
Chapter VIII

Using Zeolites in Agriculture

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Using Zeolites in Agriculture

INTRODUCTION

AS agriculturalists the world over increase their effort to expand crop and animal production, more and more attention is being paid to various mineral materials as soil amendments and as dietary supplements in animal husbandry. The close relationship between the agricultural and geological sciences is not new--crop production depends on the existence and maintenance of fertile soil and agronomists rely on knowledge of mineralogy and geochemistry of clays and other soil constituents. In the animal sciences, the addition of crushed limestone to chicken feed to strengthen egg shells is well known, as is the use of bentonite as a binding agent in pelletized animal feed stuffs.

Recently, one group of minerals has emerged as having considerable potential in a wide variety of agricultural processes. This group of minerals is the zeolite group. The unique ion-exchange, dehydration-rehydration, and adsorption properties of zeolite materials promise to contribute significantly to many years of agricultural and aquacultural technology (60).

Most of the initial research on the use of zeolites in agriculture took place in the 1960s in Japan. Japanese farmers have used zeolite rock for years to control the moisture content and malodor of animal wastes and to increase the pH of acidic volcanic soils. The addition of small amounts of the zeolites clinoptilolite and mordenite to the normal protein diet of pigs, chickens, and ruminants gave noticeable in-

creases in the body weight and general "health" of the animals (52). The use of zeolites in rations also appeared to reduce odor and associated pollution problems and to provide a means of regulating the viscosity and nitrogen retentivity of animal manure. These same zeolites were also found to increase the ammonium content of rice paddy soils when added with normal fertilizers.

Although most of these were preliminary results and often published in rather obscure journals or reports from local experiment stations, they did suggest that zeolites could act as traps or reservoirs for nitrogen both in the body and in the soil. The growing awareness of such phenomena and of the availability of inexpensive natural zeolites in the Western United States and in geologically similar parts of the world has aroused considerable commercial interest. Zeolites are fast becoming the subject of serious investigation in dozens of agricultural laboratories both here and abroad. Some of the ways in which zeolites can contribute to more efficient crop and livestock production are discussed below, along with their role in the rapidly expanding areas of fish breeding and aquiculture. At this stage, the number of published papers dealing with "zeo-agriculture" is quite small, and hard data are few; however, the potential of these materials in such areas is apparent, and zeolites show promise of contributing directly to increased agricultural productivity in the years to come.

NATURAL ZEOLITES

Zeolites are crystalline, hydrated aluminosilicates of alkali and earth metals that possess infinite, three-dimensional crystal structures. They are further characterized by an ability to lose and gain water reversibly and to exchange

some of their constituent elements without major change of structure. Zeolites were discovered in 1756 by Freiherr Axel Fredrick Cronstedt, a Swedish mineralogist, who named them from the Greek words meaning "boiling

stones," in allusion to their peculiar frothing characteristics when heated before the mineralogist's blowpipe. Since that time, nearly 50 natural species of zeolites have been recognized, and more than 100 species having no natural counterparts have been synthesized in the laboratory. Synthetic zeolites are the mainstays of the multimillion-dollar molecular sieve businesses that have been developed by Union Carbide Corp., W. R. Grace & Co., Mobil Corp., Norton Co., Exxon Corp., and several other companies in the last 25 years in the United States and by chemical firms in Germany, France, Great Britain, Belgium, Italy, Japan, and the Soviet Union.

Natural zeolites have long been known to members of the geological community as ubiquitous, but minor constituents in the vugs and cavities of basalt and other traprock formations. It was not until the late 1950s that the world became aware of zeolites as *major* constituents of numerous volcanic tuffs that had been deposited in ancient saline lakes of the Western United States or in thick marine tuff deposits of Italy and Japan. Since that time, more than 2,000 separate occurrences of zeolites have been reported from similar sedimentary rocks of volcanic origin in more than 40 countries. The high purities and near-surface location of the sedimentary deposits has

prompted intense commercial interest both here and abroad. Many industrial applications based on the exciting bag of chemical and physical tricks of zeolites have been developed.

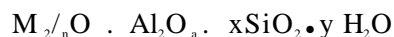
The commercial use of natural zeolites is still in its infancy, but more than 300,000 tons of zeolite-rich tuff is mined each year in the United States, Japan, Bulgaria, Hungary, Italy, Yugoslavia, Korea, Mexico, Germany, and the Soviet Union. Natural zeolites have found applications as fillers in the paper industry, as lightweight aggregate in construction, in pozzolanic cements and concrete, as ion-exchangers in the purification of water and municipal sewage effluent, as traps for radioactive species in low-level wastewaters from nuclear facilities, in the production of high purity oxygen from air, as reforming petroleum catalysts, as acid-resistant absorbents in the drying and purification of natural gas, and in the removal of nitrogen compounds from the blood of kidney patients (58).

The applications and potential applications of both synthetic and natural zeolites depend, of course, on their fundamental physical and chemical properties. These properties are in turn related directly to the chemical composition and crystal structure of individual species.

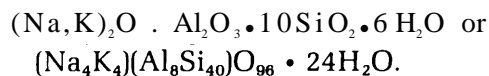
CHEMISTRY AND CRYSTAL STRUCTURE OF ZEOLITES

Along with quartz and feldspar, zeolites are "tektosilicates," that is, they consist of three-dimensional frameworks of silicon-oxygen (SiO_4)⁴⁻ tetrahedral, wherein all four corner oxygen atoms of each tetrahedron are shared with adjacent tetrahedra. This arrangement of silicate tetrahedra reduces the overall oxygen:silicon ratio to 2:1, and if each tetrahedron in the framework contains silicon as its central atom, 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 elements such as sodium (Na^+), calcium (Ca^{2+}), and po-

tassium (K^+) elsewhere in the structure. Thus, the empirical formula of a zeolite is of the type:



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



Elements or cations within the first set of parentheses in the 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, surrounding the exchangeable cations in large pore spaces.

Whereas the framework structures of quartz and feldspar are dense and tightly packed, those of zeolite minerals are remarkably open and void volumes of dehydrated species as great as 50 percent 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 tetrahedral linked together in a simple geometrical form. This particular polyhedron is known as a truncated cube-octahedron. It is more easily seen by considering only lines joining the midpoints of each tetrahedron, as shown in figure 1.

Individual polyhedra may be connected in several ways; for example, by double four-rings of oxygen atoms (figure 2a), or by double six-rings of oxygen atoms (figure 2b), 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 figures 3a, 3b.

once the water is removed from a zeolite, considerable void space is available within both the simple polyhedra building blocks and the larger frameworks formed by several polyhedra. Although water and other inorganic and organic molecules would appear to be able to move freely throughout a dehydrated zeolite framework, 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 2a, 2b, 3a, 3b).

Properties of Zeolites

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. Once the water is removed, usually by heating to **3000** to **4000** C for a few hours, molecules having diameters small enough to fit through the entry channels are readily adsorbed on the inner surfaces of the vacant 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 4).

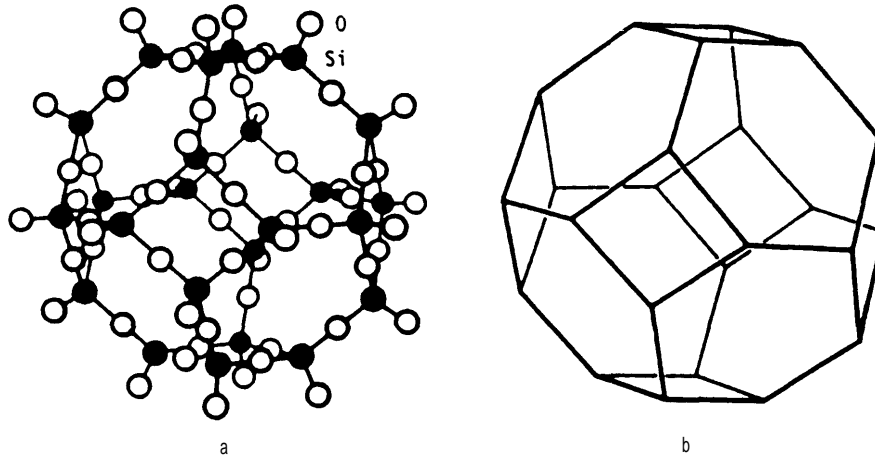
Table 1.— Representative Formulae and Selected Physical Properties of Important Zeolites

Zeolite	Representative unit-cell formula ^a	Void volume ^a	Channel dimensions ^a	Thermal stability	Ion-exchange capacity ^b
Analcime	$\text{Na}_{16}(\text{A}_{16}\text{Si}_{32}\text{O}_{96}) \cdot 16\text{H}_2\text{O}$	18%	2.6 Å	High	4.54 meq/g
Chabazite	$(\text{Na}_2, \text{Ca})_6(\text{A}_{12}\text{Si}_{24}\text{O}_{72}) \cdot 4\text{OH}_2\text{O}$	47	3.7 x 4.2	High	3.81
Clinoptilolite	$(\text{Na}_4, \text{K}_4)(\text{A}_{18}\text{Si}_{40}\text{O}_{96}) \cdot 24\text{H}_2\text{O}$	39?	3.9 x 5.4	High	2.54
Erionite	$(\text{Na}, \text{Ca}, \text{K})_9(\text{A}_{18}\text{Si}_{27}\text{O}_{72}) \cdot 27\text{H}_2\text{O}$	35	3.6 x 5.2	High	3.12
Faujasite	$\text{Na}_{56}(\text{A}_{156}\text{Si}_{384}\text{O}_{984}) \cdot 27\text{H}_2\text{O}$	47	7.4	High	3.39
Ferrierite	$(\text{Na}_2, \text{Mg}_2)(\text{A}_{18}\text{Si}_{30}\text{O}_{72}) \cdot 18\text{H}_2\text{O}$		4.3 x 5.5 3.4 x 4.8	High	2.33
Heulandite	$\text{Ca}_3(\text{A}_{18}\text{Si}_{28}\text{O}_{72}) \cdot 24\text{H}_2\text{O}$	39	4.0 x 5.5 4.4 x 7.2 4.1 x 4.7	Low	2.91
Laumontite	$\text{Ca}_4(\text{A}_{18}\text{Si}_{18}\text{O}_{48}) \cdot 16\text{H}_2\text{O}$		4.6 x 6.3	Low	4.25
Mordenite	$\text{Na}_8(\text{A}_{18}\text{Si}_{40}\text{O}_{96}) \cdot 24\text{H}_2\text{O}$	28	2.9 x 5.7 6.7 x 7.0	High	2.29
Phillipsite	$(\text{Na}, \text{K})_{10}(\text{A}_{10}\text{Si}_{22}\text{O}_{64}) \cdot 20\text{H}_2\text{O}$	31	4.2 x 4.4 2.8 x 4.8 3.3	Low	3.87
Linde A	$\text{Na}_{12}(\text{A}_{12}\text{Si}_{12}\text{O}_{48}) \cdot 27\text{H}_2\text{O}$	47	4.2	High	5.48
Linde X	$\text{Na}_{96}(\text{A}_{186}\text{Si}_{384}\text{O}_{984}) \cdot 264\text{H}_2\text{O}$	50	7.4	High	4.73

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

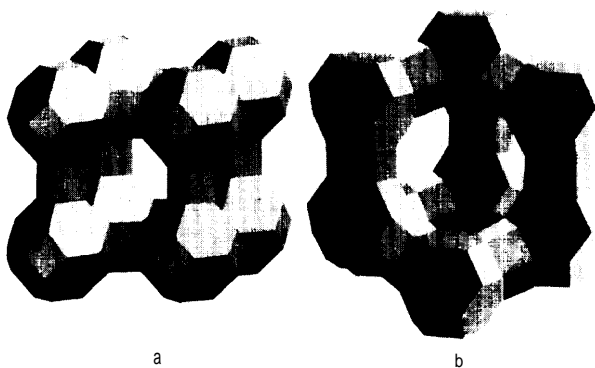
^bCalculated from unit-cell formula

Figure 1.—Simple Polyhedron of Silicate and Aluminate Tetrahedra



(a) Ball and peg model of truncated cube-octahedron. (b) Line drawing of truncated cube-octahedron, lines connect centers of tetrahedral

Figure 2.—Arrangements of Simple Polyhedra to Enclose-Large Central Cavities



(a) Truncated cube-octahedra connected by double four-rings of oxygen in structure of synthetic zeolite A. (b) Truncated cube-octahedra connected by double six-rings of oxygens in structure of faujasite.

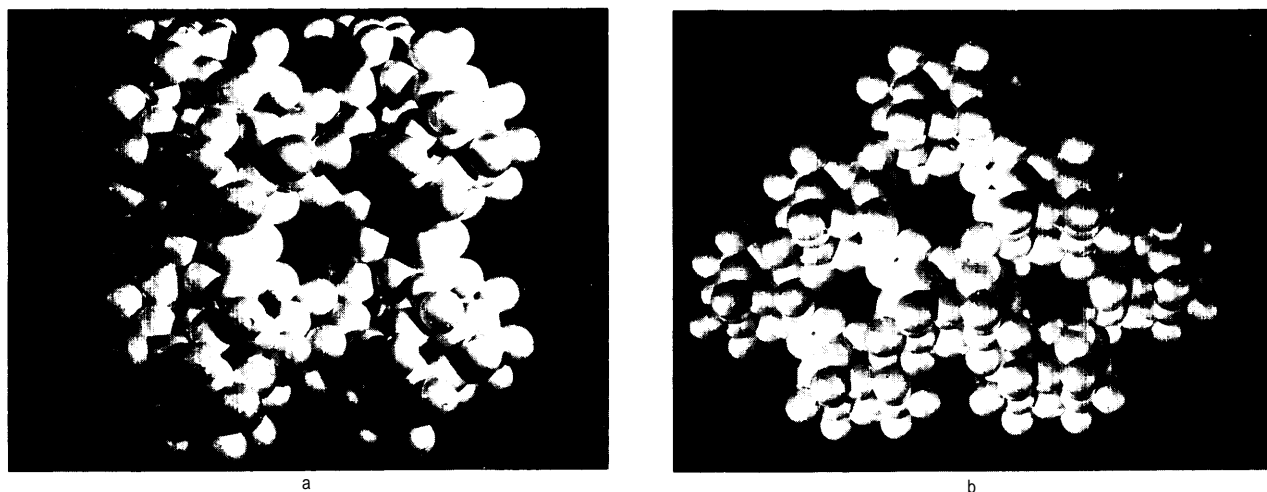
The internal surface area available for adsorption ranges up to several hundred square meters per gram, and some zeolites are capable of adsorbing up to about **30** weight percent of a gas, based on the dry weight of the zeolite.

In addition to their ability to separate gas molecules on the basis of size and shape, the unusual charge distribution within a dehydrated void volume allows many species with permanent dipole moments to be adsorbed

with a selectivity unlike that of almost all other sorbents. Thus, polar molecules such as water, sulfur dioxide, hydrogen sulfide, and carbon dioxide are preferentially adsorbed by certain zeolites over nonpolar molecules, such as methane, and adsorption processes have been developed using natural zeolites by which carbon dioxide and other contaminants can be removed from impure natural gas or methane streams, allowing the gas to be upgraded to high-Btu products. In addition, the small, but finite, quadrupole moment of nitrogen allows it to be adsorbed selectively from air by a dehydrated zeolite, producing oxygen-enriched streams at relatively low cost at room temperature. Both of the above processes may find application in agricultural technology.

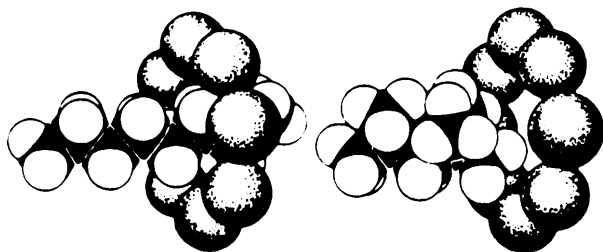
Dehydration-rehydration properties: Because of the uniform nature of the pores of structural cages, crystalline zeolites have fairly narrow pore-size distributions, in contrast to other commercial absorbents, such as activated alumina, carbon, and silica gel. Adsorption on zeolites is therefore characterized by Langmuir-type isotherms, as shown in figure 5. Here, percent of adsorption capacity is plotted against partial pressure of the adsorbate gas. Note that almost all of the zeolite's adsorption capacity for

Figure 3.—Solid Sphere Models of Synthetic Zeolite and Chabazite



(a) Solid-sphere model of the crystal structure of synthetic zeolite A (b) Solid-sphere model of the crystal structure of chabazite

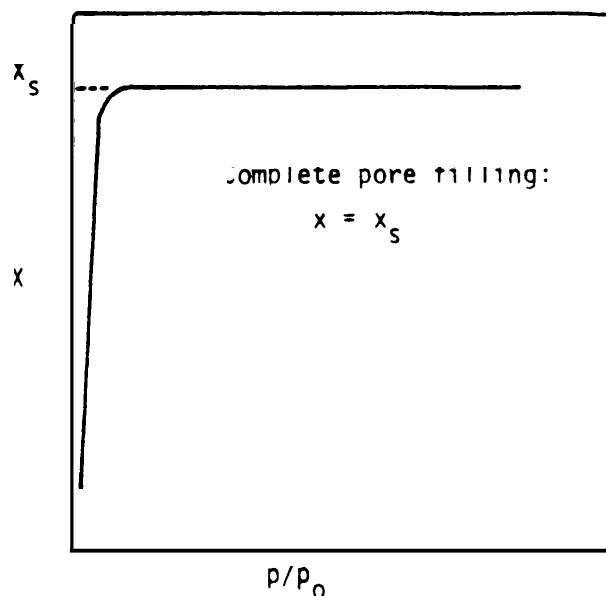
Figure 4.—Stylized Illustration of the Entry of Straight-Chain Hydrocarbons and Blockage of Branch-Chain Hydrocarbons at Channel Apertures



a particular gas (including water) is obtained at very low partial pressures, meaning that although their total adsorption capacity may be somewhat less than those of other absorbents, (e.g., silica gel), zeolites are extremely efficient adsorbents even at low partial pressures. This property has been used in the zeolitic adsorption of traces of water from Freon gas lines of ordinary refrigerators that might otherwise freeze and clog pumps and valves. The extreme nonlinearity of the water adsorption isotherms of zeolites has been exploited recently in the development of solar-energy refrigerators (81),

Ion-exchange properties: The exchangeable cations of a zeolite are also only loosely bonded to the tetrahedral framework and can be removed or exchanged from the framework

Figure 5.—Langmuir-Type Isotherm for Adsorption on Crystalline Zeolites Illustrating Almost Complete Saturation at Low Partial Pressures of the Adsorbate



x = amount adsorbed; p = pressure

structure easily by washing with a strong solution of another element. 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. This com-

pres with the 0.8 to 1.0 meq per gram cation-exchange capacity of bentonite, the only other significant ion-exchanger found in nature,

Cation-exchange capacity is basically a function of the degree of substitution of aluminum for silicon in the zeolite framework: the greater the substitution, the greater the charge deficiency of the structure, and the greater the number of alkali or alkaline earth atoms required for electrical neutrality. In practice, however, the cation-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, cation 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.

Unlike most noncrystalline ion exchangers, such as organic resins or inorganic aluminosilicate gels (mislabelled in the trade as "zeolites"), the framework of a *crystalline* zeolite dictates its selectivity toward competing ions. The hydration spheres of high-charge, small-size ions (e. g., sodium, calcium, magnesium) prevent their close approach in the cages to the seat of charge of the framework; therefore ions of low charge and large size (e. g., lead, barium, potassium), that normally do not have hydration spheres are more tightly held and selectively taken up from solution than are other ions. The small amount of aluminum in the composition of clinoptilolite, for example, results in a relatively low cation-exchange capacity (about 2.3 meq/g); however, its cation selectivity is:

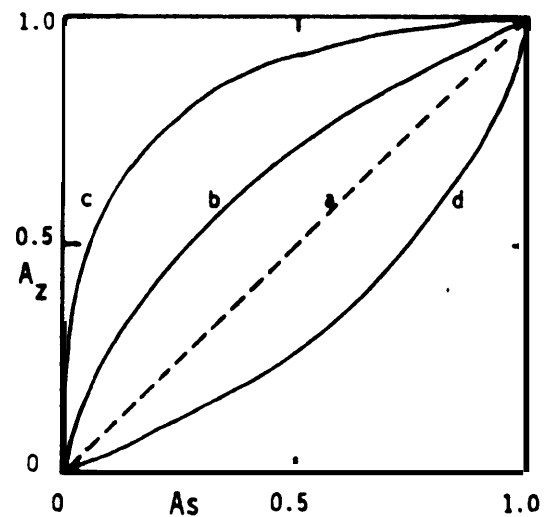
Cesium > Rubidium > Potassium > Ammonium >
Barium > Strontium > Sodium

Calcium > Iron > Aluminum >
Magnesium > Lithium (3).

Synthetic zeolite A, on the other hand, is more selective for calcium than for sodium, and thus, acts as a water softener in laundry detergents where it picks up calcium from the wash water and releases sodium (75).

Cation exchange between a zeolite (Z) and a solution (S) is usually shown by means of an exchange isotherm that plots the fraction of the exchanging ion (X) in the zeolite phase against that in the solution (figure 6). If a given cation shows no preference of either the solution or the zeolite, the exchange isotherm would be the straight line "a" at 45°. If the zeolite is moderately or very selective for the cation in solution, curve b and c would result, respectively. If the zeolite is rejective of a particular cation, curve d would result. Such is the selectivity of clinoptilolite for cesium or ammonium, for example. Clinoptilolite will take up these ions readily from solutions even in the presence of high concentrations of competing ions, a facility that was exploited by Ames (4) and Mercer, et al. (50), in their development of an ion-exchange process to remove ammoniacal nitrogen from sewage effluent.

Figure 6.—Types of Ion-Exchange Isotherms for the Reaction $A_s + B_z = A_z + B_s$



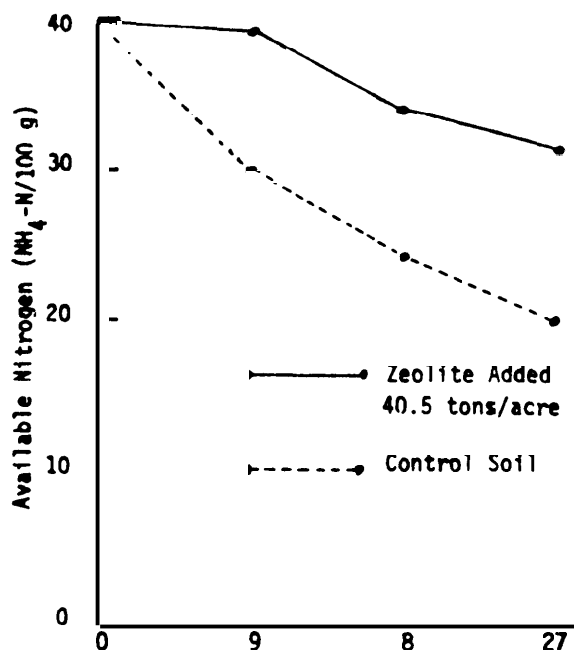
(a) no preference of the ion for either the zeolite or the solution; (b) small preference of the ion for the zeolite phase; (c) large preference of the ion for the zeolite; (d) small preference of the ion for the solution phase. (From Breck, 1974.)

APPLICATIONS IN AGRONOMY

Fertilizer and Soil Amendments

Based on their high ion-exchange capacity and water retentivity, natural zeolites have been used extensively in Japan as amendments for sandy soils, and small tonnages have been exported to Taiwan for this purpose (52,31). The pronounced selectivity of clinoptilolite for large cations, such as ammonium and potassium, has also been exploited in the preparation of chemical fertilizers that improve the nutrient-retention ability of the soils by promoting a slower release of these elements for uptake by plants. In rice fields, where nitrogen efficiencies of less than 50 percent are not uncommon, Minato (52) reported a 63 percent improvement in the amount of available nitrogen in a highly permeable paddy soil 4 weeks after about 40 tons/acre zeolite had been added along with standard fertilizer (figure 7), Turner (84), on the other hand, noted little change in the vitrification of added ammonia when clin-

Figure 7.—Change of Soil Nitrogen of Paddy Soil With Time



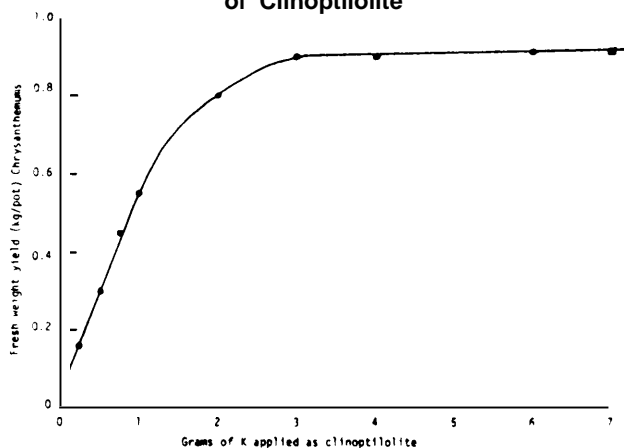
Vertical water seepage in soil = 1.35 cm/day (Yamagata Prefecture Board of Agriculture and Forestry, 1966; reported in Minato, 1968.)

optilolite was mixed with a Texas clay soil, although the overall ion-exchange capacity of the soil was increased. He attributed these conflicting results to the fact that the Japanese soils contained much less clay, thereby accounting for their inherent low ion-exchange capacity and fast-draining properties. The addition of zeolite, therefore, resulted in a marked improvement in the soil's ammonium retentivity. These conclusions support those of Hsu, et al. (31), who found an increase in the effect of zeolite additions to soil when the clay content of the soil decreased. Although additions of both montmorillonite and mordenite increase the cation-exchange capacity of upland soils, the greater stability of the zeolite to weathering allowed this increase to be retained for a much longer period of time than in the clay-enriched soils (22),

Using clinoptilolite tuff as a soil conditioner, the Agricultural Improvement Section of the Yamagata Prefectural Government, Japan, reported significant increases in the yields of wheat (13 to 15 percent), eggplant (19 to 55 percent), apples (13 to 38 percent), and carrots (63 percent) when from 4 to 8 tons of zeolite was added per acre (83). Small, but significant improvements in the dry-weight yields of sorghum in greenhouse experiments using a sandy loam were noted when 0.5 to 3.0 tons of clinoptilolite per acre was added along with normal fertilizer (47). However, little improvement was found when raising corn under similar conditions. Hershey, et al. (29), showed that clinoptilolite added to a potting medium for chrysanthemums did not behave like a soluble K source, but was very similar to a slow-release fertilizer. The same fresh-weight yield was achieved with a one-time addition of clinoptilolite as with a daily irrigation of Hoagland's solution, containing 238 ppm K, for three months (total of 7 g potassium added), with no apparent detrimental effect on the plants (figure 8).

Experiments by Great Western Sugar Co. in Longmont, CO, using clinoptilolite as a soil amendment, resulted in a significant increase

Figure 8.—Yield of Chrysanthemums as a Function of Potassium Level Supplied by One-Time Additions of Clinoptilolite



Solid square represents total of 7 g of potassium supplied by daily irrigation with Hoaglan's solution containing 234 ppm K. Total time of experiment was 3 months. (From Hershey, et al., 1980.)

in total-matter production of sugar beets, although "high" levels of zeolite were required (1). The details of these experiments are considered proprietary and have not been released. The addition of ammonium-exchanged clinoptilolite in greenhouse experiments with radishes resulted in a 59- and 53-percent increase in root weight in medium and light clay soils, respectively (45). The nitrogen uptake by plant

tops also increased with the zeolite treatment compared with an ammonium sulfate control (table 2). These authors also found that natural clinoptilolite added to soil in conjunction with urea reduced the growth suppression that normally occurs when urea is added alone (table 3). The presence of zeolites also resulted in less $\text{NO}_3\text{-N}$ being leached from the soil (figure 9).

Both zeolite treatments apparently made considerably more ammonium available to the plants, especially when clay-poor soils were employed. The authors suggested that ammonium-exchanged clinoptilolite acted as a slow-release fertilizer, whereas, natural clinoptilolite acted as a trap for ammonium that was produced by the decomposing urea, and thereby prevented both ammonium and nitrate toxicity by disrupting the bacterial nitrification process. The ammonium selectivity of zeolites was exploited by Varro (85) in the formulation of a fertilizer consisting of a 1:1 mixture of sewage sludge and zeolite, wherein the zeolite apparently controls the release of nitrogen from the organic components of the sludge.

Coupled with its valuable ion-exchange properties which allow a controlled release of micronutrients, such as iron, zinc, copper, man-

Table 2.—Growth Response of Radishes to Ammonium-Exchange Clinoptilolite^a

Parameter	130/0 clay soil ^b		6°/0 clay soil ^c	
	N H ₄ -Clinoptilolite	(NH ₄) ₂ S O ₄	N H ₄ -Clinoptilolite	(NH ₄) ₂ S O ₄
Leaf area (cm ² /plant)	243	187	187	150
Plant weight (dry weight) (g)	1.84	1.12	1.40	1.1
Root weight (g)	13.5	8.5	11.6	7.6
N uptake (mg N/plant top)	57.2	35.9	42.6	38.9

^aLewis, et al., 1980.

^bPlants sampled 36 days after planting.

^cLeached five times; plants sampled 34 days after planting.

Table 3.—Growth Response of Radishes to Natural Clinoptilolite Plus Urea^a

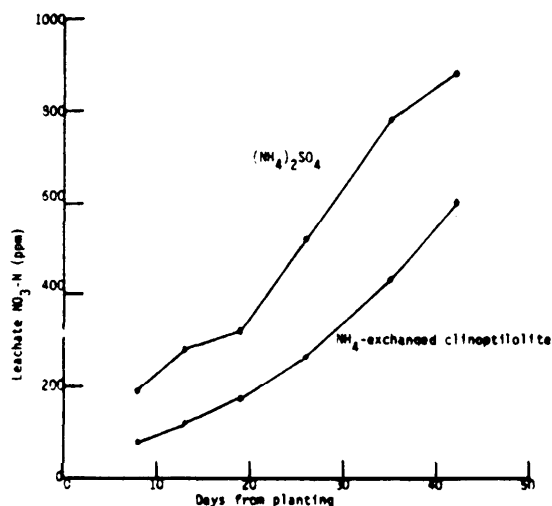
Parameter	13% clay soil ^b		6°/0 clay soil ^c	
	Zeolite + Urea	Urea	Zeolite + Urea	Urea
Leaf area (cm ² /plant)	210	187	208	116
Plant weight (dry weight) (g)	1.59	1.23	1.38	0.71
Root weight (g)	13.8	12.4	12.4	6.3
N uptake (mg N/plant top)	45.5	38.6	44.4	18.9

^aLewis, et al., 1980.

^bPlants sampled 36 days after planting.

^cLeached five times; plants sampled 34 days after planting.

Figure 9.—Cumulative Leachate $\text{NO}_3\text{-N}$ for Banded NH_4 -Exchanged Clinoptilolite and Banded Ammonium Sulfate (Lewis, et al., 1980)



ganese, and cobalt, the ability of clinoptilolite to absorb excess moisture makes it an attractive addition to chemical fertilizers to prevent caking and hardening during storage and to animal feedstuffs to inhibit the development of mold (82). Spiridonova, et al. (78), found that 0.5 percent clinoptilolite added to ammonium nitrate fertilizer decreased caking by 68 percent.

pesticides, Fungicides, Herbicides

Similar to their synthetic counterparts, the high adsorption capacities in the dehydrated state and the high ion-exchange capacities of many natural zeolites make them effective carriers of herbicides, fungicides, and pesticides. Clinoptilolite can be an excellent substrate for benzyl phosphorothioate to control stem blasting in rice (88). Using natural zeolites as a base, Hayashizaki and Tsuneji (26) found that clinoptilolite is more than twice as effective as a carrier of the herbicide benthocarb in eliminating weeds in paddy fields as other commercial products. Torii (82) reported that more than 100 tons of zeolite were used in Japan in 1973 as carriers in agriculture. A Russian patent was

issued to Aleshin, et al. (2), for grouting compound containing 3 to 5 percent clinoptilolite to control herbicide percolation from irrigation canals to ground waters.

Heavy Metal Traps

Not only do the ion-exchange properties of certain zeolites allow them to be used as carriers of nutrient elements in fertilizers, they can be exploited to trap undesirable metals and prevent their uptake into the food chain. Pulverized zeolites effectively reduced the transfer of fertilizer-added heavy metals, such as copper, cadmium, lead, and zinc, from soils to plants (18). The selectivity of clinoptilolite for such heavy metals has been noted by several workers (e. g., 74,19,1 1,76).

In view of the attempts being made by sanitary and agricultural engineers to add municipal and industrial sewage sludge to farm and forest soils, natural zeolites may play a major role in this area also. The nutrient content of such sludges is desirable, but the heavy metals present may accumulate to the point where they become toxic to plant life or to the animals or human beings that may eventually eat these plants. Cohen (12) reported median values of 31 ppm cadmium, 1,230 ppm copper, 830 ppm lead, and 2,780 ppm zinc for sludges produced in typical U.S. treatment plants. Zeolite additives to extract heavy metals may be a key to the safe use of sludge as fertilizer and help extend the life of sludge-disposal sites or of land subjected to the spray-irrigation processes now being developed for the disposal of chlorinated sewage. Similarly, Nishita and Haug (64) showed that the addition of clinoptilolite to soils contaminated with radioactive strontium (Sr^{90}) resulted in a marked decrease in the uptake of strontium by plants, an observation having enormous import in potential treatment of radioactive fallout that contaminates soils in several pacific atolls where nuclear testing has been carried out,

APPLICATIONS IN ANIMAL HUSBANDRY

Animal Nutrition

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 (73), experiments have been carried out in Japan since 1965 on the application of natural zeolites as dietary supplements for several types of domestic animals. Because much of this work was superficial or not statistically significant, it has been repeated and enlarged upon in recent years by researchers in the United States and several other countries seeking agricultural applications for zeolites.

Poultry

Using clinoptilolite from the Itaya r-nine, Yamagata Prefecture, and mordenite from Karawago, Miyagi Prefecture, Onagi (67) 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 values (FEV)¹ were markedly higher at all levels of zeolite substitution; feed-stuffs containing 10 percent zeolite gave rise to efficiencies more than 20 percent greater than those of normal rations (table 4). 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 percent less moisture than those of control groups, after a

¹ Weight gain/feed intake, excluding zeolite.

12-day drying period, making them considerably easier to handle.

Broiler chickens fed a diet of 5 percent clinoptilite from the Hector, CA, deposit gained slightly less weight over a 2-month period than birds receiving a normal diet, but average FEVs were noticeably higher (table 5) (6). Perhaps of greater significance is the fact that none of the 48 test birds on the zeolite diet died during the experiment, while 3 on the control diet and 2 on the control diet supplemented with antibiotics succumbed. In addition to an apparent feed-efficiency increase of 4 to 5 percent, the presence of zeolite in the diet appears to have had a favorable effect on the mortality of the birds.

Hayhurst and Willard (27) confirmed many of Onagi's observations and reported small increases in FEV for Leghorn roosters over a 40-day period, especially during the first 10 days. The birds were fed a diet containing 7.5 percent clinoptilolite crushed and mixed directly with the normal rations. Feces were noticeably dryer and less odoriferous. Unfortunately, only 17 birds were used in the study and extensive statistical evaluation of the results could not be made.

Swine

Kondo and Wagai (39) evaluated the use of zeolites in the diets of young and mature Yorkshire pigs in 60- and 79-day experiments, re-

Table 4.—Caloric Efficiencies of Zeolite Supplements in poultry Feeding^a

Group no.	Zeolite content of rations	Average starting wt. (g)	Average final wt. (g)	Average weight gain (g)	Average feed intake ^b (g)	Feed efficiency ratio ^c
1	10 percent Cp ^d	553.7	795.6	241.9	668	0.362
2	5 percent Cp	540.7	778	237.3	697	0.340
3	3 percent Cp	556.7	796	239.3	748	0.320
4	10 percent Mo	532.3	757.3	225.0	634	0.355
5	5 percent Mo	552.3	814.6	262.3	775	0.338
6	3 percent Mo	534.5	791.3	256.8	769	0.334
7	Control	556.5	789.3	232.8	782	0.298

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

^bExcluding zeolite.

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

^dCp = clinoptilolite, Mo = mordenite.

Table 5.—Apparent Caloric Efficiency of Zeolite in Chicken Rations^a

Treatment of_	Average	Average	Average	Survivors of 48 birds
	weight (g)	consumption (g)	F.E.V. ^c	
	4-week data ^d			
Control diet	730	1175	0.622	46
Control diet + antibiotics	708	1116	0.634	47
Control diet with 5 percent clinoptilolite	703	1070	0.657	48
	8-week data ^f			
Control diet	1869	3978	0.470	45
Control diet + antibiotics	1882	3869	0.486	46
Control diet with 6 percent clinoptilolite	1783	3647	0.489	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)

^e55 ppm zinc bacitracin

^fFinisher rations (4 to 9 weeks)

spectively, and found that the weight gain of animals of both ages receiving diets containing 5 percent clinoptilolite was from 25 to 29 percent greater than that of animals receiving normal diets (table 6). Feed supplemented with zeolites gave rise to feed efficiencies about 35 percent greater than those of normal rations when fed to young pigs, but only about 6 percent greater when given to older animals. 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 toward a more efficient conversion of feedstuff nitrogen to animal protein.

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 percent over a 12-week period (24,26). Anai, et al. (5), reported similar results using 5 percent zeolite for 8 pigs

over a 12-week period and realized a 4-percent decrease in the cost of producing body weight. They also noted a decrease in malodor and moisture content of the excrement, Toxic or other adverse effects were not noted for any of the test animals described. On the contrary, the presence of zeolites in swine rations appears to contribute measurably to the well-being of the animals. Tests carried out on 4,000 head of swine in Japan showed that the death rate and incidence of disease among animals fed a diet containing 6 percent clinoptilolite was markedly lower than for control animals over a 12-month period (83). As shown in table 7, the decrease in the number of cases of gastric ulcers, pneumonia, heart dilation, and in the overall mortality is remarkable. The savings in medicine alone amounted to about 75 cents per animal, to say nothing of the increased value of a larger number of healthy pigs.

In one test, the addition of zeolite to the diet of piglets severely afflicted with scours markedly reversed the progress of this disease within a few days (53). Four underdeveloped Laundry

Table 6.—Caloric Efficiency of Zeolite Supplements in Swine Feeding^a

	Age of pigs		Average weight		Average wt. gain (kg)	Average ^b feed intake (kg)	Average ^c F.E.V.	Zeolite improvement
	Start (days)	Finish	Start (kg)	Finish (kg)				
Experimental ^d	60	120	15.43	44.43	29.00	85.0	0.341	35 percent
Control ^e	60	120	14.85	35.78	22.93	90.6	0.253	
Experimental ^e	99	178	30.73	85.30	54.57	167.6	0.326	6 percent
Control ^e	99	178	31.20	73.50	42.30	136.2	0.308	

^aKOndo and Wagai (1968) Tests carried out using 5 percent clinoptilolite in rations of experimental groups

^bExcluded zeolite

^cFeed efficiency value = weight gain/feed intake

^dEight Yorkshire pigs

^eTwenty Yorkshire Pigs

Table 7.—Effect of Zeolite Diets on Health of Swine^a

Period	Zeolite content of rations	Sickness causes		Heart dilatation	Mortality rate (percent)	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 percent clinoptilolite	22	51	4	2.6	\$1.75

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

pigs were fed a diet containing 30 percent zeolite for the first 15 days and 10 percent 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 per head per day, no ill effects were noted, and once they had recovered from diarrhetic ailments, the pigs regained healthy appetites and became vital. A recent Japanese patent disclosure claimed a method of preventing and treating gastric ulcer in swine by the addition of zeolite to their diets (49); supportive data, however, were not reported.

Apparently the vitalizing effect of a zeolite diet can be transferred from mother to offspring. Experiments at the Ichikawa Livestock Experiment Station, where 400 g 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 8, test animals weighed from 65 to 85 percent more than control-group animals at the end of the weaning period (9). 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. The addition of 5 percent zeolite to the rations of pregnant sows 20 to 90 days after mating

gave rise to improved FEVs and increased litter weight at parturition (46). The earlier the zeolite was added, the greater was the apparent effect.

Similar studies were conducted at Oregon State University with young swine using rations containing 5 percent clinoptilolite (16). 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 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.

In a preliminary study involving 16 early weaned pigs over a 19-day period, animals on an antibiotic-free diet containing 10 percent clinoptilolite gained about 5 percent more weight per pound of feed than those on a control diet without antibiotics and about 4 percent more than those on an antibiotic-enriched diet (table 9) (70). The small number of pigs used, however, limits the significance of these findings. In another study, a 30 percent improvement in FEVs occurred for 35 young pigs on a molasses-based diet when 7.5 percent

Table 8.—Effect of Prenatal Zeolite Diet on Newborn Pigs^a

Species	No. of pigs	Group	Average weight (kg)			Weight gain improvement
			Newborn	21-days	35-days	
Yorkshire	6	Experimental	1.25	4.3	7.83	
Yorkshire	10	Control	1.10	4.2	4.81	63 percent
Laundry	6	Experimental	1.20	4.7	8.68	
Laundry	10	Control	1.10	4.0	4.67	96 percent

^aTest 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 x 100.

Table 9.—Effect of Zeolite Supplement in the Diets of Early Weaned Pigs^a

	Basal diet ^b	Zeolite diet ^c	Antibiotic diet ^d
Number of pigs	4	4	4
Average daily weight gain (g)	245	245	304
Feed efficiency value (FEV) ^e (weight gain/feed intake)	0.432	0.455	0.437

^aPond and Mumpton (1978)

^b62% ground yellow corn 10% cerelose, 23% soybean meal, 0.5% salt, 0.5% Hopro R vitamin supplement, 1.5% ground limestone, 2.5% dicalcium phosphate

^cBasal diet less 10% cerelose plus 10% clinoptilolite, -200 mesh, Castle Creek, Idaho

^dBasal diet plus 0.3% Aurofac 10 antibiotic

^eExcluding zeolite

clinoptilolite was substituted in the diet during the 35 to 65 kg growth period (table 10) (10). Feces of the zeolite-fed animals were also less liquid than those on a control diet.

The addition of zeolites had little effect on the FEVs in the 65 to 100 kg growth range. Heeney (28) supplemented normal corn-soy rations of 36 pigs with 2.5 and 5 percent clinoptilolite in a 120-day experiment (table 11). He found little overall difference in the FEVs; however, for the first 30 days after weaning, FEVs of 0.455 and 0.424 were obtained for 2.5 and 5.0 percent zeolite, respectively, compared with a value of 0.382 for the control animals, an increase of about 15 percent due to the presence of zeolites in the diet. Little improvement was noted between 30 and 120 days of the treatment.

Ruminants

In an attempt to reduce the toxic effects of high NH₄⁺ content of ruminal fluids when nonprotein nitrogen (NPN) compounds, such

as urea and diuret, are added to the diets of cattle, sheep, and goats, researchers introduced both natural and synthetic zeolites into the rumen of test animals (87). 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. Both *in vivo* and *in vitro* data showed that up to 15 percent of the NH₄⁺ in the rumen could be taken up by the zeolite. Thus, the gradual release of NH₄⁺ allowed rumen micro-organisms to synthesize cellular protein continuously for easy assimilation into the animals' digestive systems. The zeolite's ability to act as a reservoir for NH₄⁺ ". . . 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 (87).

Clinoptilolite added to the feed of young calves improved their growth rate by stimulating appetite and decreased the incidence of di-

Table 10.—Effect of Zeolite Supplement in Molasses-Based Diets of Young Pigs^a

	Zeolite level (%)				
	0	2.5	5	7.5	10
35-65 kg growth stage					
Daily gain (g)	621	694	700	704	659
Daily intake (g)	2900	3110	3090	2970	3040
Daily feed intake ^b (g)	2900	3030	2940	2750	2740
Feed efficiency value (FEV) ^d (weight gain/feed intake)	0.214	0.229	0.238	0.256	0.241
65-100 kg growth stages					
Daily gain (g)	541	582	526	562	535
Daily intake (g)	3550	3900	4260	4430	4140
Daily feed intake ^b (g)	3550	3800	4050	4100	3730
Feed efficiency value (FEV) ^d (weight gain/feed intake)	0.152	0.153	0.130	0.137	0.143

^aCastro and Elias (1978)

^bIncluding zeolite

^cIntake less zeolite

^dExcluding zeolite.

Table 11.—Effect of Clinoptilolite Supplemental in the Diet of Swine^a

	Control	2.50/o Clinoptilolite	50/0 Clinoptilolite
Average initial weight (lb)	31.6 ^c	31.7	31.7
30-days:			
Average weight (lb).....	61.0	62.2	62.5
Average daily weight gain	1.09	1.12	1.17
Feed/pound of gain (lb) ^b	2.62	2.20	2.36
Feed efficiency value ^c	0.382	0.455	0.424
60-days:			
Average weight (lb)	105.7	107.3	106.2
Average daily weight gain	1.59	1.61	1.52
Feed/pound of gain (lb) ^b	2.80	3.05	3.09
Feed efficiency value ^c	0.357	0.328	0.324
90-days:			
Average weight (lb)	153.7	149.6	150.0
Average daily weight gain	1.72	1.51	1.57
Feed/pound of gain (lb) ^b	3.33	3.43	3.67
Feed efficiency value ^c	0.300	0.292	0.272
120-days:			
Average weight (lb)	188.2	177.8	176.4
Average daily weight gain	1.56	1.28	1.27
Feed/pound of gain (lb) ^b	3.94	5.63	4.30
Feed efficiency value ^c	0.254	0.178	0.233
Overall			
Average daily weight gain	1.49	1.40	1.37
Feed/pound of gain (lb) ^b	3.42	3.45	3.34
Feed efficiency value ^c	0.292	0.290	0.299

^aFrom Heeney (1977), 6 pigs in each treatment. Control diet - 76.9% ground corn, 20% soybean 011 meal, 1.5% dicalcium phosphate, 0.5% CaCo₃, 0.5% salt, 0.1% trace mineral 0.25% vitamin premix, 0.25% ASP250 antibiotic Zeolite diets contained 25 and 5% A replacement of corn.

^bExcluding zeolite

^cWeight gain/feed Intake, excluding zeolite

arrhea and soft feces (38). 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 percent 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. The incidence of diarrhea and soft-feces was markedly less in zeolite-fed calves than in control animals (table 12)

Watanabe, et al. (86) raised six young bullocks for 329 days on a diet containing 2 percent clinoptilolite, along with 72 percent digestible nutrients and 11 percent 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 high-

er quality meat. These differences were reflected in the overall higher prices obtained for the test animals and a 20 percent 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 odorous, again testifying to the retentivity of clinoptilolite for ammonia. It is unfortunate that a higher level of zeolite was not used in these experiments; earlier studies in the United States showed that as much as 40 percent clay could be added to animal rations without adverse effects (68),

One study found increased protein digestion when 5 percent powdered clinoptilolite was added to a high-volubility protein diet of 18 Holstein steers and cows over a 118-day period; however, statistically significant weight increases were not noted. The addition of 2 percent zeolite to the rations of cows was effective in preventing diarrhea and in increasing milk production (20). These effects were appar-

Table 12.—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)

ently related to an increase in the albumin and a decrease in the urea-N content of the blood.

Excrement Treatment

In the United States, livestock production creates more than 1 billion metric tons of solid waste and nearly 400 million tons of liquid waste each year (43). Accumulations of such magnitude pose serious problems to the health of man and beast alike and can pollute 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 because of 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 the:

- reduction of malodor and associated pollution,
- c creation of healthier environments for confined livestock,
- Q control of the viscosity and nutrient retentivity of the manure, and
- c purification of methane gas produced by anaerobic digestion of the excrement.

Malodor and Moisture Control

The semifluid 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 and result in smaller and less healthy birds (15,35). In many areas of Japan clinoptilolite is now mixed with the droppings directly or packed in boxes suspended from ceilings to remove ammonia and thereby improve the general atmosphere in chicken houses (82). The net result is reported to be an overall increase in egg production and healthier birds.

One study used a zeolite-packed air scrubber to improve poultry-house environments (36). By passing ammonia-laden air over a series of trays containing crushed clinoptilolite, 15 to 45 percent of the $\text{NH}_3\text{-N}$ was removed even though the contact time was less than one second. There was an associated reduction in odor intensity. The use of such a scrubber could improve the quality of the air in poultry houses without the loss of heat that accompanies normal ventilation. The ammonium-loaded zeolite could then be used as a valuable soil amendment on disposal.

Water content, maggot population, and ammonia production can be all minimized when chicken droppings are mixed with one-third zeolite (table 13). Similar results can be obtained if powdered zeolite is added directly to the rations of the birds, all without affecting the vitality or growth rate of the chickens (67). Apparently, gaseous ammonia reacts with the hydrous zeolite to form ammonium ions that are selectively ion-exchanged and held in the zeolite structure. These experiments suggest that the addition of zeolites to poultry wastes could reduce labor costs associated with air-drying or the high energy costs of thermal treat-

Table 13.—Effect of Zeolite Additions to Chicken Droppings

Property	2:1	3:1	5:1	10:1	Control
Moisture content (%)	123	131	134	157	185
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.

ment, while at the same time retain the valuable fertilizer components and meet ecological standards.

In swine raising, pigs fed a diet containing 10 percent clinoptilolite had feces richer in all forms of nitrogen after drying than those from control groups (*vide supra*) (39). As a result of this study and of other investigations, about 25 tons of clinoptilolite per month is spread on the floors of a Sapporo swine-raising facility to adsorb urine and other liquid wastes (82). The buildings were said to be dry, clean, and considerably less odoriferous. In Akita Prefecture, Japan, a zeolitic mudstone is used to treat offensive odors and to reduce moisture content of swine excrement (30). The dried manure is then sold as an inexpensive rice fertilizer.

An innovative application of zeolites in excrement treatment was patented and involves the addition of a natural zeolite and ferrous sulfate to chicken droppings (37). 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.

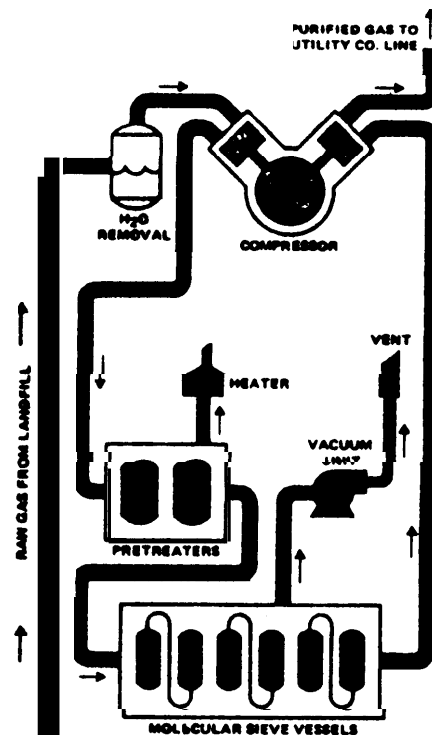
Methane Purification

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 (32). 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. Nevertheless, the process is still an attractive one, and Goepfner and Hasselmann (21) estimated that a billion cubic feet of 700 Btu/ft³ methane gas could be produced by treating the 250,000 tons of manure produced each day in the United States. The methane produced by the anaerobic digestion of the organic wastes of a typical New York State dairy farm of 60 head may be equivalent to the farm's entire fossil-fuel requirements (32).

A recent development of Reserve Synthetic Fuels, Inc., using the adsorption properties of natural zeolites, suggests that this methane 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 Pales Verde landfill near Los Angeles. As shown schematically in figure 10, raw gas containing about 50 percent methane and 40

Figure 10.—Methane-Purification System, Pales Verde Landfill



percent carbon dioxide is fed to two pretreatment vessels to remove moisture, hydrogen sulfide, and mercaptans. The dry gas is then routed through three parallel columns packed with pellets of dehydrated chabazite/erionite and carbon dioxide is removed by adsorption on the zeolite. Approximately 1 million cubic

feet of methane meeting pipeline specifications is produced each day and delivered to local utility companies (65). Such a zeolite-adsorption process to upgrade impure methane 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 is becoming a major business in the United States and other countries. Many varieties of fish, however, are extremely sensitive to minor fluctuations in such factors as water temperature, pH, O₂, H₂S, and NH₄⁺. The chemical and biological environment of aquacultural systems must be maintained within close limits at all times. Processes based on the selective adsorption and ion-exchange properties of several natural zeolites for oxygen aeration of hatchery and transport water and for the removal of toxic nitrogen from tanks and breeding ponds may contribute significantly to increased product ion for human and animal consumption.

Nitrogen Removal From Closed or Recirculation Systems

In closed or recirculating aquacultural systems, NH₄⁺ 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 parts-per-million NH₄⁺ can lead to gill damage, hyperplasia, and substantial reduction in growth rates (42). Biological vitrification is a common means of removing NH₄⁺ 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 (40). Zeolite ion

exchange might be a useful alternative to bio-filtration for NH₄⁺-removal and have the advantages of low cost and high tolerance to changing temperatures and chemical conditions (33).

Unpublished tests conducted in 1973 at a working hatchery near Newport, OR, indicated that 97 to 99 percent of the NH₄⁺ produced in a recirculating system was removed by clinoptilolite ion-exchange columns (34). Trout also remained healthy during a 4-week trial when zeolite ion exchange was used to regulate the nitrogen content of tank waters (69). Becker Industries of Newport, OR, in conjunction with the U.S. Army Corps of Engineers, has developed a single-unit purification facility for hatchery-water reuse. The system incorporates a zeolite ion-exchange circuit for nitrogen removal and is designed to handle typical concentrations and conditions encountered at most of the 200 fish hatcheries operating in the Pacific Northwest (34).

A similar ammonium-ion removal system using zeolite ion exchange for fish haulage applications, where brain damage due to excess NH₄⁺ commonly results in sterility, stunted growth, and high mortality has also been developed (63). Three-way cartridges and filters containing granular clinoptilolite will also be available for home aquaria. The U.S. Fish and Wildlife Service investigated zeolite ion-exchange processes for the treatment of recirculating waters in tank trucks used to transport channel catfish from Texas hatcheries to the Colorado River in Arizona (48). If NH₄⁺ can be removed, the number of fish hauled in such trucks can be nearly tripled.

Aeration Oxygen Production

Oxygen-enriched air can be produced by the selective adsorption of nitrogen by activated zeolites. A pressure-swing adsorption process capable of producing up to 500 m³ of 90 percent oxygen per hour was developed in Japan for secondary steel smelting (80). Smaller generators with outputs of as little as 15 liters of 50 percent O₂ per hour are also manufactured 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 (41). In closed tanks and stagnant ponds, oxygen aeration could markedly increase the number of fish that could be raised per unit volume.

Oxygen produced by small, portable units containing natural zeolite absorbents could be used to replenish free oxygen in small lakes where eutrophication endangers fish life. Fast, et al. (17), showed that the oxygen of hypolimnion zones could be increased markedly by aeration using liquid O₂ as a source. Haines (23) demonstrated side-stream pumping could improve the dissolved oxygen in the hypolimnion of a small lake in New York State.

Fish Nutrition

The high-protein rations used in commercial fish raising are quite expensive and their cost has been a limiting factor in the development

of large-scale aquacultural operations. The physiology of fish and poultry is remarkably similar, and if the results achieved with chickens can be duplicated with fish, the substitution of small amounts of inexpensive zeolites in normal fish food, with no adverse change in growth and perhaps a small increase in feed efficiency, could result in considerable savings. The quality of the water in recirculating systems should also be improved by the use of zeolite-supplemented food, as should that of the effluents. Leonard (44) reported preliminary results of experiments where 2 percent clinoptilolite was added to the normal 48 percent protein food of 100 rainbow trout: after 64 days, a 10 percent improvement in the biomass increase was noted, with no apparent ill effects on the fish (table 14).

Table 14.—Effect of Clinoptilolite Additions to the Diet of Trout^a

	Control 100% normal feed ^b	Test 98% normal feed 2% clinoptilolite
Average starting weight (g)	10.2	10.1
Average 64-day weight	48.6	52.3
Average weight gain	38.4	42.2
Mortality	4	3

^a100 rainbow trout.
^bStandard 48% protein fish food

OCCURRENCE AND AVAILABILITY OF NATURAL ZEOLITES

Geological Occurrence

Since their discovery more than 200 years ago, natural zeolite minerals have been widely recognized by geologists as cavity and fracture fillings in almost every basaltic igneous rock. Attractive crystals up to several centimeters in size adorn the mineral museums of every country; however, such traprock occurrences are generally too low-grade and heterogeneous for commercial extraction. The flat-lying and nearly monomineralic sedimentary deposits, on the

other hand, are ideally suited for simple, inexpensive, open-pit mining.

Most sedimentary zeolite deposits of economic significance were formed from fine-grained volcanic ash or other pyroclastic material that was carried by the wind from an erupting volcano and deposited onto the land surface, into shallow freshwater or saline lakes, or into the sea fairly close to the volcanic source. Much of the land-deposited material was quickly washed into lakes where it formed

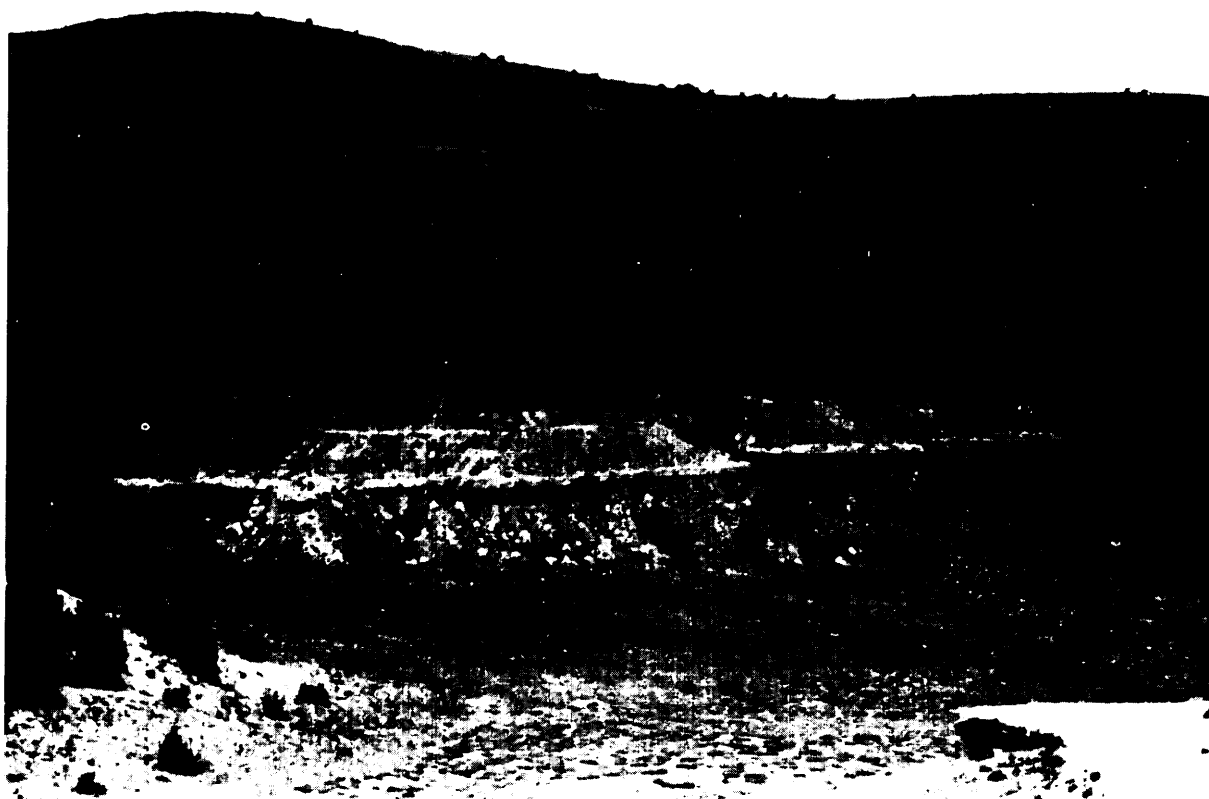
beds of nearly pure ash. Successive eruptions resulted in sequences of ash layers interstratified with normal lake or marine sediments, such as mudstones, silt stone, sandstones, and limestones, as well as beds of diatomite, bentonite, and chert (figure 1 I).

The layers of volcanic ash (called volcanic tuff) vary in thickness from less than a centimeter to several hundred meters and may stretch for 10 kilometers. Many of these bedded tuffs have been transformed almost completely into well-formed, micrometer-size zeolitic minerals. Zeolitically altered tuffs occur in relatively young sedimentary rocks in diverse geological environments. Sedimentary zeolite deposits of this kind have been classified into the following types, with many gradations between the types, Sheppard (77), Mumpton (54), and Munson and Sheppard (62):

1. deposits formed from volcanic materials in hydrologically "closed" saline lake systems;
2. deposits formed in hydrologically "open" fresh-water lake or ground water systems;
3. deposits formed in marine environments;
4. deposits formed by low-grade, burial metamorphism;
5. deposits formed by hydrothermal or hot-spring activity in bedded sediments;
6. deposits formed from volcanic materials in alkaline soils;
7. deposits formed without direct evidence of volcanic precursors.

The most common zeolites in sedimentary deposits are analcime, chabazite, clinoptilolite, erionite, heulandite, laumontite, mordenite, phillipsite, and wairakite, with clinoptilolite ranking first in abundance. Except for heulan-

Figure 11.— Field Exposure of Zeolite Beds



dite, laumontite, and wairakite, "sedimentary" zeolites are alkalic and are commonly more silicic than their igneous counterparts. Commercial interest is mainly in deposits of the first four types. Zeolite tuffs in saline-lake deposits are generally a few centimeters to a few meters thick and commonly contain nearly monomineralic zones of the larger pore zeolites, erionite and chabazite that are relatively uncommon in other types of deposits. "Open-system" deposits and marine tuffs deposited close to their source are generally characterized by clinoptilolite and/or mordenite and may be several hundred meters thick. Zeolitic tuffs are commonly soft and lightweight, although some hard, siliceous deposits of clinoptilolite and mordenite are known. Many sedimentary zeolite beds contain as much as 95 percent of a single zeolite species, while others consist of two or more zeolites with minor amounts of calcite, quartz, feldspar, montmorillonite clay, and unreacted volcanic glass.

Most zeolites in sedimentary rocks crystallized from volcanic ash by reaction of the amorphous, aluminosilicate glass with pervading pore waters derived either from saline lakes or descending ground waters. Others originated by the alteration of preexisting feldspars, feldspathoids, biogenic silica, or poorly crystalline clay minerals. Although the exact mechanism of formation is still under investigation, zeolites in sedimentary rocks probably crystallized as well-formed, micrometer-size crystals by means of a dissolution-reprecipitation mechanism, with or without an intermediate gel stage (55) (figure 12).

The factors controlling whether a zeolite or a clay mineral formed or which of several zeolites formed from a given starting material are also only poorly understood, although temperature, pressure, reaction time, and the concentrations of the dissolved species, such as H^+ , silica, alumina, and alkali and alkaline earth elements, seem to be paramount in importance. Early formed species also tend to react further with pore fluids of different composition, thereby yielding even more complex assemblages.

Figure 12.—Scanning Electron Micrograph of Clinoptilolite Laths With Minor Mordenite From a Saline-Lake Deposit Tuff Near Hector, CA (from Mumpton and Ormsby, 1976)



Geographic Distribution

The distribution of zeolite deposits in various geographic regions of the world is governed solely by the geology of those regions. Regions that have undergone past volcanic activity are likely to contain significant deposits of zeolite minerals. Although the zeolite philipsite is known to have formed within the last 10,000 years in a small saline-lake deposit at Teels Marsh, NV (79) by the alteration of volcanic ash from the explosion of Mt. Mazuma (Crater Lake), and chabazite has been identified in deposits on the walls of ancient Roman baths in France, most potentially commercial deposits of zeolites are of Tertiary or lower Pleistocene age (70,000 to 3 million years ago). Thus, any part of the Earth that was subjected to volcanic activity during this period undoubtedly contains extensive deposits of volcanic ash, and if these ash deposits had an opportunity to react with percolating ground waters or alkaline pore waters from former saline lakes, beds of high-grade zeolites are apt to exist.

Although zeolites are now considered to be some of the most abundant and widespread au-

thigenic silicate minerals in sedimentary rocks, their existence as major constituents of altered volcanic tuffs is still not common knowledge among the geologists of many countries. Because of their inherently fine crystal size, zeolites are not easily identified by ordinary microscopic techniques and have often been missed by geologists and mineralogists studying these formations. In general, zeolite identification requires sophisticated X-ray diffraction and electron microscopic equipment not available in many geological laboratories; however, once a particular soft, lightweight, clay-like rock from a particular area is identified in the laboratory as a zeolite rock, similar materials are easy to locate in the field.

Table 15 lists the countries where zeolites have been reported from sedimentary rocks of volcanic origin and estimates the chances of discovering additional deposits in these countries. Sedimentary zeolites have been found on every continent, although few have been reported from the Middle East, Latin America, or the East Indies, mainly because geologists in these regions generally have been unaware of the widespread occurrence of zeolites in altered volcanic tuffs. Wherever zeolites have been found, however, man has used the soft, lightweight tuffs for hundreds of years as easily carved stone in a variety of structures ranging from walls and foundations of buildings to barns and corrals to house livestock. Zeolitic blocks have been found in buildings associated with the Mayan pyramids at Monte Alban and Mitla in southern Mexico (56) and are used today in the construction of modern dwellings in the Tokaj region of eastern Hungary. Zeolites are mined in only a dozen countries (table 16), but the potential is much greater.

The high probability of finding minable deposits of zeolites in countries where they have not yet been reported, but where there has been considerable volcanic activity in the past, is illustrated by the discovery of major bodies of sedimentary zeolites in Mexico and in central Turkey in the early and late 1970s, respectively. Both countries show promise of becoming major suppliers of mineral raw materials in the years to come, but, as with most developing na-

tions, they have only limited in-house geological expertise to service their blossoming mineral industry.

During the late 1950s and 1960s the geological similarity of the Western United States and northern Mexico led geologists to speculate about the existence of zeolite deposits south of the border. It was not until 1972, however, that this author (56) discovered the first such deposit in southern Oaxaca after visiting a large stone quarry during an unrelated project. The rock was being used as a local dimension stone and closely resembled zeolitic tuffs that were being quarried in Japan. Subsequently, the Oaxacan rock was shown to consist of about 90 percent clinoptilolite and mordenite. Shortly thereafter, several similar deposits were discovered in this part of Mexico and Mexican scientists quickly learned to recognize zeolitic tuffs in the field. One deposit was spotted in a road cut while driving past it at 50 miles per hour, suggesting that many more await discovery with only minimal exploration efforts. As a result of these discoveries, at least three other deposits of sedimentary zeolites have been found in the northern part of the country by Mexican geologists who are now attune to the existence of zeolites in volcanogenic environments and to their potential applications in industrial and agricultural technology.

Similar to Mexico, major parts of the central Anatolian region of Turkey are covered by thick sequences of Tertiary volcanic rocks, but, with the exception of a few minor occurrences of analcime in saline-lake environments, reports of zeolites in the volcanogenic sedimentary rocks of this country have been rare. The principal reason for this is simply lack of exploration combined with a lack of knowledge about the potential applications of such materials in industry. Turkey's few geologists have been more occupied with their chrome and borate resources, which are exported in large quantities to acquire badly needed currency. In 1977, however, several low-grade occurrences of erionite and chabazite were uncovered in Turkey's Cappadocia region, along with a major deposit of clinoptilolite (7). In 1979, a second major deposit was discovered by the au-

Table 15.— Reported Occurrences of Sedimentary Zeolites

Country	Zeolite species	Minable deposit	Minor occurrence	Chances for finding deposit
Europe:				
Belgium	Laumontite		X	Poor
Bulgaria	Clinoptilolite	XXX		Excellent
	Mordenite	X		Excellent
	Analcime		X	Poor
Czechoslovakia	Clinoptilolite	X		Good
Denmark	Clinoptilolite		X	Poor
Finland	Laumontite		X	Poor
France	Clinoptilolite		XXX	Good
Germany	Chabazite	XX		Good
	Phillipsite	XX		Good
	Analcime		XX	Poor
Great Britain	Analcime		X	Poor
	Clinoptilolite		X	Poor
	Laumontite		X	Poor
Hungary	Clinoptilolite	XX		Excellent
	Mordenite	X		Excellent
Italy	Chabazite	XXX		Excellent
	Phillipsite	XXX		Excellent
	Analcime		X	Good
Poland	Clinoptilolite	XX		Excellent
Romania	Clinoptilolite	XX		Excellent
Soviet Union	Clinoptilolite	XXX		Excellent
	Mordenite	XX		Excellent
	Chabazite		X	Good
Spain	Analcime		X	Good
	Laumontite		X	Good
	Clinoptilolite		X	Good
Switzerland	Mordenite		X	Good
	Clinoptilolite		X	Poor
	Laumontite		XX	Poor
Turkey	Clinoptilolite	XX		Excellent
	Erionite		XX	Excellent
	Chabazite		XX	Excellent
Yugoslavia	Analcime	X		Excellent
	Clinoptilolite	XXX		Excellent
	Analcime	X		Good
	Mordenite	X		Excellent
Erionite		X	Good	
North America:				
Canada	Laumontite		X	Poor
	Clinoptilolite		X	Good
Cuba	Clinoptilolite	XX		Excellent
	Mordenite	X		Excellent
Guatemala	Clinoptilolite	X		Excellent
Mexico	Clinoptilolite	XX		Excellent
	Mordenite	XX		Excellent
	Analcime		X	Good
Panama	Erionite	X		Excellent
	Phillipsite		X	Excellent
	Clinoptilolite	X		Excellent
West Indies	Wairakite		X	Poor
	Clinoptilolite		X	Excellent
Africa:				
Angola	Clinoptilolite		X	Good
Botswana	Clinoptilolite		X	Good
Congo	Analcime	X		Good
Egypt	Heulandite		X	Good
Kenya	Phillipsite	X		Excellent
	Erionite	X		Excellent

Table 15.— Reported Occurrences of Sedimentary Zeolites—Continued

Country	Zeolite species	Minable deposit	Minor occurrence	Chances for finding deposit
Northwest Africa	Analcime	X		Good
	Mordenite		X	Good
Republic of South Africa	Clinoptilolite	X		Excellent
	Analcime		X	Poor
Tanzania	Clinoptilolite	XX		Excellent
	Erionite	X		Excellent
	Chabazite	X		Excellent
	Phillipsite	X		Excellent
	Analcime	X		Excellent
	Clinoptilolite	X		Excellent
Asia:				
Iran	Clinoptilolite	X		Excellent
Israel	Clinoptilolite		XX	Excellent
Pakistan	Analcime		X	Good
Australia	Clinoptilolite	X		Good
	Analcime		X	Good
China	Clinoptilolite	XX		Excellent
Formosa	Laumontite		X	Poor
	Analcime		X	Good
Japan	Clinoptilolite	XXX		Excellent
	Mordenite	XX		Excellent
	Analcime		X	Poor
	Laumontite		X	Poor
	Wairakite		X	Poor
Korea	Clinoptilolite	XX		Excellent
New Zealand	Analcime		X	Good
	Clinoptilolite	XX		Good
	Mordenite	X		Excellent
	Laumontite	X		Good
	Erionite	X		Good
Oceania	Laumontite		X	Poor
South Africa:				
Argentina	Clinoptilolite	XX		Excellent
	Analcime	X		Excellent
	Laumontite		X	Poor
Chile	Clinoptilolite		X	Excellent
Antarctica:				
Antarctica	Laumontite		X	Poor
	Phillipsite		X	Poor

thor (59) and R. A. Sheppard of the U.S. Geological Survey, accompanied by a Turkish geologist, with a minimum of field effort. This indicates a widespread distribution of such materials in volcanogenic sedimentary rocks in this country.

Mining and Milling

The mining of zeolites in bedded sedimentary deposits is a relatively straightforward process requiring only a minimum of equipment and trained personnel. Almost all of the known zeolite deposits being mined are sur-

face deposits overlain by a few to no more than 25 meters of overburden. The zeolite beds are usually flat-lying and vary only slightly in thickness along the length of the deposit. Shallow drilling is usually required to outline the areas of highest grade, but many deposits are mined by simple projection of the bed behind the outcrop. Commonly, the exposed bed can be broken in the mine by bulldozers or rippers; in places small amounts of blasting are required. In thinner deposits, care must be taken to eliminate overlying and underlying clays and volcanic ash from the ore to preserve purity, but in some of the thicker deposits this poses no problem,

Table 16.—Countries Engaged in Zeolite Mining^a

Country	Mineral	Mines	Remarks
United States	Clinoptilolite	12	Many more available.
	Chabazite	4	Single deposit, four companies.
	Erionite	2	
	Mordenite	1	
Mexico	Mordenite/Clinoptilolite	1	
Cuba	Clinoptilolite	1	
Japan	Clinoptilolite	8	Estimated.
	Mordenite	5	Estimated.
Korea	Clinoptilolite	2	
Bulgaria	Clinoptilolite	1	
Hungary	Clinoptilolite	1	
	Mordenite	1	Estimated.
Soviet Union	Clinoptilolite	3	Estimated.
	Mordenite	1	Estimated.
Yugoslavia	Clinoptilolite	2	Several more available.
South Africa	Clinoptilolite	1	
Italy	Chabazite/Phillipsite		Numerous, used for construction.
Germany	Chabazite/Phillipsite		Several, used for construction.

^aAs of 1980

Processing the raw ore is dependent on the envisioned end use. Water-purification applications require a fine-sand fraction that must be prepared from the ore by crushing and screening whereas fertilizer and animal nutrition uses will likely make use of finely powdered material. In general, preparation involves only crushing, screening, and bagging. Where particle size is critical, the screened product must be washed to remove undersize material and then dried. More sophisticated ap-

plications may require that the zeolite be ion-exchanged to an ammonium or potassium form before being shipped to the consumer. In such cases, the pulverized and screened product must be subjected to a series of washes with chloride or sulfate salts of these elements, washed with water to eliminate excess salts, filtered, dried, and bagged. In 1980, crushed ore could be produced in the United States for about \$30 to \$40/ton.

DISCUSSION

Agronomic Applications

Although zeolites have been used for many years in Japan as soil amendments, they are only now becoming the subject of serious investigation in the United States as slow-release fertilizers, moisture-control additives to low-clay soils, traps for heavy metals, carriers of pesticides, fungicides, and herbicides, and de-caking agents in fertilizer storage. As soil amendments they appear to retain moisture and improve the overall ion-exchange capacity of sandy and volcanic soils. Studies are being carried out on both pure zeolite and on zeolite that has been pretreated with nutritive elements, such as potassium or ammonium. In

either case, the zeolite appears to act as a slow-release fertilizer, selectively holding such elements in its structure for long periods of time, thereby increasing the efficiency of such additives and reducing the total cost of fertilization. Although the data available are not unequivocal, the greatest success appears to have been with root crops such as sugar beets, carrots, and radishes, where nitrogen is a vital nutrient. The optimum level of application, however, must still be determined for various types of soils and for the particular crop in question, as must the frequency and exact mode of application, the optimum particle size of the zeolite, and the nature of chemical pretreatment of the zeolite.

The ion-exchange specificity of certain zeolites for copper, lead, cadmium, and zinc suggests that the "life" of farm and forest soils amended with municipal and industrial sewage sludge can be extended by inhibiting the plant uptake of these deleterious metals. Radioactive cesium and strontium from nuclear fallout or spills may also be controlled by selective ion exchange into zeolites added to soils. Zeolites apparently are useful carriers of herbicides, pesticides, and fungicides and can prevent caking in stored fertilizers by absorbing excess moisture.

Table 17 lists organizations that have or are conducting experiments on the use of natural zeolites in agronomic applications.

Animal Nutrition Applications

Despite the lack of statistical significance, numerous studies strongly suggest that the addition of certain zeolite minerals to the diets of swine, poultry, and ruminants results in decided improvement in growth and in feed efficiency (weight gain/pounds of nutritional feed consumed). In addition, the incidence of intestinal disease among young animals appears to be less when zeolites are part of the daily diet. The most dramatic results have been reported by overseas workers where experiments may have been conducted under conditions that were somewhat less sanitary than those generally employed in the United States. Zeolite-supplemented diets appear to be most benefi-

cial in swine during the first 30 to 60 days after weaning, although there is some evidence to suggest that zeolites in the rations of pregnant sows contribute to increased litter weights and healthier offspring. In Japan, 2 to 5 percent clinoptilolite in the diets of cattle appeared to result in larger animals and fewer incidences of diarrhea. One study in the United States found a 12-percent increase in feed efficiency for cattle during the first 37 days using only 1.25 percent zeolite.

The exact function of the zeolites in both dietary and antibiotic phenomena are not well understood and await serious physiological and biochemical investigation. The ammonium selectivity of clinoptilolite suggests that in ruminants it acts as a reservoir for ammonium ions produced by the breakdown of vegetable protein and nonprotein nitrogen in rations, releasing it for a more efficient synthesis into amino acids, proteins, and other nitrogenous compounds by micro-organisms in the gastrointestinal (GI) lumen. From the concentration of ammonia in the portal blood of weanling rats fed a 5 percent clinoptilolite diet or dosed orally with this zeolite, Pond, et al. (71), postulated that the zeolite bound free ammonia in the GI tract, thereby preventing its buildup to toxic levels in the system. Such an antibiotic effect could indeed be responsible for the larger growths recorded for zeolite-fed animals.

Table 18 lists organizations that have or are conducting experiments on the use of natural zeolites in animal nutrition applications,

Table 17.—Organizations Engaged in Zeolite/Agronomic Investigations^a

Organizations	Crop	Organization	Crop
Department of Horticulture Colorado State University Fort Collins, Colorado	Radishes	Agricultural Experiment Station New Mexico State University Las Cruces, New Mexico	Corn Sorghum
Department of Agronomy Colorado State University Fort Collins, Colorado	Sorghum Corn Wheat	Department of Plant Science University of New Hampshire Durham, New Hampshire	Radishes Corn
Department of Environmental Horticulture University of California Davis, California	Chrysanthemums	Texas Agricultural Experiment Station Texas A&M University Beaumont, Texas	Rice
U.S. Sugarcane Field Laboratory U.S. Department of Agriculture Houma, Louisiana	Sugarcane	Department of Soils, Water and Engineering Tucson, Arizona	Nitrogen retention in soils

^aAs of 1980

Table 18.—Organizations Engaged in Animal Nutrition Studies Using Zeolites^a

Organization	Animal	Organization	Animal
Department of Poultry Science Colorado State University Fort Collins, Colorado	Chickens	Department of Animal Science Cornell University Ithaca, New York	Swine
Department of Animal Science Colorado State University Fort Collins, Colorado	Swine	Department of Animal Science Oregon State University Corvallis, Oregon	Swine Rabbits
Clayton Livestock Research Center	Beef Cattle	Western Washington Research and Ex- tension Center	Dairy Cattle
New Mexico State University Clayton, New Mexico		Washington State University Puyallup, Washington	
Department of Poultry Science Oregon State University Corvallis, Oregon	Chickens	Department of Animal Science University of Kentucky Lexington, Kentucky	Calves
Livestock Nutrition Service Westminster, California	Cattle	Food and Animal Research, Inc. Juneau, Wisconsin	Calves
Department of Animal Science University of Vermont Burlington, Vermont	Ruminants	Department of Biology Cleveland State University Cleveland, Ohio	Chickens Swine
U.S. Meat Animal Research Center U.S. Department of Agriculture Clay Center, Nebraska	Rats (swine)	Department of Agricultural Engineering Oregon State University Corvallis, Oregon	Odor control
Department of Animal Science Pennsylvania State University University Park, Pennsylvania	Cattle		

^aAs of 1980.

Excrement Treatment Applications

Although the results are difficult to quantify, almost all studies of the use of zeolites as dietary supplements in animal rations have reported a noticeable decrease in excrement malodor and have attributed this observation to the high selectivity of the zeolite in the feces for the ammonium ion. Similar results were noted when zeolites were added directly to cattle feedlots, suggesting that not only can healthier and less odoriferous environments be achieved by the addition of zeolites to animal manure, but that the nitrogen-retention ability of the manure can be improved as well.

Zeolite purification of low-Btu methane produced by the anaerobic fermentation of excrement and other agricultural waste products

may be a means of producing inexpensive energy on individual farms or in small communities, and zeolite ion-exchange processes may be employed in the removal of ammonium ions from recirculating or closed aquacultural systems, thereby allowing more fish to be raised or transported in the same volume of water. Aquacultural research of this type has been or is being conducted by Becker Industries, Newport, OR; the U.S. Fish and Wildlife Service, Fish Cultural Development Center, Bozeman, MT; Jungle Laboratories, Comfort, TX; the Department of Fisheries and Wildlife, New Mexico State University, Las Cruces, NM; the Narragansett Marine Laboratory, University of Rhode Island, Kingston, RI; and the Department of Zoology, Southern Illinois University, Carbondale, IL.

CONCLUSIONS AND RECOMMENDATIONS

Although they have been used locally for several years in Japan and other parts of the Far East in small amounts, the use of zeolites as soil amendments, fertilizer supplements, addi-

tives to animal rations, and in the treatment of agricultural wastes is still in the experimental stage in the United States. A number of agricultural organizations have or are investigat-

ing such uses for natural zeolites in this country. The projects have generally been sponsored by grants or contracts from companies that themselves are developing applications for zeolites in one or more areas of technology, or they have been funded by the institutions themselves and make use of zeolite products provided free or at low cost by the companies. Table 19 summarizes the agricultural research efforts of companies that hold properties of natural zeolites. In addition, other, nonproperty holding organizations, such as International Minerals & Chemical Corp., Cargill, Inc., and Lowe's, Inc., have also been involved in the development of uses of natural zeolites in agriculture.

Overseas, six to eight agricultural stations in Japan continue to investigate natural zeolites as soil amendments and dietary supplements; Pratley Perlite Mining Co., which owns a large clinoptilolite deposit in South Africa, has made several studies of the use of zeolites in the rations of swine and poultry; and a recent Bulgarian-Soviet symposium on natural zeolites contained seven papers on animal-nutrition applications and two on soil-amendment uses,

^aSecond Bulgaria n-Soviet Symposium on Natural Zeolites, Kardzhali, Bulgaria, Oct. 11-14, 1979.

Similar projects are in progress in Cuba and Hungary, where deposits of clinoptilolite and mordenite are abundant. The intense interest in the several socialistic countries mentioned above undoubtedly stems from their efforts to use their own natural resources and thereby reduce their dependency on foreign sources of expensive fertilizers and animal rations. These same objectives, of course, are desired by each developing nation—maximum use of local raw materials and minimal use of imported products that must be purchased with hard currency. Where they can be found within a particular nation or where they can be obtained from neighboring countries at minimum cost, natural zeolites have the potential to increase the agricultural productivity of that nation by reducing the need for or increasing the efficiency of chemical fertilizers and animal feedstuffs.

To convert the agricultural promise of natural zeolites into commercial reality, a concerted effort must be made in the United States and elsewhere by both the private sector and by State and Federal funding organizations. The studies to date have been mainly of a preliminary nature—radishes have been grown instead of potatoes, and rats have been raised instead of beef cattle—or of limited duration or extent.

Table 19.—Zeolite Property Holders and Zeoagricultural Research Efforts

Organization	Zeolite Species ^a	Research Effort
Anaconda Company	Clinoptilolite, Erionite, Chabazite/Erionite, <i>Clinoptilolite</i> , <i>Chabazite</i> , <i>Mordenite</i> , <i>Phillipsite</i>	In-house; sponsored
Colorado Lien Co.	Clinoptilolite	Sponsored
Double Eagle Petroleum & Mining Co.	Clinoptilolite, <i>Clinoptilolite</i>	Sponsored
Forminco	<i>Clinoptilolite</i>	None
Harris & Western Corp.	<i>Clinoptilolite</i> /A40 <i>ordenite</i>	None
Ladd Mountain Mining Co.	<i>Erionite</i> /Clinoptilolite	None
Leonard Resources	<i>Clinoptilolite</i>	Sponsored
Letcher Associates	<i>Clinoptilolite</i>	None
Minerals Research	<i>Phillipsite</i>	None
Minobras, Inc.	<i>Erionite</i>	None
Mobil Oil Corp.	Erionite	None
Monolith Portland Cement Co.	Clinoptilolite	None
NL Industries	Clinoptilolite	None
Norton Co.	Chabazite/Erionite, <i>Ferrierite</i>	None
NRG Corp.	Chabazite/Erionite	None
Occidental Minerals Corp.	Clinoptilolite, <i>Clinoptilolite</i> , <i>Erionite</i>	In-house; sponsored
Rocky Mountain Energy Co.	Clinoptilolite	Sponsored
Union Carbide Corp.	Chabazite/Erionite, Mordenite, Erionite	In-house; sponsored
U.S. Energy Corp.	<i>Clinoptilolite</i>	None
W. R. Grace & Co.	Chabazite/Erionite, <i>Ferrierite</i>	None

^aRoman type = working mines, italics = prospects

Little information has been developed to illuminate the long-term benefits or adverse impacts on food production. Many of the companies sponsoring this research have considered the results proprietary, and rightfully so, but workers in the field are therefore unable to obtain the latest information, a situation that often results in massive duplication of effort. Large-scale testing of zeolites under sustained field conditions and projects involving statistically significant numbers of animals are greatly needed at this juncture. Such projects will require continuous funding by State and Federal agencies, or perhaps, international agencies if the results are to be applied to developing nations. It would be extremely instructive to carry out such testing in several developing nations themselves, where agricultural practices are not as finely tuned as in the United States.

The actual introduction of natural zeolites into specific agricultural processes should pose no major problems. Crushed and sized material could be added to the fields directly or banded into the soil either alone or with normal fertilizers using standard equipment. Likewise, the zeolite could be mixed as a powder or fine granules with normal feedstuffs provided for livestock, or be inserted as a bolus into the stomachs of ruminants. It could also be sprinkled on or mixed with manure accumulations on a daily basis for nutrient retentivity.

None of these processes would require special machinery; in fact, all could be carried out by hand, if such were the common practice in that country. Users would, of course, need to be instructed as to the correct amount to apply to fields or to mix with normal rations, and the optimum time to apply it for specific crops, and considerable educational efforts may be necessary to convince the small farmer of the benefits of zeolite additives. In this regard, zeolites are no different than any innovative procedure that many farmers are slow to accept.

Because the use of zeolites in agricultural processes has not yet reached the proven or commercial stage, any scenario developed to introduce this promising technology into developing nations would involve contributions

from both the United States and the developing nations. The contribution of the United States would be both geological and agricultural expertise in zeolite technology, whereas the contribution of the developing nations would be a willingness to search for deposits of zeolites and a willingness to carry out some necessary long-term or large-scale testing under field conditions. Any implementation plan should begin with a series of visits by a team of zeolite experts from the United States to selected developing nations in the world where zeolites are known or have a high probability of occurring. In addition to a leader who would have a broad background in zeolite technology, the team would consist of four to eight geologists, agronomists, animal nutritionists, and agricultural engineers who are not only experienced in the use of zeolites in agriculture or in the occurrence of zeolites in volcanogenic sedimentary formations, but who can incite an enthusiasm in others for the wonderful things that zeolites can do. The team would include:

- a geologist who is not only knowledgeable about the occurrence of zeolites in such environments, but who is capable of working with local resource people to find and evaluate potential deposits of zeolites in these countries;
- an agronomist or plant scientist with considerable experience in the use of zeolites to improve crop productivity;
- an animal nutritionist with the necessary expertise in the use of zeolites as dietary supplements in animal nutrition; and
- an agricultural engineer who has worked with zeolites in excrement treatment to improve the health of confined livestock or the ammonium retentivity of animal wastes. The agricultural engineer would also provide practical experience to the team.

Prior to the first visit to a developing nation, the team would arm itself with the latest information in the field by visiting the leading experiment stations and research laboratories in this country and abroad where zoagricultural investigations are being carried out. Special emphasis would be placed on the recent work in Japan and in countries of Eastern Europe.

Each visit would be for a 10-day period, wherein the first 2 days would be spent in the company of local geologists and/or agronomists examining the general terrain of the country and gaining a brief impression of the geology and the agricultural conditions. A third day would be devoted to a series of talks by each of the team members on his specialty before an audience of local geologists, agriculturalists, government officials, labor union leaders, and bureaucrats and anyone else who would be interested in finding out about this new technology. During the next several days the team would split into small groups for individual consultations in the field with local technical people responsible for the implementation of the technology. The geologists would, perhaps, visit suspected areas of zeolite formations, whereas the agronomist could inspect potential sites for study, providing samples of zeolite for initial investigation. The last day of each visit would be devoted to round table discussions by local agricultural experts, geologists, and team members to determine what had been accomplished and the next steps to take.

It is vital that the introduction of zeoagriculture into a developing nation not end with the visit of a team of U.S. experts. On the contrary, the initial visit should be followed up as soon as possible with specific plans for implementing the technology into the nation's agricultural processes. Although the implementation scenario of all innovative technologies would appear to be similar from this point on, the zeolite scenario would involve a search for these materials in the developing nation if such materials had not already been reported from that country. Such exploration would probably be carried out by the local geological survey or mining agency, but should be assisted in the field by a geologist familiar with the occurrence of zeolites. If zeolites are known in the country or if they can be obtained from neighboring regions without difficulty, plans should be made with the country's agricultural people to field test the technology under optimum conditions. Such plans and tests should also be made with the assistance of agronomists or animal scientists already familiar with the use of zeolites in these processes.

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