

TUTORIAL

What is It About Shaly Sands?

Shaly Sand Tutorial 1 of 3

E. C. Thomas

Editor's comment: This article is the second in a series of short "tutorial-like" notes styled to mentor users of digital well log data in becoming confident practitioners of *Petrophysics*.

Some may ask: Why do we need to understand the petrophysics of shaly sands? The best answer I can give is to relate a true story that happened to me while I was on a broadening assignment in the Coastal Division of Shell Oil Company, located in New Orleans. These offices were in Gentilly, and if I had rated a window, it would have overlooked the Jewish Cemetery. I was struggling to understand formation evaluation in practice with help from Brian Ausburn, John Stieber, Roy Coles and many others who freely mentored me while I was "learning the ropes." I had quite a large learning curve coming from a laboratory environment. I made many, many mistakes and was teased about someone with a PhD not being able to master the "easy stuff." So they gave me the nickname of 'Easy' until I could prove I had learned the easy stuff. After suffering through many false starts I finally understood how to interpret low-resistivity pay. My job entailed counting pay thickness and computing porosity and water saturation. It was fun finding pay where none had tried before. The first time I called a sand with a resistivity of $0.6 \Omega\cdot\text{m}$ pay, the Division Production Engineer called me crazy and bet that if that zone was perforated it would flow all water. Of course I had an ace in the hole! Chris Clarke was the geologist on our team was the one to propose drilling the well. He knew this location was updip from a producing well and would find a section of the fault block that had not been swept. Well, he was right and so was I—the well flowed 95% oil. The Division Production Engineer came to my office to say he was sorry to have doubted me and would not have any more qualms about perforating intervals I selected. He then changed my nickname to 'Easy Money,' which I proudly wore the rest of my time in New Orleans. The Thomas-Stieber method was accepted and used by the staff to never miss a low-resistivity shaly sand again. Understanding how the geological deposition of the sand affected the logs and their resulting capillary pressure proved to be a very profitable technique. I hope these three tutorials will make understanding shaly sands much easier and remove the "magic" from their interpretation.

A comprehensive treatise explaining the petrophysics of shaly sands would require a rather thick book, so it is obvious that I will need to abridge such a manuscript for a short tutorial trilogy. I shall assume that the reader has working knowledge of the standard Archie evaluation

scheme that is based upon empirically derived equations established with the use of electrical measurements on 1-in. sample plugs cut from 4-in. whole core. The lithology of these samples consists of homogeneous, clean, slightly consolidated sandstone. Thus, such a dataset and the derived equations therefrom are empirical and valid only over the range of experimental conditions used. Consequently, when using these equations to interpret electric well logs the two most important restrictions are (1) the reservoir rock must be homogeneous, and (2) the only electrical conductor for the rock sample is the brine solution contained in the pore network. A large number of reservoir sandstones and carbonates approximately satisfy the above two conditions such that Archie's equations have been good enough for over 60 years. However, most of these "easy" rock types have been thoroughly examined in the past, leaving many rock types that violate (1) or (2) or both (1) and (2).

More sophisticated physics-based mathematical methods are needed to handle exceptions to condition (1), i.e., anisotropic rock types, and/or condition (2), i.e., rock types with clay minerals that introduce additional electrical conductivity paths. Of course these two sets of rock types are not the only ones left to pique our investigative experimental skills and mathematical forte to explain and apply in practice. We have neither the time nor the expertise to make an exhaustive list of all the candidates. However, I will mention two that are entering the petrophysical literature with great promise: methods to handle interpretation for (1) partial oil-wetting, and (2) random layers of sand, shale and silt. I encourage your careful perusal and consideration of these new ideas.

Let us turn our attention to the cause of the exception to condition (2), i.e., the presence of clay minerals. Clay minerals are a very large family of crystalline, layer-cake assemblage of other pure minerals, some with interlayer water, most with impurities entrained into their crystalline structure and/or adsorbed onto their surfaces, which incidentally, exhibit specific surfaces 10^5 to 10^6 times larger than the mineral quartz. Fortunately, we have but a small subset of clay minerals of this very large family that constitute the dominant clay minerals in siliciclastic reservoir rocks. Thus, the task of describing this subset of clay minerals and deducing their physical chemical properties, is likewise greatly reduced. Nonetheless, this small subset of clay minerals is more

than sufficient to affect the measurement of other physical chemical properties we make in the subsurface, such that the interpretation of reservoir properties is no longer simple. The siliciclastic reservoir rocks that contain 5% > clay minerals > 50% of their grain volume have become known as ‘shaly sands’ and ‘shaly sandstones.’ (Note: the British spelling is ‘shaley’ rather than shaly.)

We now move on to describing the chemical structures of the four main clay minerals: kaolinite, smectite, illite, and chlorite. I call these clay minerals the “Big-Four”. The etymology of the strange sounding names of the clay minerals is quite interesting but belongs in a separate book on clay minerals. Even these four names are themselves family names and have a large number of subsets, but their structures are similar and have differing dominate cations associated with their chemical structures.

In order to discuss the Big-Four we must first discuss the individual minerals that make up their layer-cake tiers, like in a real cake, one layer vanilla, one layer jam, and repeated one atop the other until reaching the desired size. There are two groupings of these mineral layers that are used to describe many families of clay minerals including the Big-Four mentioned above: (1) 1:1 as the repeating unit, e.g., AB AB etc., and (2) 2:1 as the repeating unit, e.g., ABA ABA etc. In my analogy above, A is the vanilla cake and B is the jam. Chemically, the B layers are silica and the A layers are alumina. These two minerals have different structures. Silica is composed of silicon, Si, and oxygen, O. Silicon is a carbon analog; it falls directly below carbon in Group IV in the periodic table of elements. Thus, when silicon bonds with oxygen, it forms four-covalent bonds arranged such that these four silicon–oxygen bonds are directed toward the corners of a regular tetrahedron, with Si in the center and O at the four apexes, and we write it chemically as $\text{SiO}_4^{=}$. Figure 1 shows a naked tetrahedron and a silica molecule.

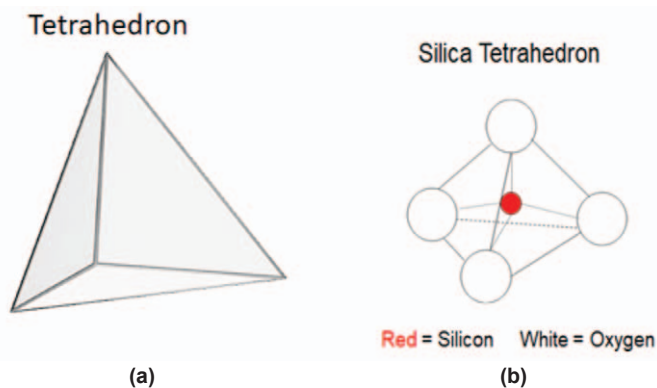


Fig. 1—(a) depicts a tetrahedron; a geometrical shape composed of four equilateral triangular sides. (b) Shows how the silica molecule fits in this tetrahedral shape. All Si-O bonds are of equal length, all four oxygens are equidistant from each other, and the silicon resides in the geometrical center of the tetrahedron.

I am sure you that are aware that the chemical formula for quartz is SiO_2 and that it is electrically neutral, but I have shown you a depiction of silica as a molecule of $\text{SiO}_4^{=}$ with a double negative charge. Well there is more to the story. When silica starts to grow into a crystal, first six silica tetrahedrons join together by sharing a single apex of each tetrahedron and forming a hexagon grouping, as shown in Fig. 2.

Six Silica Tetrahedrons share an apex to form a hexagon – notice hole

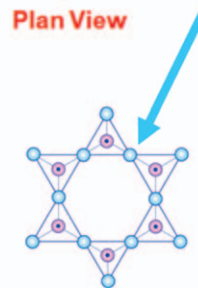


Fig. 2—First step the silica molecule makes as it starts to grow into a crystalline shape. Six silica molecules share a single apex oxygen and form an hexagonal structure. This is a very common chemical structure in nature.

If you now think of them as small hexagon-shaped tiles, you can see that many of these tiles can grow together in a plane leaving no space between the tiles. It is a common structure seen in many crystals and is referred to as “tiling space.” Scalene triangles or pentagons cannot do this. The result is shown in Fig. 3. Thus, when using this scheme the mineral grows outward in the plane of the paper, limited only by the amount of silica, and the structural strength of the resulting wafer. Growth in the third dimension (as it does in quartz) is inhibited by the simultaneous growth of the alumina layer. But let us take a closer look at this structure in Fig. 3. The center of the hexagon grouping of silica molecules is void. There is nothing there. I hope it reminds you of an empty honeycomb. It is also the shape of the inside braces of aluminum sheets (really sandwiches) used to make airplanes—light weight but very strong. Secondly, I now ask you to look at Fig. 4 in which we have taken a single hexagon of silica and look at it from the side. In reality, we observe that one side of the hexagon is in a plane (flat) while the other is pointed like a child’s version of a crown. Because the hexagon has a hole in the center, the child can actually put this crown on his/her head. This shape is important, so store it away and remember it. We know that quartz is a 3D crystal, but in clay minerals the layer structure keeps the silica from propagating up and only allows it to grow laterally. Hence, a silica layer starts to grow upon the alumina layer preventing its 3D expansion, which in turn

provides a platform for alumina to grow, and the process repeats for hundreds of repeating units to give rise to the clay mineral platelet. The silica layer, or “B” layer from above is now described, and we can turn our attention to the “A” layer, alumina.

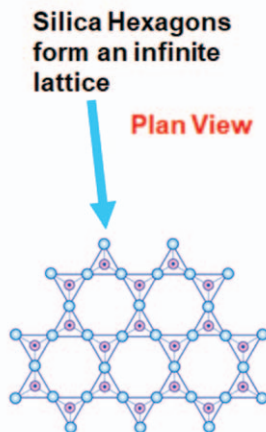


Fig. 3—A silica hexagon combines into an infinite lattice by sharing an oxygen apex between hexagonal structures. Hexagons only grow in the X-Y plane.

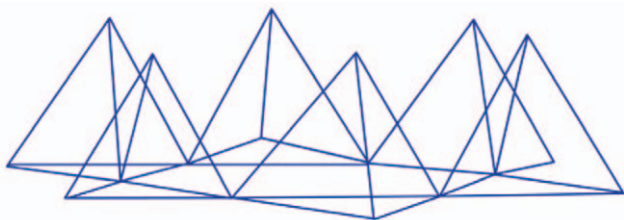


Fig. 4—A different view of the hexagonal ring of alumina molecules. The hexagonal ring forms a pointed crown-like structure on the upper side, while the bottom side is flat. Note the large void in the center of the ring.

Alumina is composed of aluminum Ions (Al^{+3}), oxygen Ions ($\text{O}^{=}$) and hydroxyl Ions (OH^-), where H represents the element hydrogen. Because of aluminum’s place in Group III in the periodic table, when it forms covalent bonds it makes six bonds, all the same length, and directed toward the apexes of a regular octahedron. Figure 5 shows a picture of a naked octahedron. The best way I can describe this structure is two square pyramids, bottom to bottom like two cymbals. Also in Fig. 5, I have shown you the octahedron with the seven ions in place: one aluminum in the center, four hydroxyls in a plane at the corners of the shared pyramid bases, and two oxygen ions one above and one below the plane of the shared pyramid bases. We can write the chemical formula as $\text{Si}^{+3}\text{O}^{=}\text{4OH}^-$ and we observe that we have yet again an imbalanced negative charge in the molecule. Despair not, we now have to grow this alumina octahedron in a plane to make the second layer, and sharing of oxygens with other octahedrons and with the silica layer evens out the charges. In Fig. 6 we observe how the octahedrons propagate in a

plane. They can share faces and leave no vacant space at all.

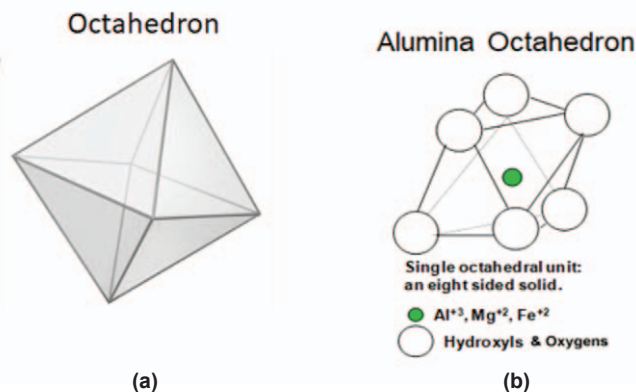


Fig. 5—(a) depicts the geometrical shape of an octahedron, a geometrical shape composed of eight equilateral triangles. (b) The alumina molecule configures to this shape with oxygens and hydroxyl ions residing at the six apexes and the aluminum ion residing at the geometrical center of the octahedron. All six of the Al-O bonds are of equal length and the oxygens are equidistant from each other.

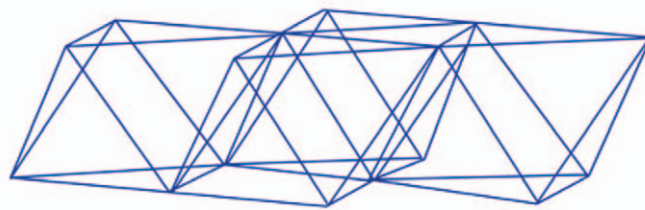


Fig. 6—Geometrical projection of the alumina octahedra showing how the crystal grows in the X-Y plane by sharing one of its eight faces. By doing so, the lattice grows without leaving any gaps between the octahedra.

Now we are ready to assemble the entire clay mineral crystal. Let us start with the simplest case: a two-layer clay mineral; the AB AB case. Let us abandon the surrogate letters, A and B, and use a more recognizable symbology by using T to represent the silica tetrahedron and O to represent the alumina octahedron (see Fig. 7, which describes this new symbolism). The alumina structure is symmetrical and this fits the symmetrical “O” symbol. However, the silica hexagonal growth unit is not symmetrical; remember the analogy of a crown. One face is flat while the other has six points. Thus the “T” symbol mimics this behavior by having a flat top and a pointed bottom. We can now see that points of the hexagonal silica layer aligns with the oxygens in the octahedral layer and can share this covalent bonding, finally resulting in electrical balance. Additionally, this repeating unit is now flat on top and bottom. Mechanically we now stack the repeating units one upon the other to give rise to the clay mineral platelet. But there is no chemical bonding between the repeating units. What keeps them together? The attractive force that keeps these repeating units together is van der Waal’s forces, i.e., the electrostatic attraction arising from fluctuating molecular dipole moments.

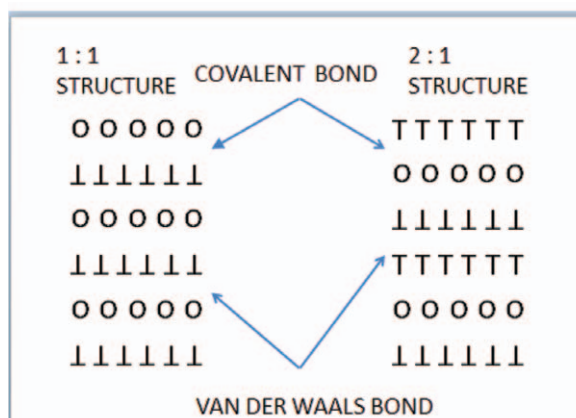


Fig. 7—The silica tetrahedral and alumina octahedra combine in three dimensions to form two types of clay minerals, 1:1 and 2:1. The “T” has been turned upside down to symbolize that the shaft of the “T” is the point of the crown and the bottom of the “T” is the flat bottom of the six tetrahedra. In the 1:1 mineral, alternating layers of silica and alumina chemically combine into one unit. This unit then repeats in the Z plane. The only attractive force holding the repeating units together comes from van der Waals attractions—very weak compared to the covalent bonds resulting from sharing of oxygens between the silica and alumina molecules. In the 2:1 mineral, two silica tetrahedra chemically attach to the central alumina molecules to form a three-layer repeating unit. Again, the only bond between the repeating units arises from van der Waals attractions.

We follow a similar process to describe 2:1 clay minerals and start by glancing at Fig. 7 which shows the arrangement of silica tetrahedrons, T, and alumina octahedrons, O, in a 2:1 assemblage. This configuration is arrived at by inverting a silica tetrahedron and placing it atop the alumina octahedral layer of a 1:1 clay mineral. We can chemically join it by sharing oxygens just as we did to join the silica tetrahedrons at the bottom of the octahedral layer to make 1:1 clay minerals. Therefore, now the repeating unit is three layers: one alumina and two silica layers.

Before we get into the next subtopic, I wish to remind

you that the use of geometric figures, such as a tetrahedron and octahedron, in drawings in the structure of clay mineral platelets is only a teaching aide. The lines shown are not bonds, just geometrical place holders to aide you in correctly placing the components of the discussed clay mineral platelets; for example, silica ($\text{SiO}_4^{=}$) resides inside the tetrahedron with the silicon atom at the geometrical center while the oxygen atoms reside at the apexes (one oxygen per apex), resulting in all silicon-oxygen bonds being of equal length, which in turn gives rise to a completely symmetrical arrangement. The geometry of the alumina similarly places the aluminum atom at the geometric center of an octahedron and places oxygens and hydroxyls at the six apexes, resulting in equal aluminum-oxygen bond lengths, which in turn lead to a symmetrical molecule. The lines shown in the alumina structure are NOT bonds, but are intended to identify the correct placement of the atoms. If one leaves out these “training aides” it is most difficult to look at all the atomic spheres and know what goes with what.

After having mastered the messy arrangements of empty geometrical figures, I will abandon them. We can actually make our discussions of clay mineral structures somewhat simpler because we know that each layer is growing outward in a plane, hence nothing is changing in the X-Y plane in its geometrical arrangement and we choose not to draw all this sameness which makes the figures much smaller and clearer. We can concentrate on the vertical arrangements, Z-axis, which do vary and give the various characteristics that we identify with each clay mineral type (crystallographers use a different nomenclature and refer to this vertical axis as the C axis.) The late, great clay mineralogist, Professor R.E. Grim of the University of Illinois, advocated the use of this short-hand method in his famous textbook on clay mineralogy (Grim, 1968), and we have adopted it in our discussion on the structure of clay minerals.

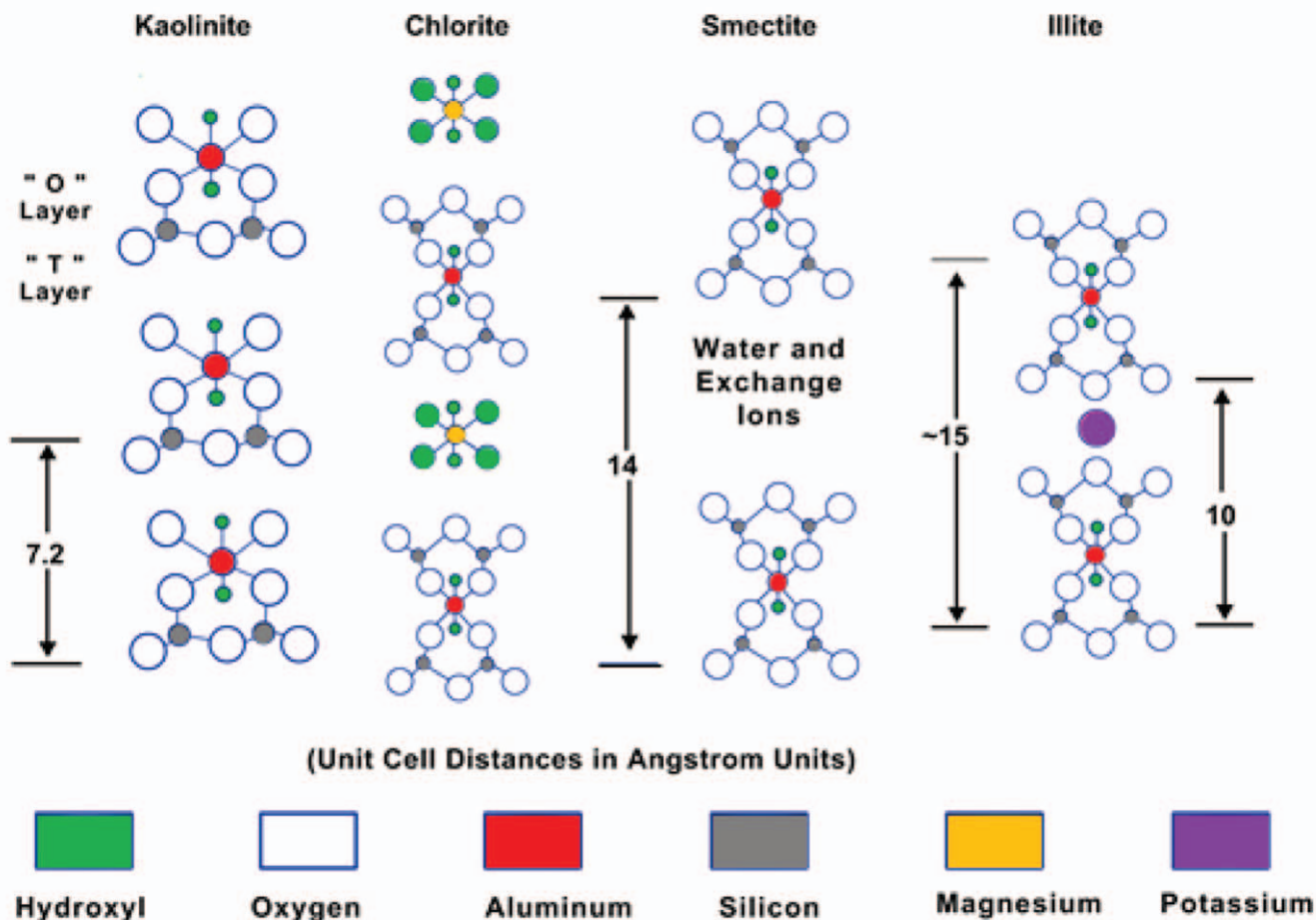


Fig. 8—The chemical structures of the “Big Four” clay mineral species using Grim’s (1968) notation. Left to right: kaolinite, chlorite, smectite, and illite. The legend shows the correspondence between color and atomic species.]

One of the first things to observe is that kaolinite and chlorite are grouped together as 1:1 clay mineral structures, while smectite and illite are grouped as 2:1 clay mineral structures. The thickness of layers and repeating units are shown in Angstrom units (10^{-12} m). We use this nomenclature because one Angstrom is about the size of the ions in the chemical structures. Please note the size of the repeating unit in kaolinite compared to smectite, e.g., 7 Å for kaolinite, and 14 Å for smectite in a salty brine. Because a not uncommon thickness of a clay mineral platelet is 0.1 μm (10^{-7} m) and if we let the average size of the repeating unit to be 10 Å or 10^{-11} m, we must stack about 10,000 repeating units atop one another to make this typical clay mineral thickness (who are the masons and where is their scaffolding?)

In the laboratory, it is simple to artificially make a pure crystal as we have control of reagent purity, solvent purity, temperature, and pressure. In the earth, however, where clay minerals originate, purity is hardly a byword, more like a witch’s brew of chemicals and temperature and pressure are “as is” for a given location. Hence we really have to take what nature gives us to grow such minerals. Silica and alumina

are relatively insoluble ions, hence they must be generated “on-the-fly” as the crystal grows. We believe the dominant ions in these brews to be sodium, magnesium, calcium, chlorine, carbonate, bicarbonate, iron, and hydrogen and hydroxyl from water. The combinations are infinite and will be controlled locally by deep, hot, circulating brines and the minerals they have to dissolve and later seep to shallower formations via faults and fractures. The assembly of these minerals is probably quite fast when appropriate chemical concentrations are present. Silica and alumina ions being the least soluble will be the first ones to crystallize out of the mix, but why certain clay minerals form and not others is a question I cannot answer. However, once formed they leave behind the more soluble ions mentioned above. Well, not quite. This on-the-fly assembly can be interloped upon by the soluble ions, if their size allows them to replace, say Al^{+3} with Fe^{+2} and not strain the growing crystal, all is fine. Such a behavior, which is referred to as isomorphic substitution, i.e., same size substitution, can be observed in Fig. 9. I liken it to making a brick wall—it turns out okay as long as the bricks are all the same size and it does not matter what the

color of the brick is. As in life, size really does matter. The layer structure is fine mechanically, but because we have used a smaller valence ion, we leave behind a negative defect in the crystal. This is a random process and depends upon the concentrations of the ions in the crystallizing brew. Such a negative defect gets buried in the growing process, and life goes on. The result is sort of like a plum pudding, with negative defects spreading throughout the crystal platelet (see Fig. 10). Because the crystal assemblage contains many, many ions, we can never sense those deep within the crystal due to shielding effects. The result is that only the defects near the surface or on the surface can be sensed from outside the clay platelet. Soluble cations such as sodium are drawn to these negative defects where the brine solution contacts the clay mineral platelets, and hence locally keeps the area electrically neutral.

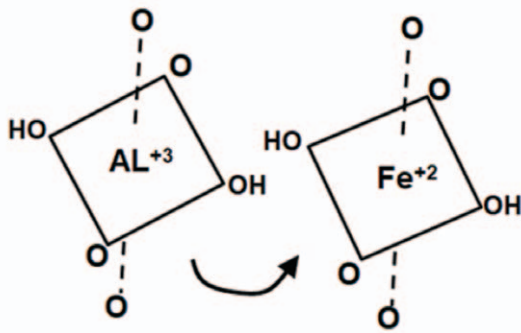


Fig. 9—Illustration of how isomorphous substitution occurs in the alumina layer resulting in the generation of a negative charge defect in the crystal lattice without disrupting the structural strength of the resulting clay mineral platelet. This can happen when the two ions are roughly equal in size.

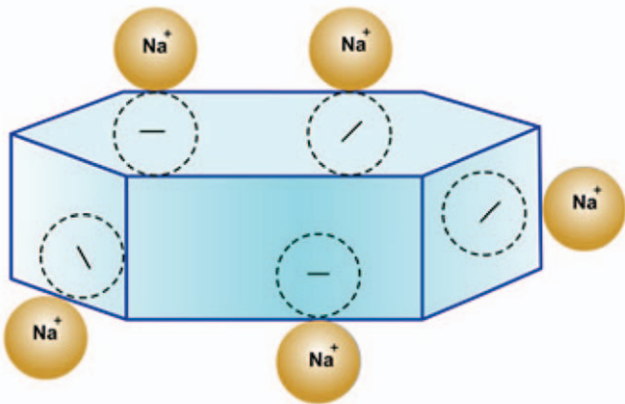


Fig. 10—Illustration of how the hexagonal clay platelet only exhibits negative charge defects on or near the surface of the platelet due to shielding from overlaying ions in the structure. These negative defects attract hydrated sodium ions from the brine solution.

Of course, to keep sodium in solution, six water molecules surround each sodium cation, and the “p” orbitals (sorry about the quantum mechanical reference) orient the six water molecules into an octahedral complex ion configuration with the water aligning at the apexes of the octahedron, negative oxygen pointing in toward the positive sodium ion at the center of the octahedral complex. Figure 11 shows the corresponding configuration.

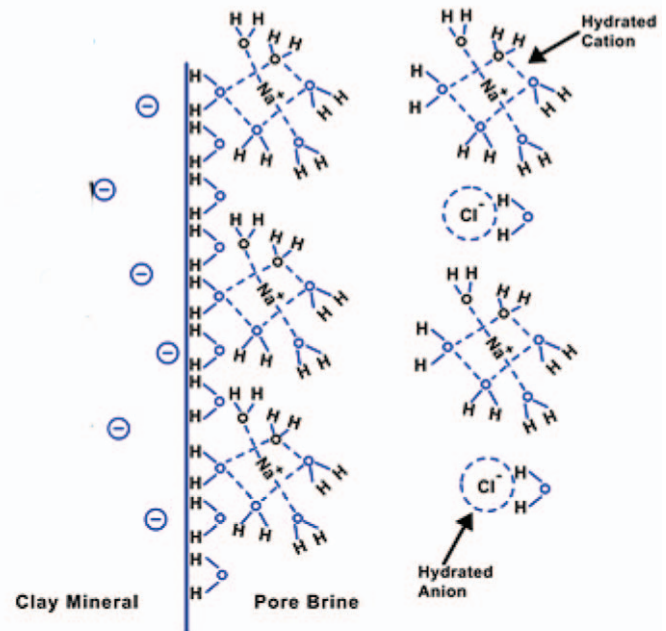


Fig. 11—Depiction of the water molecules, as well as the ions, to show how messy the distribution becomes. Each sodium ion requires six water molecules to stay in solution. The electronegative end of the water molecule (the oxygen end) aligns toward the positively charged cation and is held in a pseudocomplex-ion arrangement aligned and positioned at the apexes of an octahedron. This alignment is driven by the unfilled “p” orbitals of the sodium ion. The figure also shows the electropositive ends of water (the hydrogens) aligning toward the electronegative surface of the clay mineral and quartz as well resulting in capillary attraction of the water to the surface of the pore walls.

The combination of the negative defects within the clay mineral platelet and the hydrated sodium cation (also some plain water being held by van der Waals forces, i.e., capillary-trapped water) is referred to as the “electrical double layer” or EDL. The amount of water in this EDL is controlled by the brine salinity, roughly proportional to the inverse of the square root of the sodium chloride concentration. The effect is explained by noticing that as the concentration of sodium and chlorine ions increase, they shield the negative defect from the solution and hence attract fewer hydrated sodium ions. Therefore, the EDL is at its maximum in very fresh brine and at its minimum in very salty brines. These hydrated cations that are attracted to the negative charges of the clay minerals are referred to as gegen or counter ions. They are not bonded to the surface, but only held by

weak electrostatic forces (van der Waal's forces) while the thermal energy of the surrounding environment is enough to supply energy to the hydrated sodium ion to cause it to leave the surface and be replaced immediately by another hydrated sodium ion. This process, which is referred to as cation exchange (the ions are referred to as exchange ions), is shown graphically in Fig. 12.

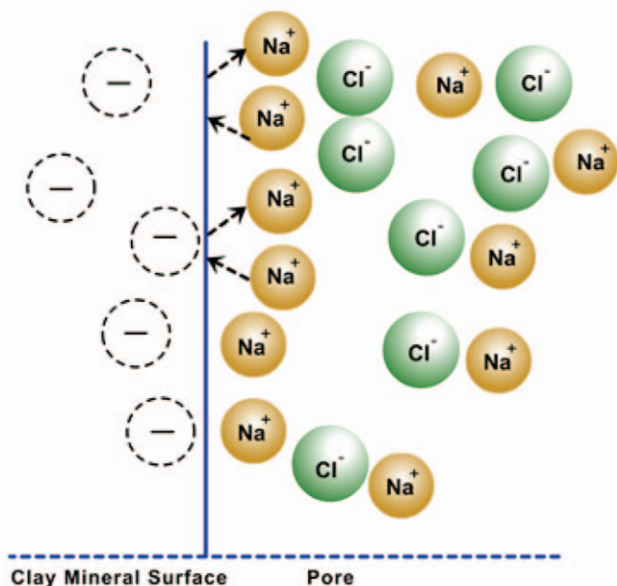


Fig. 12—Illustration of how cation exchange occurs on the surface of the clay minerals when in contact with brine. It is a simultaneous process keeping the surface electrically neutral. For simplicity, the figure does not included the water molecules. This process is diffusion controlled; the translation motion is dependent upon both the temperature of the rock-brine assemblage and the concentration of hydrated ions in solution.

This exchange process is occurring continuously as long as brine is in contact with the clay mineral surface. As the temperature goes up, the exchange process increases as more energy is available to be partitioned to the soluble ions. If an electric field is applied, these exchange ions can carry electrical current along the surface of the clay mineral by hopping from one exchange site to the next. Having available ions in the brine then allows the exchange process to aid this electrical conduction. Thus brine-containing shaly sands have normal conductivity through the brine, and in addition, some extra conductivity along the surface of the clay mineral platelets. It is this extra conductivity from the exchange ions that cause interpretation difficulties from measured conductivity of a formation being transformed into water saturation. This extra conductivity is then proportional to the concentration of negative defects sensed by the brine and this is referred to as the cation exchange capacity of a given clay mineral. So the source of exchange capacity seen in clay minerals is due to isomorphous substitution of the central ion in the alumina complex ion by an ion of lower

positive valence resulting in a local negative charge defect in the clay mineral structure. These negative defects attract hydrated cations in the brine resulting in an electrically neutral crystal. However, these electrostatic bonds are weak and can swap places with other hydrated positive ions in the brine. This “swap” is called exchange, and the number of negative defects seen on the surface is measured as its exchange capacity in equivalents per gram of clay minerals. Each of the Big-Four clay minerals has quite different levels of exchange capacity. The average values are shown in Table 1. The higher the number of exchange sites leads to larger extra conductivity in a shaly sand. Because the development of charge defects is random, the range of observed exchange capacity in some of the Big-Four is large. We show this behavior for smectite in Table 2. Thus, even if we know the relative amount of a given clay mineral in a rock, we cannot predict the value of cation exchange capacity until it is actually measured. This brings some excitement to the life of a petrophysicist when he/she learns that the constant values shown in textbooks must now be considered variables in our interpretations. Of course, the simple explanation given in the paragraphs above does not provide you with the analytical tools needed to make corrections to measured electrical conductivities for the extra conductivity due to cation exchange ions, hence there is still much more to come.

Table 1—Exchange Capacity of the Big-Four Clay Minerals

Clay Type	Range of CEC (meq/100 g rock)
Smectite	80 to 100
Illite	20 to 30
Kaolinite	2 to 3
Chlorite	0 to 1

These average values are relative in magnitude and exhibit variability.

Table 2—Values of Exchange Capacity of Smectite from Six Locations Across the United States

Clay Formation	Exchange Capacity (meq/100 g clay)
Belle Fourche, South Dakota	85
Upton, Wyoming	100
Otay, California	52
Bayard, New Mexico	127
Polkville, Mississippi	63
Cheto, Arizona	96

This table emphasizes the futility of assuming a single average value for all smectites.

We have now come to the end of the first of three tutorials on shaly sands. Worry not; we have yet to scratch the surface of effects that these clay minerals cause to our logging tool responses. The chemical structures shown in Fig. 8 and the knowledge of exchange capacity of clay minerals will lead us into understanding the cause of various perturbations of

tool responses caused by clay minerals and what we can do about them. Stay tuned.

ACKNOWLEDGEMENT

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ABOUT THE AUTHOR



E.C. Thomas is a consulting petrophysicist and owner of Bayou Petrophysics and provides technical training in shaly sand analyses and all other areas of petrophysics for Petroskills. E.C.'s professional career interests and publications have spanned the entire field

of formation evaluation/reservoir characterization, i.e., petrophysics. In 1992, he wrote a biographical sketch of Gus Archie for *The Log Analyst* to commemorate the 50th anniversary of the publication of the Archie Equation.

E.C. retired from Shell E&P Technology Company as a Petrophysical Advisor where he actively pursued research and field evaluation topics in the area of Petrophysics for over 32 years. He also authored and taught basic, intermediate and advanced courses in petrophysics for more than seven years at Shell's Training Center. E.C.'s academic background includes a BS in Chemistry from LSU, a PhD in Physical Chemistry from Stanford University, and a year of postdoctoral research in Physical Chemistry at Princeton University.

E.C. has served SPWLA and SPE in many capacities, including SPE Distinguished Lecturer and chairman of the 1998 Archie Conference. Professional recognitions have included invitations to serve as keynote speaker at several SPE and SPWLA regional and topical conferences, and at the 2005 SPWLA Annual Symposium. In 2000, E.C. received

the SPWLA Distinguished Technical Achievement Award; and in 2004, the SPWLA Gold Medal Award for Technical Achievement. E.C. served as a Petrophysical Consultant to the President's Commission investigating the BP-Deepwater Horizon blowout and resulting oil spill. E.C. currently serves as a technical reviewer for *Petrophysics* and *SPE Reservoir Evaluation & Engineering*.