

THE APPLICATION OF NATURAL ZEOLITES IN ANIMAL SCIENCE AND AQUACULTURE

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SUMMARY

As agriculturalists increase their efforts to expand crop and animal production, numerous mineral materials are receiving greater attention as soil amendments and as dietary supplements in animal husbandry. The zeolite group of minerals stands out among the rest, and its exciting bag of physical and chemical tricks promises to contribute to many areas of agriculture and aquaculture in the next decade. Their abundance and availability has aroused considerable interest in experiment stations of several nations, although the number of publications and amount of "hard" data on their usefulness in agriculture are still small. A review of this subject reveals that both the ion-exchange and adsorption properties of natural zeolites can be exploited to make more efficient use of feed nitrogen in animal nutrition, to reduce intestinal diseases prevalent in young swine and ruminants, to control moisture and ammonia content of animal manure, to purify recirculating hatchery waters in aquaculture, to provide oxygen-enriched air for fish breeding and transportation, and to reduce the nitrogen content of feedlot- and hatchery-runoff waters.

Most of this work has been carried out in Japan where zeolitic tuffs have been used for years to control the malodor of animal wastes and to raise the pH of acidic volcanic soils. The addition of about 10% clinoptilolite to the diets of chickens and pigs appears to increase feed efficiency by as much as 25%. Studies in Japan

and in the United States suggest that the incidence of scours in young swine may be substantially reduced by adding zeolites to the animals' rations. These same zeolites can be used to extract NH_4^+ from animal wastes and hatchery waters by ion exchange. Numerous deposits of natural zeolites are known in the U.S. totaling several hundred million metric tons. Their flat-lying nature and closeness to the surface suggests a large supply of inexpensive zeolite are available to the industry in the \$50.00 to \$75.00 per metric ton price range.

(Key Words: Zeolites, Animal Nutrition, Aquaculture, Excrement Treatment, Ion Exchange, Ammonia.)

INTRODUCTION

Despite the fact that Agricola, the noted 16th century author of *De Re Metallica* and *De Natura Fossilium*, was a farmer in name only (Georg Bauer of Freiberg, Saxony), there has always been a close relationship between the agricultural and geological sciences. The strong dependency of crop production on the existence and maintenance of fertile soils has led agronomists deep into the mineralogical and geochemical aspects of clays and other soil constituents. Likewise, the addition of crushed limestone to chicken feed to strengthen egg shells is well known, as is the use of bentonitic clays as binding agents in pelletized animal feedstuffs. As agriculturalists the world over increase their efforts to expand crop and animal production, numerous mineral materials are receiving greater attention as soil amendments and as dietary supplements in animal husbandry. One group of minerals stands out among the rest, and its exciting bag of physical and chemical tricks promises to contribute to many areas of agricultural and aquacultural technology in the next decade. This group is the zeolite group of minerals, and the research and development efforts aimed at the possible utilization of zeolites in animal science and aquaculture

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has been labeled by some as "zeo-agriculture."

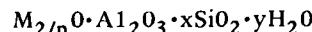
Most of the past activities in zeo-agriculture have taken place in Japan where farmers have used zeolite rock for years to control the moisture content and malodor of manure and to increase the pH of acidic volcanic soils. The growing awareness of the abundance and availability of inexpensive natural zeolites in the United States has prompted considerable interest, and zeolites are becoming the subject of serious agricultural experimentation around the country. Some of the ways in which zeolite minerals can contribute to more efficient livestock and crop production are discussed here, along with their role in the rapidly expanding areas of fish breeding and aquaculture. At this stage in its development, the number of papers on "zeo-agriculture" in the literature is small, and hard data are few; however, despite these drawbacks, the potential of zeolite raw materials seems apparent, and may be of interest to many in the field of agricultural technology.

NATURAL ZEOLITES

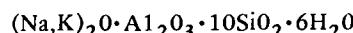
Zeolites are crystalline, hydrated aluminosilicates of alkali and alkaline earth cations, having infinite, three-dimensional structures. They are further characterized by an ability to lose and gain water reversibly and to exchange constituent cations without major change of structure. Zeolites were discovered in 1756 as well-formed crystals in cavities of basal rock by Baron Axel Fredrick Cronstedt, a Swedish mineralogist, who named them from the Greek words $\zeta\omega$ and $\lambda\theta\sigma\sigma$, meaning "boiling stones," in allusion to their peculiar frothing characteristics when heated before the blowpipe. Since that time, nearly 40 natural species have been recognized, and an equal number have been synthesized in the laboratory. Synthetic zeolites are the mainstays of the multimillion dollar molecular sieve businesses that have blossomed in the last 15 years in this and other countries. The potential applications of both synthetic and natural zeolites stem, of course, from their fundamental physical and chemical properties, which in turn are related directly to their individual crystal structures and chemical compositions.

Crystal Structure of Zeolites. Along with quartz and feldspar minerals, zeolites are tektosilicates, that is, they consist of three-dimensional frameworks of SiO_4^{-4} tetrahedra, wherein all four corner oxygen ions of each tetrahedra are shared with adjacent tetrahedra, as

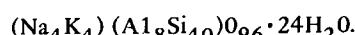
shown in figure 1. This arrangement of silicate tetrahedra reduces the overall Si:O ratio to 2:1, and if each tetrahedron in the framework contains silicon as the cation, the structures are electrically neutral, as is quartz (SiO_2). In zeolite structures, however, some of the quadrivalent silicon is replaced by trivalent aluminum, giving rise to a deficiency of positive charge. This charge is balanced by the presence of mono- and divalent cations, such as Na^+ , Ca^{++} , and K^+ , elsewhere in the structure. Thus, the oxide empirical formula of a zeolite is of the type:



where M is any alkali or alkaline earth cation, n is the valence of that cation, x is a number from 2 to 10, and y is a number from 2 to 7. The oxide and unit-cell formulae of clinoptilolite, the most common of the natural zeolites, follow:



or



Ions within the first set of parentheses in the unit-cell formula are known as exchangeable cations; those within the second set of parentheses are called structural cations, because with oxygen they make up the tetrahedral framework of the structure. Loosely bound molecular water is also present in the structures of all natural zeolites.

Whereas the framework structures of quartz

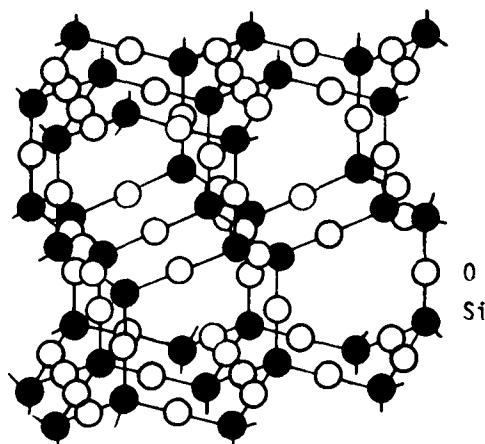


Figure 1. Three-dimensional arrangement of silicate tetrahedra in tektosilicates. Crystal structure of the beta-tridymite form of SiO_2 .

TABLE 1. REPRESENTATIVE FORMULAE AND SELECTED PHYSICAL PROPERTIES OF IMPORTANT ZEOLITES

Zeolite	Representative unit-cell formula ^a	Void volume ^a	Channel dimensions ^a	Thermal stability	Ion-exchange capacity ^b
Analcime	$\text{Na}_{1.6}(\text{Al}_{1.6}\text{Si}_{3.2}\text{O}_{9.6}) \cdot 16\text{H}_2\text{O}$	18%	2.6 Å	High	4.54 meq/g
Chabazite	$(\text{Na}_2,\text{Ca})_6(\text{Al}_{1.2}\text{Si}_{1.4}\text{O}_{7.2}) \cdot 4\text{OH}_2\text{O}$	47	3.7 X 4.2	High	3.81
Clinoptilolite	$(\text{Na}_4\text{K}_4)(\text{Al}_6\text{Si}_{4.0}\text{O}_{9.6}) \cdot 24\text{H}_2\text{O}$	39?	3.9 X 5.4	High	2.54
Erionite	$(\text{Na},\text{Ca},\text{K})_9(\text{Al}_9\text{Si}_{1.2}\text{O}_{7.2}) \cdot 27\text{H}_2\text{O}$	35	3.6 X 5.2	High	3.12
Faujasite	$\text{Na}_{5.8}(\text{Al}_{5.8}\text{Si}_{1.4}\text{O}_{3.84}) \cdot 27\text{H}_2\text{O}$	47	7.4	High	3.39
Ferrierite	$(\text{Na}_2\text{Mg}_2)(\text{Al}_6\text{Si}_{3.0}\text{O}_{7.2}) \cdot 18\text{H}_2\text{O}$		4.3 X 5.5 3.4 X 4.8 4.4 X 7.2 4.1 X 4.7	High	2.33
Heulandite	$\text{Ca}_4(\text{Al}_6\text{Si}_{2.8}\text{O}_{7.2}) \cdot 24\text{H}_2\text{O}$	39	4.0 X 5.5 2.9 X 5.7 6.7 X 7.0	Low	2.91
Laumontite	$\text{Ca}_4(\text{Al}_6\text{Si}_{1.6}\text{O}_{4.8}) \cdot 16\text{H}_2\text{O}$		4.6 X 6.3	Low	4.25
Mordenite	$\text{Na}_6(\text{Al}_6\text{Si}_{4.0}\text{O}_{9.6}) \cdot 24\text{H}_2\text{O}$	28	4.2 X 4.4 2.8 X 4.8 3.3	High	2.29
Phillipsite	$(\text{Na},\text{K})_{1.0}(\text{Al}_{1.0}\text{Si}_{2.2}\text{O}_{6.4}) \cdot 20\text{H}_2\text{O}$	31		Low	3.87
Linde A	$\text{Na}_{1.2}(\text{Al}_{1.2}\text{Si}_{1.2}\text{O}_{4.8}) \cdot 27\text{H}_2\text{O}$	47	4.2	High	5.48
Linde X	$\text{Na}_{8.6}(\text{Al}_{8.6}\text{Si}_{1.06}\text{O}_{3.84}) \cdot 264\text{H}_2\text{O}$	50	7.4	High	4.73

^aTaken mainly from Breck, 1974; Meier and Olson, 1971. Void volume is determined from water content.

^bCalculated from unit-cell formula.

and feldspar are dense and tightly packed, those of zeolite minerals are remarkably open, and void volumes of dehydrated species as great as 50% are known (table 1). Each zeolite species has its own unique crystal structure and, hence, its own set of physical and chemical properties. Most structures, however, can be visualized as SiO_4 and AlO_4 tetrahedra linked together in a

simple geometrical form, such as that shown in figure 2a. This particular polyhedron is known as truncated cubo-octahedron. It is more easily seen by considering only lines joining the midpoints of each tetrahedron, as shown in figure 2b. Individual polyhedra may be connected in several ways; for example, by double four-rings of oxygen ions, as shown in figure 3a,

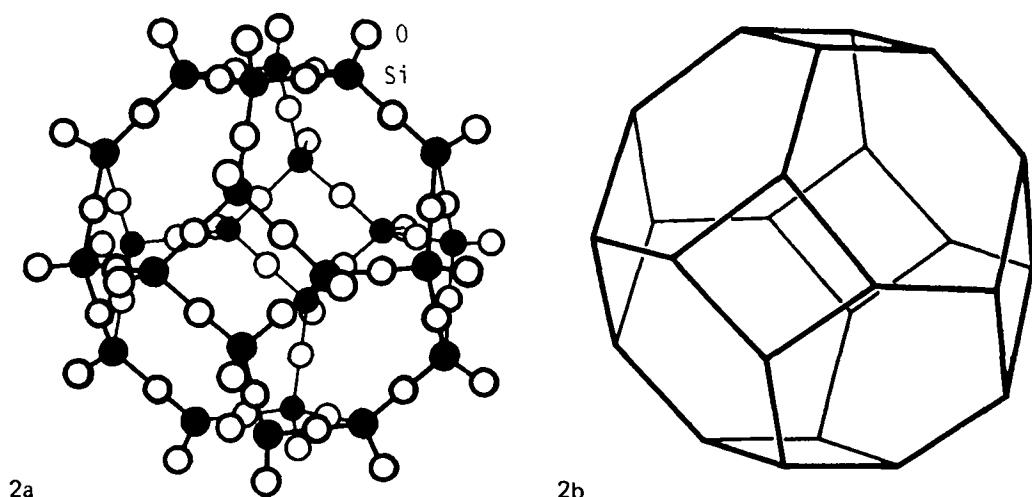


Figure 2. Simple polyhedron of silicate and aluminate tetrahedra. (a) Ball and peg model of truncated cubo-octahedron. (b) Line drawing of truncated cubo-octahedron; lines connect centers of tetrahedra.

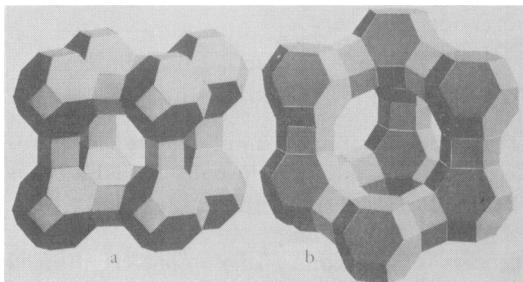


Figure 3. Arrangements of simple polyhedra to enclose large central cavities. (a) Truncated cubo-octahedra connected by double four-rings of oxygen in structure of synthetic zeolite A. (b) Truncated cubo-octahedra connected by double six-rings of oxygens in structure of faujasite.

or by double six-rings of oxygen ions, as shown in figure 3b, the framework structures of synthetic zeolite A and the mineral faujasite, respectively. Solid-sphere models of synthetic zeolite A and of the mineral chabazite are illustrated in figure 4.

It is evident (figures 2 to 4) that there is considerable void space within both the simple polyhedra building blocks and within the larger frameworks formed by several polyhedra. The passageways leading into the simple polyhedra are too small for all but the smallest molecules to pass; however, ports or channels up to 8 Å in diameter lead into the large, three-dimensional cavities (figures 3, 4a, 4b).

Adsorption Properties. Under normal conditions, the large cavities and entry channels of zeolites are filled with water molecules forming hydration spheres around the exchangeable cations. If the water is removed, usually by heating to 300 to 400°C for a few hours, molecules having effective cross sectional diameters small enough to fit through the entry channels are readily adsorbed on the inner surfaces of the dehydrated central cavities. Molecules too large to pass through the entry channels are excluded, giving rise to the well-known "molecular sieving" property of most crystalline zeolites (figure 5). The surface area available for adsorption ranges up to several hundred square meters per gram, and some zeolites are capable of adsorbing up to about 30% of a gas, based on the dry weight of the zeolite.

In addition to their ability to separate gas molecules on the basis of size, the unusual charge distribution within a dehydrated central

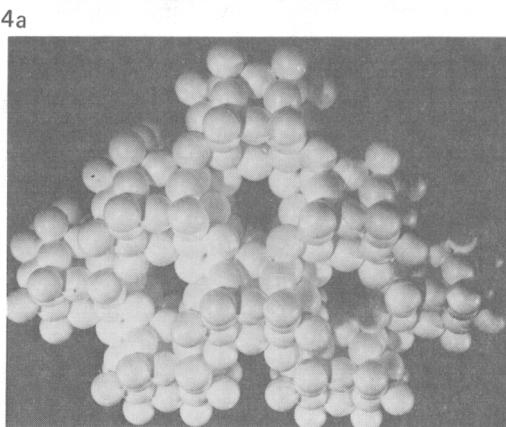
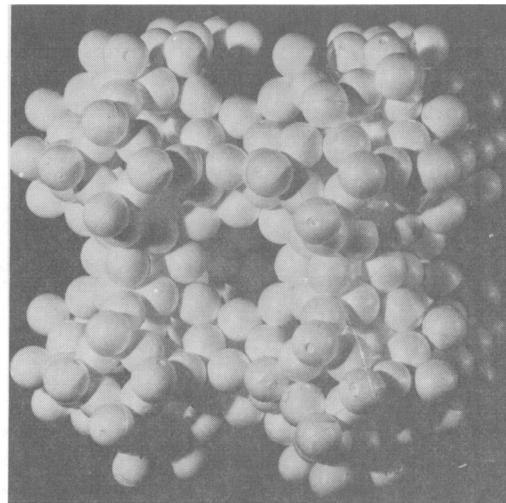


Figure 4. (a) Solid-sphere model of crystal structure of synthetic zeolite A. (b) Solid-sphere model of crystal structure of chabazite.

cavity allows many species with permanent dipole moments to be adsorbed with a selectivity unlike that of almost all other sorbents. Thus, CO₂ is preferentially adsorbed by certain

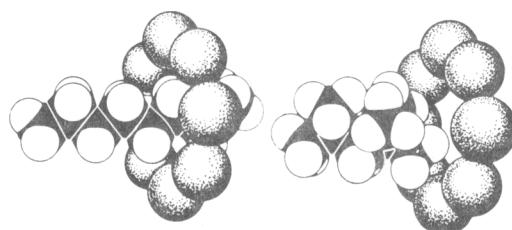


Figure 5. Stylized illustration of the entry of straight-chain hydrocarbons and blockage of branch-chain hydrocarbons at channel apertures.

zeolites over CH₄, providing a means by which impure natural gas or methane streams can be upgraded to high-BTU products. In addition, the small, but finite, quadripole moment of N₂ allows it to be adsorbed selectively from air, producing oxygen-enriched streams at relatively low costs. Both of the above processes may find application in agricultural technology (*vide infra*).

Ion-Exchange Properties. The exchangeable cations of a zeolite are also only loosely bonded to the tetrahedral framework and can be removed or exchanged easily by washing with a strong solution of another ion. As such, crystalline zeolites are some of the most effective ion exchangers known to man, with capacities of 3 to 4 meq per gram being common. Ion-exchange capacity is basically a function of the degree of substitution of aluminum for silicon in the framework structures; the greater the substitution, the greater the charge deficiency, and the greater the number of alkali or alkaline earth cations required for electrical neutrality. In practice, however, the ion-exchange capacity is dependent on a number of other factors as well. In certain species, cations can be trapped in structural positions that are relatively inaccessible, thereby reducing the effective exchange capacity of that species for that ion. Also, ion-sieving may take place if the size of the exchanging cation is too large to pass through the entry channels into the central cavities of the structure. Analcime, for example, will exchange almost completely its Na⁺ for Rb⁺ (ionic radius = 1.49 Å), but not at all for Cs⁺ (ionic radius = 1.65 Å) (Breck, 1974).

Unlike most *non-crystalline* ion exchangers, such as organic resins or inorganic aluminosilicate gels (mislabeled in the trade as 'zeolites'), the framework of a crystalline zeolite dictates its selectivity towards competing ions. The hydration spheres of high field-strength ions prevent their close approach to the seat of charge in the framework; therefore ions with low field strengths are more tightly held and selectively exchanged than other ions. The small amount of aluminum in clinoptilolite, for example, results in a relatively low ion-exchange capacity (about 2.3 meq/g); however,

its cation selectivity is:



Thus, clinoptilolite has a decided preference for larger cations, and its selectivity for NH₄⁺ ions was exploited by Ames (1967) and Mercer *et al.* (1970) in the development of an ion-exchange process for the removal of ammoniacal nitrogen from municipal sewage. This same affinity of clinoptilolite for NH₄⁺, of course, is the basis of many of the uses of this zeolite that are being developed in the agricultural field.

ANIMAL-HUSBANDRY APPLICATIONS

Animal Nutrition

Since 1965, experiments have been in progress in Japan on the use of natural zeolites as dietary supplements for poultry, swine and cattle. Based on the successful use of montmorillonite clay in slowing down the passage of nutrients in the digestive system of chickens and the resultant improvement in caloric efficiency, as reported by Quisenberry (1968), clinoptilolite and mordenite have been added to the normal protein diets of pigs, chickens, and ruminants at several agricultural stations and livestock farms in Japan. Significant increases in the gain of body weight per unit of feed consumed (feed efficiency) and in the "general health" of the animals have been achieved (Minato, 1968).

Poultry. Using clinoptilolite from the Itaya mine, Yamagata Prefecture, and mordenite from Karawago, Miyagi Prefecture, Onagi (1966) found that Leghorn chickens required less food and water and still gained as much weight in a 2-week trial as birds receiving a control diet. Feed efficiency ratios (weight gain/feed intake)⁴ were markedly higher at all levels of zeolite substitution; feedstuffs containing 10% zeolite giving rise to efficiencies more than 20% greater than those of normal rations (table 2). Adverse effects on the health or vitality of the birds were not noted, and the droppings of groups receiving zeolite diets contained up to 25% less moisture than those of control groups, after a 12-day drying period, making them considerably easier to handle.

Arscott⁵ found that broiler chickens fed a diet of 5% clinoptilolite from the Hector, California, deposit gained slightly less weight over a 2-month period than birds receiving a

⁴Excluding zeolite.

⁵Arscott, G. H. 1975, 1976. Dept. Poul. Sci., Oregon State Univ., Corvallis, (*Personal communication*).

TABLE 2. CALORIC EFFICIENCIES OF ZEOLITE SUPPLEMENTS IN POULTRY FEEDING^a

Group no.	Zeolite content of rations	Avg starting wt	Avg final wt	Avg weight gain	Avg feed intake ^b	Feed efficiency ratio ^c
1	10% Cp ^d	553.7g	795.6g	241.9g	668g	.362
2	5% Cp	540.7	778	237.3	697	.340
3	3% Cp	556.7	796	239.3	748	.320
4	10% Mo	532.3	757.3	225.0	634	.355
5	5% Mo	552.3	814.6	262.3	775	.338
6	3% Mo	534.5	791.3	256.8	769	.334
7	Control	556.5	789.3	232.8	782	.298

^aOnagi (1966). Tests carried out on 48-day-old Leghorns over a 14-day period, 30 birds/group. Normal rations consisted of 16.5% crude protein and 66% digestible nutrients.

^bExcluding zeolite.

^cFeed efficiency = weight gain/feed intake (excluding zeolite).

^dCp = clinoptilolite; Mo = mordenite.

normal diet, but average feed-efficiency values were noticeably higher (table 3). Perhaps of greater significance is the fact that none of the 48 test birds on the zeolite diet died during the experiment, while three on the control diet and two on the control diet supplemented with antibiotics succumbed. In addition to an apparent feed-efficiency increase of 4 to 5%, the presence of zeolite in the diet appears to have had a favorable effect on the mortality of the birds.

Swine. Kondo and Wagai (1968) evaluated the use of zeolites in the diets of young and mature Yorkshire pigs in 60-day and 79-day experiments, respectively, and found that the weight gain of animals of both ages receiving diets containing 5% clinoptilolite from Futatsui, Akita Prefecture, Japan, was from 25 to 29% greater than that of animals receiving normal diets (table 4). Feed supplemented with zeolites gave rise to feed efficiencies about 35% greater than those of normal rations when fed

TABLE 3. APPARENT CALORIC EFFICIENCY OF ZEOLITE IN CHICKEN RATIONS^a

Treatment data	Avg weight	Avg consumption ^b	Avg F.E.V. ^c	Survivors of 48 birds
4-week data ^d				
Control diet	730g	1175g	.622	46
Control diet + zntibiotic ^f	708g	1116g	.634	47
Control diet with 5% clinoptilolite	703g	1070g	.657	48
8-week data ^e				
Control diet	1869g	3978g	.470	45
Control diet + antibiotics ^f	1882g	3869g	.486	46
Control diet with 5% clinoptilolite	1783g	3647g	.489	48

^aAdapted from data of Arscott (1975).

^bFeed consumed, excluding zeolite.

^cFeed efficiency value = weight/feed consumed (excluding zeolite).

^dStarter rations (0 to 4 weeks).

^eFinisher rations (4 to 8 weeks).

^f55 ppm zinc bacitracin.

TABLE 4. CALORIC EFFICIENCY OF ZEOLITE SUPPLEMENTS IN SWINE FEEDING^a

Group	Age of pigs		Average weight		Avg wt. gain	Avg ^b feed intake	Avg ^c F.E.V.	Zeolite improvement
	Start	Finish	Start	Finish				
Experimental ^d	60 days	120	15.43kg	44.43kg	29.00kg	85.0kg	.341	
Control ^d	60	120	14.85	35.78	22.93	90.6	.253	
Experimental ^e	99	178	30.73	85.30	54.57	167.6	.326	
Control ^e	99	178	31.20	73.50	42.30	136.2	.308	6%

^aKondo and Wagai (1968). Tests carried out using 5% clinoptilolite in rations of experimental groups.

^bExcluded zeolite.

^cFeed efficiency value = weight gain/ feed intake.

^dEight Yorkshire pigs.

^eTwenty Yorkshire pigs.

to young pigs, but only about 6% greater when given to older animals. All pigs on the zeolite diet displayed polished hair and slightly reddish skin. In addition, the particle size of the feces of the control group was noticeably coarser than that of the experiment group, suggesting that the digestive process was more thorough when zeolites were added to the diet. The feces of animals in the control group were also richer in all forms of nitrogen than zeolite-fed animals, indicating that the zeolites contributed towards a more efficient conversion of feed-stuff nitrogen to animal protein. Han *et al.* (1975, 1976) found that the digestibility of crude protein and nitrogen-free extracts tended to be improved as zeolite was substituted for wheat bran in swine diets at levels from 1 to 6% over a 12-week period.

Toxic or other adverse effects were not noted for any of the test animals described above. On the contrary, the presence of zeolites in swine rations appears to contribute measurably to the well-being of the animals. According to Torii (1977), tests carried out at the Keai Farm near Morioka, Iwate Prefecture, Japan, where 4,000 head of swine are bred,

showed that the death rate and incidence of disease among animals fed a diet containing 6% clinoptilolite was markedly lower than for control animals in experiments conducted over a 12-month period. As shown in table 5, the decrease in the number of cases of gastric ulcers, pneumonia, heart dilation, and in the overall mortality rate is remarkable. The savings in medicine alone amounted to about 75¢ per animal, to say nothing of the increased value of a larger number of healthy pigs. Although no control groups were monitored, Morita (1967) reported that the addition of zeolite to the diet of piglets severely afflicted with scours markedly reversed the progress of this disease within a few days. Four underdeveloped Laundry pigs were fed a diet containing 30% zeolite for the first 15 days and 10% zeolite for the remaining part of a month-long experiment. The severity of the disease decreased almost at once, and feces of all pigs were hard and normal after only 7 days. Although the pigs consumed an average of 1.75 kg of zeolite/head/day, no ill effects were noted, and once they had recovered from diarrhetic ailments, the pigs regained healthy appetites and became vital.

TABLE 5. EFFECT OF ZEOLITE DIETS ON HEALTH OF SWINE^a

Period	Zeolite content of rations	Sickness causes			Heart dilation	Mortality rate	Medicine cost/ head
		Gastric ulcer	Pneumonia				
2/72 to 1/73	0	77	128	6		4.0%	\$2.50
2/73 to 1/74	6% clinoptilolite	22	.51	4		2.6%	\$1.75

^aTest carried out on 4,000 swine at Keai Farm, Morioka, Iwate Prefecture, Japan (Torii, 1974).

Apparently the vitalizing effect of a zeolite diet can be transferred from mother to offspring. Experiments at the Ichikawa Livestock Experiment Station, where 400g of clinoptilolite was fed each day to pregnant sows and continued through the 35-day weaning period of their offspring, showed substantial increase in the growth rate of the young pigs. As shown in table 6, test animals weighed from 65 to 85% more than control-group animals at the end of the weaning period (Buto and Takehashi, 1967). The authors reported that young pigs whose dams received the zeolite diet also suffered almost no attacks of diarrhea, while those in control groups were severely afflicted with scours, greatly inhibiting their normal growth.

Similar studies were conducted at Oregon State University (England, 1975) with young swine using rations containing 5% clinoptilolite from the Hector deposit. Although lesser increases in growth rates were found than in the Japanese studies, the incidence of scours was significantly reduced for animals receiving the zeolite diet. Currently, heavy doses of prophylactic antibiotics are used to control such intestinal diseases, which, left unchecked, result in high mortality rates among young swine after they are weaned. Federal regulations are becoming increasingly stringent in this area, and if antibiotics are prohibited, other means must be found to control such diseases. Natural zeolites may be the answer.

The exact functions of the zeolites in both dietary and antibiotic phenomena are not well understood and await serious physiological and biochemical examination. The ammonium se-

lectivity of clinoptilolite suggests that in ruminants it acts as a nitrogen reservoir in the animals' digestive systems, resulting in a slower release and more efficient use of ammonium ions produced by the breakdown of ingested protein-containing rations. Zeolite particles might also stimulate the lining of the stomach and intestinal tract, causing the animal to produce more antibodies and thereby inhibit diseases such as scours, et cetera.

Ruminants. In an attempt to reduce the toxic effects of high NH_4^+ content of ruminal fluids when non-protein nitrogen (NPN) compounds, such as urea and diuret, are added to the diets of cattle, sheep, and goats, White and Ohlrogge (1974) introduced both natural and synthetic zeolites into the rumen of test animals. Ammonium ions formed by the enzyme decomposition of NPN were immediately ion exchanged into the zeolite structure and held there for several hours until released by the regenerative action of Na^+ entering the rumen in saliva during the after-feeding fermentation period. From both *in vivo* and *in vitro* experiments, they found that up to 15% of the NH_4^+ in the rumen could be taken up by the zeolite. Thus, the gradual release of NH_4^+ allowed rumen microorganisms to synthesize cellular protein continuously for easy assimilation into the animal's digestive system. The zeolite's ability to act as a reservoir for NH_4^+ "... permits the addition of supplemental nitrogen to the animal feed while protecting the animal against the production of toxic levels of ammonia" in the rumen (White and Ohlrogge, 1974).

The amount of zeolite used in these experiments depended on the size of the animal, the

TABLE 6. EFFECT OF PRENATAL ZEOLITE DIET ON NEWBORN PIGS^a

Species	No. of pigs	Group	Average weight (kg)			Weight- gain improve- ment
			New- born	21- days	35- days	
Yorkshire	6	Experimental	1.25	4.3	7.83	63%
	10	Control	1.10	4.2	4.81	
Laundry	6	Experimental	1.20	4.7	8.68	86%
	10	Control	1.10	4.0	4.67	

^aTests carried out at Ichikawa Livestock Experiment Station, Japan. Four hundred grams of clinoptilolite given to sows in experimental group per day and continued to end of weaning period (Buto and Takenashi, 1967).

^bWeight-gain of experimental animals ÷ weight-gain of control animals × 100.

expected concentration of ammonium ions, and the NH_4^+ -exchange capacity and selectivity of the zeolite. Approximately 500 g of a synthetic zeolite was introduced into the 50-liter rumen of a cow; lesser amounts sufficed for sheep. The zeolite was added in the form of a foraminous bolus or as a finely divided powder with the normal rations, the latter method requiring periodic replenishment. Although natural chabazite and clinoptilolite were found to be effective in this application, synthetic F zeolite (Milton, 1961) appeared to work best of all. Synthetic F and W zeolites both have superior ion selectivities and total NH_4^+ -exchange capacities. Considering the current non-availability of these products, however, and their probable high price when they become available, it is apparent that certain NH_4^+ -selective natural zeolites, such as clinoptilolite or phillipsite, may find definite application in ruminant feeding, especially if powdered zeolite can be mixed directly with the normal rations of the animals. The price would be only a few cents per kilogram.

In this same area, Kondo *et al.* (1969) found that clinoptilolite added to the feed of young calves improved their growth rate by stimulating appetite and decreased the incidence of diarrhea and soft-feces. Five percent zeolite was added to the normal grass and hay diets of 10- and 184-day-old heifer calves over a 180-day period. The animals on the zeolite-supplemented diets gained approximately 20% more weight than those in control groups, and although the test calves consumed more feed, the feeding costs per kilogram of weight gained were significantly less than for control animals.

No deleterious effects were noted, and the feces of the test animals contained slightly less water and fewer particles of undigested solids in the >5 mm size-range. The incidence of diarrhea and soft-feces was markedly less in zeolite-fed calves than in control animals (table 7).

Watanabe *et al.* (1971) raised six young bullocks for 329 days on a diet containing 2% clinoptilolite, along with 72% digestible nutrients and 11% crude protein. Although little difference in the final weights of test and control animals was noted, test steers showed slightly larger body dimensions and reportedly dressed out to give slightly higher quality meat. These differences were reflected in the overall higher prices obtained for the test animals and a 20% greater profit. In addition, diarrhea and other intestinal ailments were noticeably less prevalent in the animals on the zeolite diet, and the excrement from these animals was significantly less odiferous, again testifying to the retentivity of clinoptilolite for ammonia. It is unfortunate that a much higher level of zeolite was not used in these experiments; earlier studies in the United States showed that as much as 40% clay could be added to animal rations without adverse effects (Ousterhout, 1970).

Excrement Treatment

The rising demand for animal protein in worldwide diets is attended by several on-going problems, not the least of which is what to do with the mountains of animal wastes produced each day on farms and in feedlots. In the United States alone, livestock production cre-

TABLE 7. OCCURRENCE OF DIARRHEA AND SOFT-FECES AMONG CALVES ON DIETS SUPPLEMENTED WITH 5% CLINOPTILOLITE^a

Time (days)	Incidence of diarrhea			Incidence of soft-feces		
	Grass-fed + zeolite (2 calves)	Hay-fed + zeolite (2 calves)	Control group (6 calves)	Grass-fed + zeolite (2 calves)	Hay-fed + zeolite (2 calves)	Control group (6 calves)
30	0	0	4	0	0	4
36-60	0	1	2	9	4	13
61-90	0	0	2	1	1	13
91-120	1	0	1	2	0	13
121-150	0	0	4	4	0	8
151-184	0	0	0	0	0	0
Total	1	1	13	16	5	51

^aData summarized from Kondo *et al.* (1969).

ates more than one billion metric tons of solid wastes and nearly 400,000,000 tons of liquid wastes each year (Laporte, 1975, p. 365). Accumulations of such magnitude pose serious problems to the health of man and beast alike and are the source of pollution of nearby streams and rivers. In addition, the large amount of undigested protein remaining in the excrement represents a valuable resource that for the most part is being wasted, due to our growing dependence on chemical fertilizers. The physical and chemical properties of many natural zeolites lend themselves to a wide variety of applications in the treatment of animal wastes, including (1) the reduction of malodor and associated pollution, (2) the creation of healthier environments for confined livestock, (3) the control of the viscosity and nutrient retentivity of the manure, and (4) the purification of methane gas produced by anaerobic digestion of the excrement.

Malodor and Moisture Control. The semi-fluid droppings in large poultry houses commonly emit a stench that is discomforting to farm workers and to the chickens themselves. The noxious fumes of ammonia and hydrogen sulfide contribute to decreased resistance to respiratory diseases resulting in smaller and less healthy birds (Ernst, 1968; Kling and Quarles, 1974). Japanese farmers with access to local deposits of zeolitic tuff have sprinkled zeolite on farmyards and manure piles for years to control both the odor and the moisture content (Minato, 1968, 1971). Torii (1974) reported that in many areas of Japan, clinoptilolite is now being mixed with the droppings directly or packed in boxes suspended from ceilings to remove ammonia and thereby improve the general atmosphere in chicken houses. The net

result is reported to be an overall increase in egg production and healthier birds.

Using clinoptilolite from Itaya, Onagi (1965) noted that the water content, maggot population, and ammonia production were all minimized when chicken droppings were routinely mixed with one-third zeolite (table 8). He found that similar results could be obtained if powdered zeolite was added directly to the rations of the birds, all without affecting the vitality or growth rate of the chickens (Onagi, 1966). Apparently, gaseous ammonia reacts with the hydrous zeolite to form ammonium ions which are selectively ion-exchanged and held in the zeolite structure. Onagi (1965) suggested from these experiments that the addition of zeolites to poultry wastes would substantially reduce labor costs associated with air-drying or the high energy costs of thermal treatments, while at the same time retain valuable fertilizer components and meet ecological standards. Similar studies are in progress in the Department of Poultry Science, Oregon State University (Arscott⁶).

In swine raising, Kondo and Wagai (1968) found that the feces of pigs fed a diet containing 10% clinoptilolite were richer in all forms of nitrogen after drying than those from control groups (*vide supra*). As a result of this study and of other investigations, about 25 tons of clinoptilolite per month are spread on the floors of a Sapporo swine-raising facility to adsorb urine and other liquid wastes (Torii, 1974). The buildings are said to be dry, clean, and considerably less odoriferous. Nishimura (1973) reported that mordenite was used in treating liquid swine-wastes. Not only was 90% of the suspended solids removed, but significant reductions in the NH_4^+ , B.O.D., and C.O.D. contents were also achieved, as shown in table 9. In Akita Prefecture, Japan, a zeolitic mudstone is used to treat offensive odors and to reduce moisture content of swine excrement

⁶Ibid, 1976.

TABLE 8. EFFECT OF ZEOLITE ADDITIONS TO CHICKEN DROPPINGS^a

Property	Droppings/zeolite ratio				
	2:1	3:1	5:1	10:1	Control
Moisture content (%)	12.3	13.1	13.4	15.7	18.5
Maggot content (counts per unit area)	38	101	172	387	573
Ammonia generation (relative quantities)	315	370	245	500	450

^aOnagi (1965). Clinoptilolite was spread on droppings of Leghorn chickens every third day for a 15-day period. The total amount of droppings is the same in all tests, including the control.

TABLE 9. EFFECT OF ZEOLITE TREATMENT
ON LIQUID SWINE WASTES^a

	N (ppm)	COD (ppm)	BOD (ppm)	Trans- parency (%)
Original solution	554	1907	3600	0
Zeolite-treated effluent	19	24	21	24

^aNishimura (1973).

(Honda and Koizumi, 1976). The dried manure is then sold as an inexpensive fertilizer for the cultivation of rice.

An innovative application of zeolites in excrement treatment was recently patented in the United States by Komakine (1974) and involves the addition of natural zeolites and ferrous sulfate to chicken droppings. The ferrous sulfate inhibits zymosis and decomposition of the droppings, and the zeolite stabilizes the hygroscopic nature of this compound and captures NH_4^+ produced in the manure. The mixture is dried at 120 to 150°C and used as an odorless, organic fertilizer. It is also used as a protein-rich feedstuff for fish, fowl, and domestic animals. The zeolite-, ferrous sulfate-treated droppings contain 4.5% N, 4.5% P_2O_5 , 2.4% K_2O , and 22% useable protein and have been successfully substituted for as much as 20% of the normal rations of swine, poultry and edible carp.

Methane Purification. Although it is well known that anaerobic digestion of animal excrement and other organic wastes produces an impure methane-gas product, this source of energy has generally been ignored for anything except local or in-house use (Jewell, 1974). Automobiles that run on chicken droppings and lamps that burn manure-pile gases are common in the popular science magazines, to be sure, but commercial operations based on the utilization of such gases face both technical difficulties and economic hurdles that have not yet been resolved. One major drawback is the fact that in addition to methane, copious quantities of carbon dioxide and sulfur compounds are also produced during the digestion process, giving rise to low-BTU products that are extremely corrosive to pumps, valves, and other hardware needed in the operation. Nevertheless,

the process is still an attractive one, and Goepner and Hasselmann (1974) estimated that a billion cubic feet of 700 BTU/ft³ of methane gas could be produced by treating the 250,000 tons of manure produced each day by the 12,000,000 cattle penned in feedlots of the United States. Jewell (1974) also suggested that the methane produced by the anaerobic digestion of the organic wastes of a typical New York State dairy farm of 60 head would be equivalent to the farm's entire fossil fuel requirements.

A recent development by Reserve Synthetic Fuels, Inc., utilizing the adsorption properties of natural zeolites, suggests that such methane streams can be economically upgraded to high-BTU products. In 1975 this company opened a methane-recovery and purification plant to treat methane gas produced by decaying organic matter in the Palos Verde sanitary landfill near Los Angeles. Raw gas containing about 50% CH_4 and 40% CO_2 is fed to 2 pre-treatment vessels to remove moisture, H_2S , mercaptans, et cetera. The dry gas is then routed through three parallel adsorption columns packed with pellets of dehydrated chabazite/erionite from a deposit near Bowie, Arizona, and CO_2 is removed by pressure-swing adsorption on the zeolite. Approximately one million cubic feet of methane meeting pipeline specification is produced each day and delivered to utility company pipelines (NRG, 1975). Such a zeolite-adsorption process to upgrade impure methane streams produced by the digestion of animal manure appears to be technically feasible and awaits detailed economic and engineering evaluation.

AQUACULTURAL APPLICATIONS

In recent years, more and more fish products have found their way to the dinner tables and feeding troughs of every country, and the commercial breeding and raising of fish as a source of protein and for hobby and recreational purposes is becoming a major business in the United States. Many varieties of fish, however, are extremely sensitive to minor fluctuations in such factors as water temperature, pH, O_2 , H_2S , and NH_4^+ , and the chemical and biological environment of aquacultural systems must be carefully maintained within close limits at all times. Processes based on the selective adsorption and ion-exchange properties of several natural zeolites for the oxygen aeration of hatchery and transport waters and for the

removal of toxic nitrogen from tanks and breeding ponds may contribute significantly to increased fish production for human and animal consumption.

Nitrogen Removal. In closed or recirculating aquacultural systems, NH_4^+ produced by the decomposition of excrement and unused food is one of the leading causes of disease and mortality in fish. In oxygen-poor environments, even a few ppm NH_4^+ can lead to gill damage, hyperplasia, and substantial reduction in growth rates (Larmoyeux and Piper, 1973). Biological nitrification is a principal means of removing NH_4^+ from culture waters; however, processes similar to those used in municipal sewage-treatment plants based on zeolite ion-exchange have been found to be effective in controlling the nitrogen content of hatchery waters (Konikoff, 1973). Johnson and Sieburth (1974) proposed that zeolite ion-exchange might be a useful backup and/or alternative to bio-filtration for NH_4^+ removal and have the advantages of low cost and high tolerance to changing temperatures and chemical conditions.

Unpublished tests conducted in 1973 at a working hatchery near Newport, Oregon, indicated that 97 to 99% of the NH_4^+ produced in a recirculating system was removed by clinoptilolite ion-exchange columns from waters containing .34 to 1.43 mg $\text{NH}_3\text{-N}/\text{liter}$ (Kaprinos⁷). Peters and Bose (1975) substantiated these results and found that trout remained healthy during a 4-week trial when zeolite ion-exchange was used to regulate the NH_4^+ content of tank waters. Becker Industries of Newport, Oregon, in conjunction with the U.S. Army Corps of Engineers, is developing a single unit, purification facility for hatchery-water reuse. The system will incorporate a zeolite ion-exchange circuit for nitrogen removal and is designed to handle concentrations of 20 to 30 ppm $\text{NH}_3\text{-N}$ at flow rates of 10 to 15 Mgd, typical of the conditions encountered at most of the 200 fish hatcheries now operating in the Pacific Northwest (Kaprinos)⁷. Piper⁸ also reports progress

in the development of a nitrogen purification unit for trout and salmon hatcheries using clinoptilolite from a New Mexico deposit. Here NH_4^+ is reduced from about 5 ppm to less than .1 ppm, at flow rates of 2.2 to 4.5 Mgd. The system is said to be economically superior to biofiltration and much more reliable under colder climatic conditions.

Jungle Laboratories of Comfort, Texas, is working on a similar ammonium-ion removal system using zeolite ion-exchange for fish haulage applications, where brain damage due to excess NH_4^+ ions commonly results in sterility, stunted growth, and high mortality (Nichols)⁹. Throw-away cartridges and filters containing granular clinoptilolite will also be available for the removal of NH_4^+ from home aquaria and are expected to come onto the market shortly. The U.S. Fish and Wildlife Service of the Department of the Interior is investigating zeolite ion-exchange processes for the treatment of recirculating waters in tank trucks used to transport channel catfish from Texas to the Colorado River in Arizona (McCraren¹⁰). Currently, about 2,000 kg of 20 to 25 cm fish are carried in 45,000 liters of water (about .04 kg/L or 35 kg of fish per cubic meter). If NH_4^+ can be removed, the number of fish hauled in such trucks can be nearly tripled. Slone *et al.* (1975) were able to achieve biomass concentrations of more than .112 kg/L (or 35 kg/m³) for catfish (*Ictalurus punctatus*) after 7 months in a vertical raceway using recycled water and a zeolite ion-exchange process to remove ammonium ions after biofiltration. Ammoniacal nitrogen concentrations of less than 5 mg/liter were easily maintained.

Aeration Oxygen Production. As mentioned above, oxygen-enriched air can be produced by the selective adsorption of nitrogen by activated zeolites. A pressure-swing adsorption process (p.s.a) capable of producing up to 500 m³ of 90% O_2 per hour was developed in Japan (Tamura, 1970) for secondary smelting operations. Smaller generators with outputs of as little as 15 liters of 50% O_2 per hour are also manufactured by the Koyo Development Company, Ltd. and used to aerate fish breeding tanks and in the transportation of live fish. Carp and goldfish raised in such environments are said to be livelier and to have greater appetites (Koyo Kaihatsu, 1974). It is obvious that in closed tanks and stagnant ponds, oxygen aeration might markedly increase the number of fish that can be raised per unit volume.

⁷Kaprinos, W. 1976. Becker Industries, Portland, OR. (Personal communication).

⁸Piper, R. G. 1976. Fish Cultural Development Center, U.S. Fish and Wildlife Service, Bozeman, MT. (Personal communication).

⁹Nichols, R. A. 1976. Jungle Laboratories, Comfort, TX. (Personal communication).

¹⁰McCraren, J. 1976. U.S. Fish and Wildlife Service, San Marcos, TX. (Personal communication).

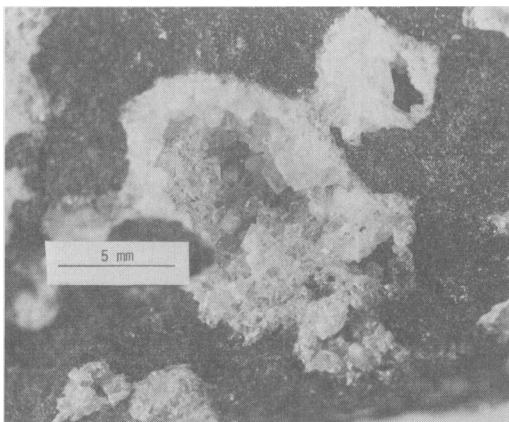


Figure 6. Hand specimen of typical "igneous" zeolite, filling vugs and cavities in a basalt.

Oxygen, produced by small, portable p.s.a. units containing natural zeolite adsorbents, could also be used to replenish free oxygen in small lakes where eutrophication endangers fish life. Fast *et al.* (1975) showed that the oxygen content of hypolimnion zones could be increased markedly by aeration using liquid oxygen as a source. Haines¹¹ demonstrated side-stream pumping as a means of improving the dissolved oxygen in the hypolimnion of a small lake in western New York and utilized approximately 32 kg/day of liquid oxygen at a water flow-rate of 340 liters/minute.

ZEOLITE AVAILABILITY

Since their discovery more than 200 years ago, zeolite minerals have been recognized as minor, but ubiquitous constituents in the vugs and cavities of basaltic igneous rocks (figure 6). Attractive crystals up to several centimeters in size are found in the museum collections of every country; however, occurrences of such materials are generally too low-grade and heterogeneous to mine on a commercial scale. In the late 1950's, natural zeolites were discovered as major constituents of numerous volcanic tuffs in ancient saline-lake deposits of the western United States and of thick, marine tuffs of Japan and Italy. Since that time, more than 1,000 occurrences of zeolites have been reported from sedimentary rocks of more than 40

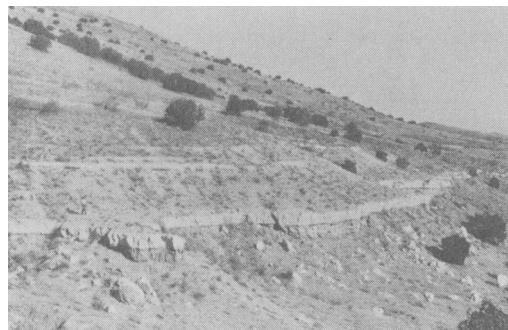


Figure 7. Clinoptilolite deposit, 1 m thick, near Buckhorn, NM.

countries. The flat-lying nature and high purity of the sedimentary deposits have aroused considerable commercial interest, both here and abroad, and numerous applications have and are being developed for them in many areas of industrial technology which take advantage of the low mining costs and availability of the near-surface deposits (Mumpton, 1975, 1977).

Most deposits of sedimentary zeolites of economic significance were formed from fine grained volcanic ash which was carried by the wind from an erupting volcano and deposited into shallow freshwater or saline lakes or into the sea close to the source. Discrete beds of nearly pure ash were built up in this manner, varying in thickness from less than a centimeter to several hundred meters (figures 7 to 9). After deposition, the non-crystalline volcanic ash (glass) reacted with pervading saline and alkaline pore waters or with permeating groundwaters and transformed into micrometer-size crystals of zeolites (figures 10 to 11). Sedimentary zeolites are commonly soft and light weight, although some silicified deposits of

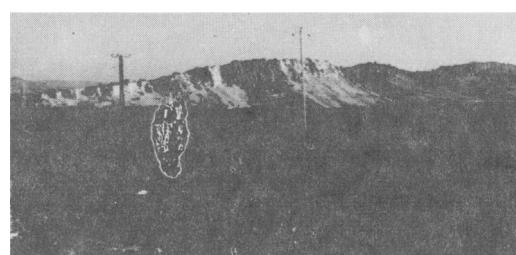


Figure 8. Mordenite/clinoptilolite deposit, 50 m thick, near Oaxaca, Mexico.

¹¹Haines, T. A. 1976. State University College, Brockport, New York. (Personal communication).

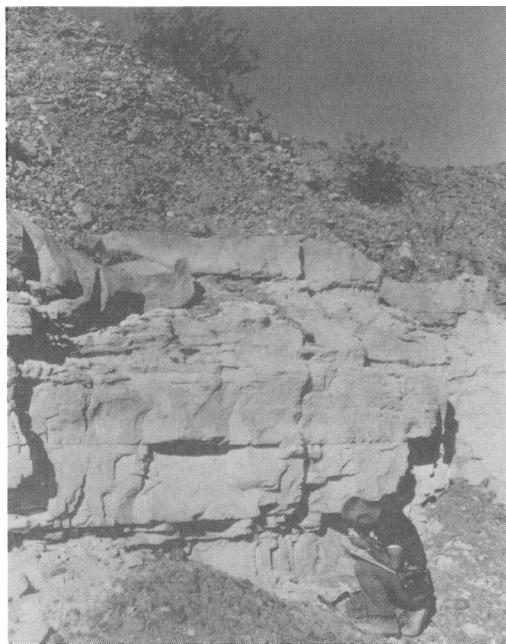


Figure 9. Clinoptilolite deposit, 4 m thick, near Wellton, AR.

clinoptilolite and mordenite are known. The deposits are extensive and can be traced for as much as 5 km in some basins. Many contain as much as 95% of a single zeolite; however, others consist of 2 or more zeolites with minor amounts of calcite, quartz, feldspar, montmorillonite and unreacted volcanic ash.

Numerous deposits of clinoptilolite are in



Figure 10. Scanning electron micrograph of clinoptilolite laths with minor amount of mordenite fibers from a lacustrine tuff near Hector, CA. (Mumpton and Ormsby, 1976).



Figure 11. Scanning electron micrograph of chabazite rhombs from a lacustrine tuff along Beaver Divide, WY. (Mumpton and Ormsby, 1976).

the several million metric-ton range, and there appears to be an unlimited supply of this zeolite in the western part of the country (figure 12). Deposits of mordenite, erionite, chabazite, phillipsite and analcime are less common and somewhat smaller in size, but several are currently being developed by various companies. In general, only those deposits of a near-monomineralic nature are mined, but for many agricultural applications, it may be possible to use lower-grade ores or those containing a mixture of zeolites having the same or similar ion-exchange or adsorption properties.



Figure 12. Map showing locations of mineable clinoptilolite deposits in the United States. (1) Hector, CA. (2) Stone Corral, AR. (3) Wellton, AR. (4) Horseshow Dam, AR. (5) Buckhorn, NM. (6) Dwyer, NM. (7) Marfa, TX. (8) Tilden, TX. (9) Campbell, AL. (10) Creede, CO. (11) Panguitch, UT. (12) Fish Creek Mountains, NV. (13) Mountain Green, UT. (14) Sheaville, OR. (15) Castle Creek, ID. (16) Lysite, WY. (17) Beaver Divide, WY.

Mining operations are relatively simple. The ore is exposed by the removal of overlying clays and siltstones and stockpiled by small bulldozers or frontend loaders. It is then crushed and screened to size. For many ion-exchange applications the desired size range is 20 × 50 mesh (850 to 300 µm) which has been found to optimize contact time and hydraulic characteristics of packed columns. Although the coarse screened material is somewhat more expensive unscreened, <300 µm size material is usually available at a price significantly less than high-protein animal or fish rations. Increased demand should yield reduced prices for pulverized clinoptilolite.

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