, 179
- reaction with cement, 266
- reaction with lime, 269, 271, 272
- saponite group, 107
- sedimentary cycle and, 66
- selective sorption, 157
- shape, 376
- slides and, 34
- structural clay products and, 299
- surface area estimation, 389
- swelling pressure, 185, 189
- transportation of, 39
- Mounting and treatment of samples for X-ray analysis, 332-339
- Mud, 1, 51
- flows, 32
- stone, 1, 75
- Mullite, 304, 305, 309, 336
- Muscovite, 61, 110, 111, 305
- Nacrite, 105
- Nature and classification of clays and soils, 1-19
 - of water and ionic solutions, 168-171
- Negative adsorption, 157
 - charge, 104, 107, 108, 152
- Neolithic period, 285
- Nepheline, 50
- Nesosilicates, 98
- Neutron diffraction, 170
- Neutron-moisture meter, 403
- New England, 23
- Newtonian liquid, 223, 225, 226-228
- Ninevah, 285
- Nomographic charts, in particle-size analysis, 384
- Non-crystalline solids, 113, 114, 157
 - see also amorphous
- coatings, 329
- Newtonian systems, 225
- Nontronite, 64, 107
- Normal pressure, 77
- stress, 219, 220
- Normally consolidated, 72, 424
- North American clays, 115 - see also United States
- Norwegian clays, 34, 115, 242
- Nuclear methods and density, 392
- Numerical aperture, 363
- Ocean, 29
- Octahedral group, 95, 100
 - layer, 100-108
- Oedometer, 421, 423
- Oklahoma, U.S.A., drill lime stabilization, 267
- Olivine, 50, 64, 98, 336
- One-dimensional disorder, 95
 - layer monoclinic, 77, 110
 - point method, 407
- Opal, 114
- Optimum density, 401
 - water content, 190, 298, 428, 429
- Orders, in pedological soil classification, 15
- Organic compounds, complexes, 108, 161
 - , consolidation affected, 427
 - , exchange and, 154, 159-161, 157
 - , flocculation and, 152
 - , index properties and, 12
 - , removal of, 330
 - , soil stabilization and, 255, 264, 265, 271
 - , sorting and, 67
 - , X-ray analysis and, 335
- Orientation diagram, 373
 - of clay minerals, 362, 382
 - of fabric elements, 361
 - of water molecules, 186
- Oriented sample, 332
 - water molecules, 180, 186, 235, 236
- Origin and evolution of clay minerals and clays, 49-89
- Oscillation volume theory, 158
- Osmotic pressure, 171, 187
- Overburden pressure, and mineralogical changes, 77, 78
- Overconsolidated, 72, 222, 402, 420, 425, 426, 427, 428
- Overconsolidation and frost-action, 203-204
- Overpressured zones, 79
- Overtones, 347
- Oxidation, 56
- Oxides, 49, 92
- Oxygen, tetrahedral group, 95, 98

- Packing geometry, 70
- Palygorskite, 98, 297, 343, 344
- Paragonite, 110
- Parent material of clays and soils, 49-52, 57, 59
- Particle association, 152, 153
- Particle-size analysis, 379-386
 - , consolidation and, 70, 252
 - , frost susceptible soils and, 204
 - , moisture interaction and, 175
 - , surface area and, 390
- Patterns in soil, 125
- Pauling's Rules, 95
- Peat, 91
- Pediment, 23, 24
- Pediplain, 23
- Pedogenesis, 56
- Pedological soil classification, 15-18
- Pelitic, 1
- Pellets and agglomerations, 30, 114, 116
- Pendulate water, 25
- Peneplain, 23, 24
- Penetration tests, 413
- Perched water table, 25
- Periods, geological, 21
- Permafrost, 201
- Permeability, 37, 125, 178-181, 179, 390, 402
 - , coefficient of, 69, 178, 403, 404, 424, 425
 - , consolidation and, 70, 421, 424, 404
 - , effective, 402
 - , measurement, 403-405
 - , mineralogical changes and, 77-78
 - , primary, 402, 403
 - , secondary, 402, 403
 - , soil structure and, 120, 129, 203-204
- Permeameter, 404
- Permeametry, 390
- Persistence of minerals on weathering, 59, 61, 103
- Petrographic microscope, 361, 363-364
- Petrography, 263
- pF, 173-174, 199, 200
- Phase diagram, ceramic use, 303, 306
 - , of water, 168
- Phase transformations, reconstructive, displacive, 306
- Phengite, 110
- Phlogopite, 110, 155
- Phosphates, 114, 157, 254, 273-274
- Photoelectric cell, 364
- Phreatic surface, 25, 172, 405
- Phyllite, 50
- Phyllosilicates, 98, 100-113
 - , classification, 103, 100-104
 - , thermal changes and, 304-307, 343
- Physical analysis of clays, 361-399
 - changes in clays after deposition, 74-76
 - chemistry of clays, 143-166
 - geology, 21-47
 - processes and clay mineral formation, 53-54
 - Piezometer tubes, 421
 - Pipette method, 382-384, 386
 - Pitches, 257
 - Plagioclase, 51, 59, 61, 64
 - Plane shear-strain apparatuses, 414
 - Planes, defined, 104
 - Plants, transpiration from, 200
 - Plastic limit, 12, 262, 271, 408 - see index properties
 - , re-defined, 410
 - model, 228
 - properties represented, 14
 - soils and consolidation, 68
 - Plasticity, 224, 225, 235, 267
 - , ceramic industry and, 297
 - chart, 13, 14
 - , economic importance, 285
 - , experimental study of, 224
 - index, 13, 225, 258, 272, 406
 - , mechanism, 235, 236
 - , reduced by salts, 254
 - Plastico-viscous properties, 229
 - Pleistocene, 23, 39-42, 73, 241
 - Plucking by ice, 41
 - Plutonic rocks, 49, 50
 - Poisson's ratio, 223
 - Polarization of ions, 101, 143-144
 - Polarized light, 363
 - Polar organic compounds, 154 - see also organic compounds
 - Pole figure diagram, 114, 115, 374
 - Polyhedral groups, 95
 - Polymerization, 98, 100
 - Polymorphs, 95
 - Polystyrene plastic in control of frost heave, 275 - see also frost action
 - Polytypes, 95, 104, 105, 106, 110, 339
 - Pop-outs, 312
 - Pore moisture tension, 173
 - size distribution, 180, 367, 390, 391
 - solutions, 77-78, 224
 - volume, 70
 - water pressure, 34, 229, 232, 253, 403, 413, 416, 418, 428
 - Pores, as fabric elements, 114, 120, 361
 - , best methods of measurement, 391
 - , in gel-like materials, 113
 - Porosity, 129, 367, 390-391
 - Portland cement, composition, 302
 - , manufacture, 285, 299-301
 - , production in terms of raw materials, 299

- , release of alkalis, 312
- , soil stabilization and, 254, 261-266
- Positive edge charge, 148, 149, 152
- Post depositional changes in clays, 68, 69
- Potassium, 65, 66, 107, 155, 156, 157
- Powder method, diffraction geometry, 328
- Power shovel, 286
- Pozzolan, 273, 313
- Pre-consolidation, 72, 424, 426, 427
- Preferred orientation, 114, 119, 361, 373, 401
- Pressure-void ratio relationship, 423, 424
- Pre-treatment of clay, 288
- Primary, minerals, 92, 105, 409
- Principal plane, 220
 - stress, 220, 410, 415
- Principles of consolidation theory, 69-74
- Proctor test, 252, 253, 429
- Properties of colloidal particles, 143-145
- Proportional limit, 221
- Proving ring, 414, 416
- Pseudomorphs, 64
- Pseudoplastic fluid, 226
- Psychrometer, 406
- Pumping test, 405,
- Pyrite, 57, 68, 125, 130
- Pyrometric cone equivalent, 14, 303
- Pyrophyllite, 103, 104, 106, 186, 311
- Pyroxenes, 50, 64, 98, 311
- Quantitative mineralogical analysis, 339-341
- Quartiles, 381
- Quartz, 50, 56, 64, 144, 306
- Quartzite, 50
- Quattara depression, 39
- Quick clays, 34, 35, 226, 227, 234, 240, 242
- Quicklime, 267, 268, 269
- Radial distribution analysis, 170
- Radioactive waste disposal, 65
- Radius ratio, 94, 95, 100
- Rainwash, 36
- Rainwater, composition, 26
- Random fabric arrangement, 75, 114 - see also fabric
 - interstratification - see mixed layer minerals
- Rapidity number, 234
- Rate of sedimentation, 67
- Raw materials, 290-297
 - , moisture expansion, 310, 311
- Ray paths in light and electron microscopes compared, 365
- Recoil, in rheology, 228
- Reconstructive phase transformations, 306
- Rectorite, 106
- Refractory, 14, 303, 307
- Refractoriness, 14, 351
- Regolith, 1
 - Relationship between liquid limit and plasticity index for typical soils, 13
- Relative density, 391, 392, 430
- Relative humidity, soil moisture and, 173, 405, 406
 - , X-ray analysis and, 334
- Replica techniques, 370
- Repulsive forces, 94, 152
- Residual earth materials, 2
 - strength, 222, 237, 410, 415, 419
 - stress in silicates, 102, 103
- Resolution, 363-367
- Resolving power, 363
- Retention of moisture, 171-177 - see also moisture
- Rheological behaviour and models, 227-230
- classification of materials, 227
- Rheology, 219, 227-230
- Rheopexy, 226
- Rigidity, modulus of, 223
- River, capacity, 36
 - dispersion in, 39
 - flow data, 36
 - load, 36
 - vertical velocity gradient, 37
- water composition, 27, 65
- Road construction, 267
- Rock, chemical composition, 52
 - defined, 49
 - falls, 29
 - flour, 3, 13, 42
 - forming minerals, 92
 - igneous, 49-52, 59, 66, 98, 112
 - metamorphic, 49, 50, 112
 - sedimentary, 49, 51, 112
- Rollers, 256, 257
- Rotational slips, 32
- Rutile, 59
- Saint-Venant body, 223, 228
- Saline soils, 177
- Salinity and boron sorption, 67-68
- Salt content, 79
- Saltation, 36
- Sample preparation for electron microscope, 367-372
 - for microscope, 363
 - , for X-ray analysis, 327, 328, 331
- Sand, 1, 2, 51, 174, 238, 329

- Sand drains, 253
- Sands, locked, 238
- Sandstone, 51, 52, 74, 77, 79
- Saponite, 108
- Saturated minerals, 50
- Sauconite, 108
- Scalar parameters, 361
- Scandinavia, 34, 115, 226, 242
- Scanning electron microscope, 365, 366, 385
- , supplementary methods, 372
- micrographs, 193-197
- Schist, 50, 52
- Schulze-Hardy rule, 151
- Seasons, effects of, 167
- Sea-water, 28, 33, 65, 292
- Sedimentary rocks, 49-52, 112
- Sediment, classification, 2
- , transport, 2, 36, 37, 65
- Selective sorption, 66, 157
- Sensitive clays, Canadian, 34, 35, 177, 226, 241, 243, 373
- , Scandinavian, 34, 226, 242
- , slides in, 34
- Sensitivity, 34, 232-234, 242, 253
- , clay classification in terms of, 233
- Sepiolite, 98, 343, 376, 344
- Septechlorite, 106, 112 - see also chlorites
- Serpentines, 64, 98, 106, 343, 344, 347
- Settlement, 67, 68, 401
- Sewage disposal, 39
- Shadow casting, 370, 371
- Shale, 1, 52, 53, 72, 77
- black, 125
- planer, 287
- stockpile, 290
- Shape of minerals, analysis of, 374-379
- Shear-failure by rotational slide in cohesive strata, 32
- , angle of, 231
- , fabric and bonding, 237
- forces, 220
- modulus, 223
- , pure, 221
- resistance, 73, 238
- , simple, 221, 414
- strains, 414
- strength and Mohr-Coulomb hypothesis, 230-234
- , change in, 73
- , determination of, 410-420
- stress, 77, 219, 220, 224, 231, 410, 414 - see also stress
- types of, 221
- Shearing resistance, angle of, 231
- Sheepsfoot roller, 256
- Sheetfloods, 36
- Sheets, defined, 104
- Short firing range, 296
- Shrink-swell potential, 387
- Shrinkage, 177, 252
- cracks, 75
- diagram, 199
- limit, 12, 200, 285, 409
- potential, 200
- SiC, 95
- Silanol surface, 145
- Silica, 56, 98, 99, 100, 113, 145, 154, 171
- , solubility, 272
- Silicates, 92, 114
- , classification, 98-113
- , crystal chemistry, 98-100
- , isomorphous substitution, 100
- , structural combinations, 96, 97
- Siliceous compounds, removal prior to mineral analysis, 330
- Silicon, 57, 67, 95, 98, 99
- Sillimanite, 50, 303
- Sills, 49
- Siloxane, 144
- Silts, 1, 2, 13, 74, 204, 238, 329
- Sintering, 269, 307
- Site investigations, 401
- Sixth power law, 37
- Size analysis, 379-386
- distribution and surface measurement methods, 380
- fractions, for mineralogical analysis of clay grade, 329
- Slag, 254
- Slaked lime, 267
- Slate, 1, 50, 54
- Slide, aerial photographs before and after, 35
- Slides, 32-36
- Slip-planes due to failure, 231
- Slope cycle 33
- stability, 33
- Slump and slide structures, 74
- Smectite group, 107-108
- Smectites, 62, 65, 77, 78, 103, 105, 107, 108, 109, 111, 158, 237, 263, 329 - see also bentonites, montmorillonite
- , acid attack on, 329
- , analysis, 335, 344
- and vermiculites, distinction, 109
- , index properties, 13
- , layer charge, 104, 107, 108
- , plasticity affected by, 224
- , surface area, 144
- , water uptake by, 107, 185
- Sodium chloride in stabilization, 254
- silicate in stabilization, 254
- Soil, 1
- , as a mass of interconnected capillaries, 171

- asphalt, 257-261
- atmosphere, 91
- cement, 261-266
- classification, 2-4, 15-18
- collapse, 192-198
- composition, 91
- creep, 29-32
- families, 15
- formation, 56
- , frost-susceptibility of, 204-205
- horizons, 15, 56, 125, 129
- mechanics, 401
- moisture, 72, 167, 172, 177, 178, 206, 405, 406 - see also moisture
- orders, 17
- organisms, 261
- parent material, 15, 56, 57, 59
- profile, 15, 129, 263
- residual, 4
- series, 15
- soft, 3
- stabilization, 251-283
- structure, 134
- solutions, 91
- subgroups, 15
- survey maps, 15
- , transported, 2
- water potential, 171
- water removal, 69-74, 191-201
- Solar system, 21
- Solid solution, 103
- Solifluction, 29, 32
- Solutions, 169-170
 - , colloidal, 145-153
- Sorosilicates, 98
- Sorption, by minerals, 66
 - , specific, 154, 157
- Sorting, 67, 125, 133, 379
- Space lattice, 93
- Special refractories, 14
- Specific adsorption, 154
 - affinity, 157
 - surface, 54, 113, 143, 144, 387, 407
 - gravity, 391
 - , of clay minerals, 382
- Sphene, 50
- Spherical aberration, 363
- Spinel, 304, 305, 336
- Spring-dashpot models, 229
- Stability of minerals, 56-61, 103
 - soil, 129
- Stabilization by electrokinetics, 274
 - , mechanical, 251-254
 - with additives, 254-274
 - bituminous materials, resinous materials, and chemicals, 257-261
 - cement, 254, 261-266
 - lime, 254, 267-273
 - phosphates, 273, 274
- Stabilizer, in-place, multiple pass, 257
- Stable channel, 36
- Standard compaction test, 429
- Staurolite, 50
- Stereographic net compared with equal area net, 375
 - projection, 373
- Stokes' Law, 143, 381, 382
- Strain, 157, 220, 222
 - controlled shear test, 414, 418
 - hardening, 231
 - softening, 222, 231
 - triaxial test, 415
 - ellipsoid, 220
 - rate, 225, 237
- Straumanis technique, 327
- Stream contamination, 39
- Strength, 219-250
 - and rheology of clays, 219-250
 - gain of clay with CaO and Ca(OH)_2 , 268
 - of pure cement compounds, 265
 - , residual, 222, 237, 410, 415, 419
 - soils with cement, 262-266
 - soils with lime, 269, 270, 272
 - of materials made from clay, 299, 308-310
 - of undisturbed and remoulded Leda clay, 241
 - tests, 401, 410-420
- Stress, 219-223, 231, 236, 427
 - and strain, 219-223
 - concentration, 308, 310
 - controlled shear test, 414, 418
 - path, 412
 - , triaxial, 415
 - difference, 219, 411
 - , effective, 232
 - history, 238
 - , normal, 231, 411
 - , peak, 221
 - , principal, 219, 410, 411, 415
 - relaxation, 228, 426
 - , shear, 77, 219, 220, 231, 410, 411, 414 - see also shear
 - strain curve, 221
 - strain curves of clays of various sensitivities, 233
 - strain relationships for soil, 222
 - , tensile, 231, 238
 - , types of, 220
 - , ultimate, 221, 222
- Structural arrangements of linked tetrahedra, 99 - see also tetrahedra
 - clay products, 289, 290, 295, 299
 - combination in silicates, 96-97
 - skeleton of clay, 234, 237
- St. Venant body, 223, 228
- Subaerial weathering, 125
- Subaqueous shrinkage cracks, 75
- Subgroups, in phyllosilicates, 103

- Sublimation, 367
- Submarine canyons, 30
- Suborders of soils, 15
- Suction, 72, 172, 178, 205, 206, 232, 405, 406
 - , defined, 172
 - , freezing point and, 205-206
 - , ice lenses and, 206
 - , index properties and moisture content, 200
 - measurement, 200, 402, 405, 406
- Sulphates, concrete and, 177
- , fired clay products and, 311
- , soil cement and, 264
- Sulphides, 56
- Sulphur concrete, 275
- Sumer, 285
- Sun, 21
- Surface active agents, 254, 261
 - , and double layer water on clay crystals, 188
 - area, estimation, 287-390
 - of clay minerals, 388
 - of colloids, 143
 - of kaolinite, 144
 - of smectites, 144
 - variation with particle shape, 114, 116
 - atoms, 143
 - charge density, 155
 - forces, 71, 206, 405
 - ions deformed by assymetric force field, 145
 - of bulk samples, 367, 370, 371
 - phenomena, 144
 - tension, 143, 171, 192, 367
 - water, 26
- Swelling capacity and burial, 77
 - chlorites, 112, 185, 335
 - fabric and, 115
 - pressures, 107, 185, 189
- Symmetry of fabric, 114
 - illustrated by contoured equal area projections, 115
- Syneresis, 68, 74, 147
- Systems, geological, 21
 - with variable viscosity and yield point, 225-227
- Tactoids, 189
- Taeniolite, 110
- Talc, 104, 106, 186, 311
- Tars, 257
- Tektosilicates, 99
- Tensile forces, 219
 - strength, 308
 - stress, 231, 238
- Tensiometer, and soil moisture content, 403
 - , and soil moisture suction, 405, 406
- Tetrahedra group, 98, 101, 102
 - layer, 100-102, 108
 - , structural arrangements of, 96, 97, 99, 101
- Texture, 79
 - coefficients, 375
 - goniometer, 375
 - onion skin, 59
- Thaw, 207
 - break-up of road surface, 208
- Thermal effects associated with clay minerals, 343
 - changes affecting phyllosilicates, 305
 - conductivity and soil moisture measurement, 403
- Thermal methods of analysis, 341-346
- Thermocouple, in DTA, 342
- Thermodynamic functions, 54-55
 - methods, 172
- Thermograms of some clay minerals, 345
- Thermogravimetry, 341, 344
- Thixotropy, 221, 226, 235, 240
- Tholeiites, hydrothermal alteration, 64
- Three-dimensional frameworks, 97, 99
- Till, 2, 42, 51, 203, 381 - see also Boulder clay
- Tobermorite, 266
- Tonsteins, 14
- Topotactic, 55
- Torsion tests, 410, 419-420
- Tourmaline, 68
- Transpiration, 191, 200
- Transport, 1, 29-42, 65
- Treasure island lagoon, 179
- Triaxial apparatus, 415, 417
 - body, 297
 - compression test, 232, 410, 415-419
 - diagram, 298
- Trioctahedral structure, 61, 105-112
 - , defined, 104
 - , recognition, 104, 339
- True cohesion, 232
 - internal friction, 232
- Turbidity currents, 30
- Turbostratic, 119
- Turbulent flow, 40
- Twinning, 58
- Two-layer monoclinic, 77
- Tyndall effect, 145
- Types of shear, 221
 - stress, 220
- Ultra microscope, 145, 150
 - microtomy, 370
 - sonic (sound), 329, 375
 - thin sections, 363, 370
- Unconfined compression test, 252, 419
- Unconsolidated earth material, 1

- Underconsolidated, 72
- Undisturbed sample, 361, 392, 401, 415
- Undrained triaxial test, 416
- Unified soil classification system, 5-12
- Uniform soil, 379
- Unit cell, 92, 93
- United States, ceramic mix, 311
 - fullers earth, 297
 - kaolin deposit, 292
 - lime stabilization, 267
 - major categories of clay products, 297, 298
 - uses of various clays in terms of quantity, 294
 - value of various clays, 293
- Unsaturated minerals, 50
- Vaiont reservoir disaster, 36
- Value of various clays used in U.S.A., 293
- Vanadium, 296, 311
- Van der Waals forces, 93, 104, 106, 152, 160, 186
- Vane shear apparatus, 420
 - test, 410, 413, 420
- Van't Hoff's principle, 57
- Vapour pressure, curvature of meniscus, water column height and p_f relationships, 174
- Variable head permeameter, 404
- Varved clays, 3, 115, 117-118, 123, 428
- Vector parameters, 361
- Venus, 21
- Vermiculite, 102, 108-109
 - ammonium fixation, 157
 - analysis, 335
 - and smectites, distinction, 109
 - compared with chlorites, 109, 112, 335
 - exfoliation, 303
 - interlayer complexes, 336-339
 - layer charge, 104, 109
 - water uptake by, 185
- Visco-elastic, 227, 228
- Viscosity, 225-227
 - variable, 225, 226, 234, 238
- Viscous bonds, 234
- Void fraction, 421, 428
- Voids, observation, 391
 - as fabric element, 114
 - ratio, 70-74, 390
 - change on compression of normally consolidated and overconsolidated clay, 424
 - defined, 390
 - overburden pressure relationship, 71
- Volume change characteristics, 167-168, 181
 - coefficient, 424
 - consolidation and, 424
 - due to moisture migration, 181-201
 - decrease, 191-201
 - increase, 181-191
- Wad, 114
- Wash slopes, 24
- Water, adsorbed, 234, 343
 - connate, 25, 125
 - content, 167, 402
 - erosion and transportation and, 29-39
 - gravitational, 25
 - ground, 26, 30
 - jet washing out kaolin, 287
 - juvenile, 25
 - meteoric, 25, 171
 - molecule, structure of, 168-171
 - oriented near surfaces, 180, 186, 235, 235
 - structural role of, 93
 - pendulate, 25
 - phase diagram, 168
 - pore - see pore water pressure
 - proofers, 254, 258, 275
 - properties, 168
 - rain, 26
 - removal of, 367
 - river, 19, 27, 65
 - run-off, 26
 - sea, 26, 28, 33, 65, 292
 - sensitive beds, 180
 - surface, 26
 - table, 25, 34, 57, 172, 205, 405
 - and frost-action, 205
 - transportation agent, 2, 29-42
- Wavenumber, in infrared analysis, 346
- Waves, 29, 67
- Weathering, classification and, 4
 - clay mineral formation and, 56, 105, 111
 - exchange and, 156
 - fabric and, 125
 - index, 53
 - lateritic, 295
 - stability of minerals, 58-62, 103
- Weight changes on heating, see thermogravimetry, 344, 346
- Well-graded, 379
 - sorted, 381
- Whisker crystals, 308
- Whiteware, 14, 298
- Wilting point, 173, 200
- Wind, 2, 29, 39
- Winning and pre-treatment of clay, 288-290
 - processing clay for brick manufacture, 292
- clays, equipment for, 286-288
- Wollastonite, 311

- Wulff (stereographic) net compared with Lambert (equal area) net, 373, 375
- Xanthophyllite, 100
- X-ray camera, 326, 327
- , coherent, 324
- , diffraction analysis, 103, 323-339
- , background, reduction of, 332, 333
- , quantitative, 339-341
- , fabric studies and, 361, 372-374
- , particle-size estimation and, 386
- , sensitivity, 341
- , shape estimation and, 379
- , fluorescent, 325
- identification of principal groups of clay minerals, 338
- interaction with matter, 324
- Yield point, 220-223, 226, 227
- Young's modulus, 223, 308
- Zeolites, 62, 64, 99
- Zinc, 157
- Zircon, 50, 59, 98
- Zone of weathering, 56