La roca magica: Uses of natural zeolites in agriculture and industry

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ABSTRACT For nearly 200 years since their discovery in 1756, geologists considered the zeolite minerals to occur as fairly large crystals in the vugs and cavities of basalts and other traprock formations. Here, they were prized by mineral collectors, but their small abundance and polymineralic nature defied commercial exploitation. As the synthetic zeolite (molecular sieve) business began to take hold in the late 1950s, huge beds of zeolite-rich sediments, formed by the alteration of volcanic ash (glass) in lake and marine waters, were discovered in the western United States and elsewhere in the world. These beds were found to contain as much as 95% of a single zeolite; they were generally flat-lying and easily mined by surface methods. The properties of these low-cost natural materials mimicked those of many of their synthetic counterparts, and considerable effort has made since that time to develop applications for them based on their unique adsorption, cation-exchange, dehydration–rehydration, and catalytic properties. Natural zeolites (i.e., those found in volcanogenic sedimentary rocks) have been and are being used as building stone, as lightweight aggregate and pozzolans in cements and concretes, as filler in paper, in the take-up of Cs and Sr from nuclear waste and fallout, as soil amendments in agronomy and horticulture, in the removal of ammonia from municipal, industrial, and agricultural waste and drinking waters, as energy exchangers in solar refrigerators, as dietary supplements in animal diets, as consumer deodorizers, in pet litters, in taking up ammonia from animal manures, and as ammonia filters in kidney-dialysis units. From their use in construction during Roman times, to their role as hydroponic (zeoponic) substrate for growing plants on space missions, to their recent success in the healing of cuts and wounds, natural zeolites are now considered to be full-fledged mineral commodities, the use of which promise to expand even more in the future.

The discovery of natural zeolites 40 years ago as large, widespread, mineable, near-monomineralic deposits in tuffaceous sedimentary rocks in the western United States and other countries opened another chapter in the book of useful industrial minerals whose exciting surface and structural properties have been exploited in industrial, agricultural, environmental, and biological technology. Like talc, diatomite, wollastonite, chrysotile, vermiculite, and bentonite, zeolite minerals possess attractive adsorption, cation-exchange, dehydration–rehydration, and catalysis properties, which contribute directly to their use in pozzolanic cement; as lightweight aggregates; in the drying of acid-gases; in the separation of oxygen from air; in the removal of NH_3 from drinking water and municipal wastewater; in the extraction of Cs and Sr from nuclear wastes and the mitigation of radioactive fallout; as dietary supplements to improve animal production; as soil amendments to improve cation-exchange capacities (CEC) and water sorption capacities; as soilless zeoponic substrate for greenhouses and space missions; in the deodorization of animal litter, barns, ash trays, refrigerators, and athletic footwear; in the removal of ammoniacal nitrogen from saline hemodialysis solutions; and as bactericides, insecticides, and antacids for people and animals. This multitude of uses of natural zeolites has prompted newspapers in Cuba, where large deposits have been discovered, to refer to zeolites as the magic rock, hence the title of this paper.

The present paper reviews the critical properties of natural zeolites and important uses in pollution control, the handling and storage of nuclear wastes, agriculture, and biotechnology. The paper also pleads for greater involvement by mineral scientists in the surface, colloidal, and biochemical investigations that are needed in the future development of zeolite applications.

PROPERTIES

A zeolite is a crystalline, hydrated aluminosilicate of alkali and alkaline earth cations having an infinite, open, three-dimensional structure. It is further able to lose and gain water reversibly and to exchange extraframework cations, both without change of crystal structure. The large structural cavities and the entry channels leading into them contain water molecules, which form hydration spheres around exchangeable cations. On removal of water by heating at 350–400°C, small molecules can pass through entry channels, but larger molecules are excluded—the so called "molecular sieve" property of crystalline zeolites. The uniform size and shape of the rings of oxygen in zeolites contrasts with the relatively wide range of pore sizes in silica gel, activated alumina, and activated carbon, and the Langmuir shape of their adsorption isotherms allows zeolites to remove the last trace of a particular gas from a system (e.g., H_2O from refrigerator Freon lines). Furthermore, zeolites adsorb polar molecules with high selectivity. Thus, polar CO_2 is adsorbed preferentially by certain zeolites, allowing impure methane or natural gas streams to be upgraded. The quadrupole moment of N_2 contributes to its selective adsorption by zeolites from air, thereby producing O_2-enriched products. The adsorption selectivity for H_2O, however, is greater than for any other molecule, leading to uses in drying and solar heating and cooling.

The weakly bonded extraframework cations can be removed or exchanged readily by washing with a strong solution of another cation. The CEC of a zeolite is basically a function of the amount of Al that substitutes for Si in the framework tetrahedra; the greater the Al content, the more extraframework cations needed to balance the charge. Natural zeolites have CECs from 2 to 4 milliequivalents/g (meq/g), about twice the CEC of bentonite clay. Unlike most noncrystalline ion

FIG. 1.   Scanning electron micrograph of plates of clinoptilolite from Castle Creek, ID [Reproduced with permission from ref. 3 (Copyright 1976, The Clay Minerals Society)].

exchangers, e.g., organic resins and inorganic aluminosilicate gels (mislabeled in the trade as "zeolites"), the framework of a crystalline zeolite dictates its selectivity toward competing ions. The hydration spheres of high field-strength cations prevent their close approach to the seat of charge in the framework; hence, cations of low field strength are generally more tightly held and selectively exchanged by the zeolite than other ions. Clinoptilolite has a relatively small CEC ($\approx$2.25 meq/g), but its cation selectivity is

$$Cs > Rb > K > NH_4 > Ba > Sr > Na > Ca > Fe > Al > Mg > Li.$$

This preference for larger cations, including NH_4^+, was exploited for removing NH_4-N from municipal sewage effluent and has been extended to agricultural and aquacultural applications (1, 2). Clinoptilolite and natural chabazite have also been used to extract Cs and Sr from nuclear wastes and fallout.

Most zeolites in volcanogenic sedimentary rocks were formed by the dissolution of volcanic glass (ash) and later precipitation of micrometer-size crystals, which mimic the shape and morphology of their basalt counterparts (Fig. 1; ref. 3). Sedimentary zeolitic tuffs are generally soft, friable, and lightweight and commonly contain 50–95% of a single zeolite;

however, several zeolites may coexist, along with unreacted volcanic glass, quartz, K-feldspar, montmorillonite, calcite, gypsum, and cristobalite/tridymite. Applications of natural zeolites make use of one or more of the following properties: (*i*) cation exchange, (*ii*) adsorption and related molecular-sieving, (*iii*) catalytic, (*iv*) dehydration and rehydration, and (*v*) biological reactivity. Extrinsic properties of the rock (e.g., siliceous composition, color, porosity, attrition resistance, and bulk density) are also important in many applications. Thus, the ideal zeolitic tuff for both cation-exchange and adsorption applications should be mechanically strong to resist abrasion and disintegration, highly porous to allow solutions and gases to diffuse readily in and out of the rock, and soft enough to be easily crushed. Obviously, the greater the content of a desired zeolite, the better a certain tuff will perform, *ceteris paribus*. (See Table 1 for more information on the properties of zeolites.)

APPLICATIONS

Construction

Dimension Stone. Devitrified volcanic ash and altered tuff have been used for 2,000 years as lightweight dimension stone. Only since the 1950s, however, has their zeolitic nature been recognized. Their low bulk density, high porosity, and homogeneous, close-knit texture have contributed to their being easily sawed or cut into inexpensive building blocks. For example, many Zapotec buildings near Oaxaca, Mexico, were constructed of blocks of massive, clinoptilolite tuff (4), which is still used for public buildings in the region. The easily cut and fabricated chabazite- and phillipsite-rich *tuffo giallo napolitano* in central Italy has also been used since Roman times in construction, and the entire city of Naples seems to be built out of it (Fig. 2). Numerous cathedrals and public buildings in central Europe were built from zeolitic tuff quarried in the Laacher See area of Germany. Early ranch houses (Fig. 3) in the American West were built with blocks of locally quarried erionite; they were cool and did not crumble in the arid climate. Similar structures made of zeolitic tuff blocks have been noted near almost every zeolitic tuff deposit in Europe and Japan (5).

Cement and Concrete. The most important pozzolanic raw material used by the ancient Romans was obtained from the *tuffo napolitano giallo* near Pozzuoli, Italy (6, 7). Similar

Table 1.   Representative formulae and selected physical properties of important zeolites*

Zeolite	Representative unit-cell formula	Void volume, %	Channel dimensions, Å	Thermal stability (relative)	CEC, meq/g[†]
Analcime	$Na_{10}(Al_{16}Si_{32}O_{96})\cdot16H_2O$	18	2.6	High	4.54
Chabazite	$(Na_2Ca)_6(Al_{12}Si_{24}O_{72})\cdot40H_2O$	47	3.7×4.2	High	3.84
Clinoptilolite	$(Na_3K_3)(Al_6Si_{30}O_{72})\cdot24H_2O$	34	3.9×5.4	High	2.16
Erionite	$(NaCa_{0.5}K)_9(Al_9Si_{27}O_{72})\cdot27H_2O$	35	3.6×5.2	High	3.12
Faujasite	$(Na_{58})(Al_{58}Si_{134}O_{384})\cdot240H_2O$	47	7.4	High	3.39
Ferrierite	$(Na_2Mg_2)(Al_6Si_{30}O_{72})\cdot18H_2O$	28	4.3×5.5	High	2.33
Heulandite	$(Ca_4)(Al_8Si_{28}O_{72})\cdot24H_2O$	39	4.0×5.5 4.4×7.2 4.1×4.7	Low	2.91
Laumonitte	$(Ca_4)(Al_8Si_{16}O_{48})\cdot16H_2O$	34	4.6×6.3	Low	4.25
Mordenite	$(Na_8)(Al_8Si_{40}O_{96})\cdot24H_2O$	28	2.9×5.7 6.7×7.0	High	2.29
Phillipsite	$(NaK)_5(Al_5Si_{11}O_{32})\cdot20H_2O$	31	4.2×4.4 2.8×4.8 3.3	Medium	3.31
Linde A	$(Na_{12})(Al_{12}Si_{12}O_{48})\cdot27H_2O$	47	4.2	High	5.48
Linde X	$(Na_{86})(Al_{86}Si_{106}O_{384})\cdot264H_2O$	50	7.4	High	4.73

*Modified from refs. 103 and 104. Void volume determined from water content.
[†]Calculated from unit-cell formula.

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FIG. 2. Castel Nuovo (Naples, Italy) constructed of *tuffo giallo napolitano* [Reproduced with permission from ref. 105 (Copyright 1995, International Committee on Natural Zeolites)].

FIG. 4. Clinoptilolite-filled columns at a Denver, CO, water-purification plant [Reproduced with permission from ref. 106 (Copyright 1997, AIMAT)].

materials have been used in cement production throughout Europe. The high silica content of the zeolites neutralizes excess lime produced by setting concrete, much like finely powdered pumice or fly ash. In the U.S., nearly $1 million was saved in 1912 during the construction of the 240-mile-long Los Angeles aqueduct by replacing ≤25% of the required portland cement with an inexpensive clinoptilolite-rich tuff mined near Tehachapi, CA (8, 9).

Lightweight Aggregate. Much like perlite and other volcanic glasses are frothed into low-density pellets for use as lightweight aggregate in concrete, zeolitic tuff can be "popped" by calcining at elevated temperature. Clinoptilolite from Slovenia and Serbia yields excellent aggregates of this type on firing to 1,200–1,400°C. Densities of ≥0.8 g/cm³ and porosities of ≤65% have been reported for expanded clinoptilolite products (10). These temperatures are somewhat higher than those needed to expand perlite, but the products are stronger (11). The Russian Sibeerfoam product is expanded zeolitic tuff and is used as lightweight insulating material (12). In Cuba, mortars for ferrocement boats and lightweight aggregate for hollow prestressed concrete slabs contain indigenous clinoptilolite (13, 14). The mortars have compressive strengths of ≤55.0 MPa; the ferrocement boats can withstand marine environments.

Water and Wastewater Treatment

Municipal Wastewater. Large-scale cation-exchange processes using natural zeolites were first developed by Ames (1) and Mercer *et al.* (2), who demonstrated the effectiveness of

clinoptilolite for extracting NH_4^+ from municipal and agricultural waste streams. The clinoptilolite exchange process at the Tahoe–Truckee (Truckee, CA) sewage treatment plant removes >97% of the NH_4^+ from tertiary effluent (15). Hundreds of papers have dealt with wastewater treatment by natural zeolites. Adding powdered clinoptilolite to sewage before aeration increased O_2-consumption and sedimentation, resulting in a sludge that can be more easily dewatered and, hence, used as a fertilizer (16). Nitrification of sludge is accelerated by the use of clinoptilolite, which selectively exchanges NH_4^+ from wastewater and provides an ideal growth medium for nitrifying bacteria, which then oxidize NH_4^+ to nitrate (17–19). Liberti *et al.* (19) described a nutrient-removal process called RIM-NUT that uses the selective exchange by clinoptilolite and an organic resin to remove N_2 and P from sewage effluent.

Drinking Water. In the late 1970s, a 1-MGD (million gallons per day) water-reuse process that used clinoptilolite cation-exchange columns went on stream in Denver, CO, (Fig. 4) and brought the NH_4^+ content of sewage effluent down to potable standards (<1 ppm; refs. 20–22). Based on Sims and coworkers' (23, 24) earlier finding that nitrification of sewage sludge was enhanced by the presence of clinoptilolite, a clinoptilolite-amended slow-sand filtration process for drinking water for the city of Logan, UT, was evaluated. By adding a layer of crushed zeolite, the filtration rate tripled, with no deleterious effects. At Buki Island, upstream from Budapest, clinoptilolite filtration reduced the NH_3 content of drinking water from 15–22 ppm to <2 ppm (25, 26). Clinoptilolite beds are used regularly to upgrade river water to potable standards at Ryazan and other localities in Russia and at Uzhgorod, Ukraine (27, 28).

FIG. 3. Abandoned ranch house in Jersey Valley, NV, constructed of quarried blocks of erionite-rich tuff [Reproduced with permission from ref. 5 (Copyright 1973, Industrial Minerals)].

FIG. 5. Methane-purification pressure-swing adsorption unit, NRG Company, Palos Verde Landfill, Los Angeles, CA [Reproduced with permission from ref. 106 (Copyright 1997, AIMAT)].

The selectivity of several natural zeolites for Pb^{2+} suggests an inexpensive means of removing lead from drinking water.

Adsorption and Catalysis

Two principal uses of synthetic molecular sieves are the purification of gaseous hydrocarbons and the preparation of catalysts for petroleum refining. In general, natural zeolites do not compete with their synthetic counterparts in adsorption or catalytic applications because of their inherent lower adsorption capacities and, to some extent, to the presence of traces of Fe and other catalyst "poisons." Most natural materials have smaller pore openings than the synthetics. Despite the low cost of the natural materials (a few cents per kilogram), the economics of hardware construction, activation, and regeneration favor the more expensive synthetics, even at $2.00/kg, for most adsorption applications.

By using certain natural zeolites, however, researchers have made headway in the drying and purification of acid gases. Mordenite and chabazite, for example, can withstand the rigors of continuous cycling in acid environments and have been used to remove water and carbon dioxide from sour natural gas. Union Carbide Corporation (now UOP Corporation, Tarrytown, NY) marketed an AW-500 product (natural chabazite-rich tuff from Bowie, AZ) for removing HCl from reformed H_2 streams (pH < 2), H_2O from Cl_2, and CO_2 from stack gas emissions (29). NRG Corporation (Los Angeles, CA; ref. 30) used a pressure-swing adsorption process with Bowie chabazite to remove polar H_2O, H_2S, and CO_2 from low-BTU (British thermal unit) natural gas and developed a zeolite-adsorption process for purifying methane produced by decaying garbage in a Los Angeles landfill (Fig. 5). A pressure-swing adsorption process using natural mordenite was developed in Japan to produce high-grade O_2 from air (T. Tamura, unpublished work; refs. 31 and 32). Dominé and Häy (33) showed that the quadrupole moment of nitrogen is apparently responsible for its adsorption by a dehydrated zeolite in preference to oxygen, resulting in a distinct separation of the two gases for a finite length of time. Similar processes use synthetic CaA zeolite to produce O_2 in sewage-treatment plants in several countries. In Japan, small zeolite adsorption units generate O_2-enriched air for hospitals, in fish breeding and transportation, and in poorly ventilated restaurants.

Modifying the surface of clinoptilolite with long-chain quaternary amines allowed it to adsorb benzene, toluene, and xylene in the presence of water, a process that shows promise in the clean up of gasoline and other petroleum spills (34–36). These hydrophilic products can be treated further with additional amine to produce anion exchangers capable of taking up chromate, arsenate, selenate, and other metal oxyanions from aqueous solutions.

Applications in catalysis include (*i*) a selective-forming catalyst developed by Mobil Corporation using natural erionite-clinoptilolite (37); (*ii*) a hydrocarbon conversion catalyst for the disproportionation of toluene to benzene and xylene, employing a hydrogen-exchanged natural mordenite (38); (*iii*) a catalyst using cation-exchanged clinoptilolite from Tokaj, Hungary, for the hydromethylation of toluene (39); and (*iv*) clinoptilolite catalysts for the isomerization of *n*-butene, the dehydration of methanol to dimethyl ether, and the hydration of acetylene to acetaldehyde (40).

Nuclear Waste and Fallout

Nuclear Waste. Early experiments were aimed at concentrating ^{137}Cs and ^{90}Sr from low-level waste streams of nuclear reactors and leaking repositories on clinoptilolite (41–43). The "saturated" zeolite was transformed into concrete, glass, or ceramic bodies and stored indefinitely. Natural zeolites have superior selectivity for certain radionuclides (e.g., ^{90}Sr, ^{137}Cs

^{60}Co, ^{45}Ca, and ^{51}Cr) compared with organoresins and are cheaper and much more resistant to nuclear degradation. Dozens of papers have demonstrated the ability of several natural zeolites to take up these and other radionuclides (44–47). A mixture of synthetic zeolite A and natural chabazite from Bowie, AZ, was used to take up Sr and Cs, respectively, from contaminated waters at Three Mile Island, PA (48). Clinoptilolite currently is used to remove Sr and Cs from low-level effluents from a nuclear power plant before they are released to the Irish Sea at Sellafield, U.K. (49), and to capture these isotopes from leaking repository containers at West Valley, NY (50).

Nuclear Fallout. The same selectivities for Cs and Sr by zeolites permit treatment of radioactive fallout from nuclear tests and accidents. The addition of clinoptilolite to soils contaminated with ^{90}Sr markedly reduced the strontium uptake by plants (51), and the presence of clinoptilolite inhibited the uptake of Cs in contaminated Bikini Atoll soils (52). Several zeolite processes have been developed to counteract the fallout from the 1986 Chernobyl disaster. Shenbar and Johanson (53) found that ^{137}Cs in soils was not taken up by plants after treating the soil with a zeolite, and Forberg *et al.* (54) showed that a zeolite supplement to the diets of Swedish reindeer accelerated the excretion of ^{137}Cs ingested with food contaminated by Chernobyl fallout. Zeolites added to soils reduced the uptake of ^{137}Cs by pasture plants in the vicinity of Chernobyl (55), and dietary zeolite reduced sorption of radiocesium by sheep fed fallout-contaminated rations in Scotland (56). In Bulgaria, zeolite pills and cookies were prepared for human consumption to counteract Chernobyl fallout (57). The zeolite apparently exchanges ^{137}Cs and ^{90}Sr in the gastrointestinal tract and is excreted by normal processes, thereby minimizing assimilation into the body.

Agriculture

Animal Nutrition and Health. Since 1965, studies in Japan using ≤10% clinoptilolite and mordenite as dietary supplements for swine and poultry showed that test animals generally grew faster than control groups, with simultaneous decrease in the amount and cost of the feed. Young and mature pigs fed rations containing 5% clinoptilolite gained 16% more weight than animals fed a normal diet (58, 59). The animals' excrement was less odoriferous because of the take up of NH_4^+ by the zeolite, and the number and severity of intestinal diseases decreased. To reduce the toxic effect of high NH_4^+ in ruminal fluids when nonprotein-nitrogens, such as urea and biuret, are added to animal diets, White and Ohlrogge (60) introduced both synthetic and natural zeolites into the rumen of test animals. NH_4^+ formed by the enzyme decomposition of the nonprotein-nitrogen was exchanged immediately by the zeolite and held for several hours until released by Na^+ entering the rumen in saliva. This gradual release of the excess nitrogen allowed rumen organisms to synthesize cellular protein for assimilation into the animals' digestive systems. Several hundred studies of the effect of zeolites in animal diets have been made in the U.S. and elsewhere (61). The results are mixed, but in countries in which the level of animal productivity is not as high as in the U.S. and the sanitary conditions of feed lots and production facilities are much worse, substantial increases in productivity and mortality have been achieved (62). Weight gain may be caused by the zeolite acting as an ammonium reservoir in the gastrointestinal tract, thereby allowing the animal to use ingested nitrogen more efficiently. The prevention or minimization of scours and other intestinal diseases, however, is more baffling. An NH_4^+-containing zeolite may support the growth of nitrogen-loving bacteria that contribute to the health of the animals; the zeolite may take up deleterious heavy metals, or it may simply regulate pH in the gut system, resulting in fewer or less severe stomach ailments.

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FIG. 6.   Tomatoes grown zeoponically in Havana, Cuba [Reproduced with permission from ref. 106 (Copyright 1997, AIMAT)].

These reactions await serious physiological and biochemical examination.

Natural zeolites and some clay minerals have proven to be effective in protecting animals against mycotoxins (63, 64). The apparent ability of clinoptilolite and other zeolites to absorb aflatoxins that contaminate animal feeds has resulted in measurable improvements in the health of swine, sheep, and chickens (65–67). Here also, more work is needed to verify and understand the mechanisms of such reactions.

Agronomy and Horticulture. Natural zeolites are used extensively in Japan as amendments for sandy, clay-poor soils (68). The pronounced selectivity of clinoptilolite NH_4^+ and K^+ also was exploited in Japan in slow-release chemical fertilizers. By using clinoptilolite-rich tuff as a soil conditioner, significant increases in the yields of wheat (13–15%), eggplant (19–55%), apples (13–38%), and carrots (63%) were reported when 4–8 tonne/acre zeolite was used (69). The addition of clinoptilolite increased barley yields (70); it also increased the yields of potatoes, barley, clover, and wheat after adding 15 tonne/hectare to Ukrainian sandy loams (71). Clinoptilolite amended to a potting medium for chrysanthemums behaved like a slow-release K-fertilizer, yielding the same growth for the plants as daily irrigation with Hoagland's solution (72). The addition of NH_4^+-exchanged clinoptilolite in greenhouse experiments resulted in 59% and 53% increase in root weight of radishes in medium- and light-clay soils, respectively (73). A 10% addition of clinoptilolite to sand used in the construction of golf-course greens substantially reduced NO_3-leaching and increased fertilizer-N uptake by creeping bent-grass, without disturbing the drainage, compaction, or "playability" of the greens (74–76).

In Italy, natural zeolites have been used as dusting agents to kill aphids afflicting fruit trees (J. L. Gonzalez, personal communication). The mechanism of this reaction is not known; the zeolite could be acting as a desiccant, although it is saturated almost completely with water before use, or its highly alkaline character in water could simply kill individual insects that come in contact with it.

The use of clinoptilolite as the principal constituent of artificial soil was developed in Bulgaria in the late 1970s. The growth of plants in synthetic soils consisting of zeolites with or without peat, vermiculite, and the like has been termed zeoponics. A nutrient-treated zeoponic substrate used for growing crops and the rooting of cuttings in greenhouses produced greater development of root systems and larger yields of strawberries, tomatoes, and peppers, without further fertilization (77). Tomatoes and cucumbers are grown commercially outdoors in Cuba (Fig. 6) by using zeoponic substrate (78), and vegetables currently are supplied to Moscow in the winter from greenhouses that use zeoponic synthetic soils. By using a treated Bulgarian clinoptilolite product, cabbage and radishes have been grown aboard the Russian space station Mir (79). Considerable attention has been paid to zeoponic mixtures of NH_4- or K-exchanged natural zeolites and spar-
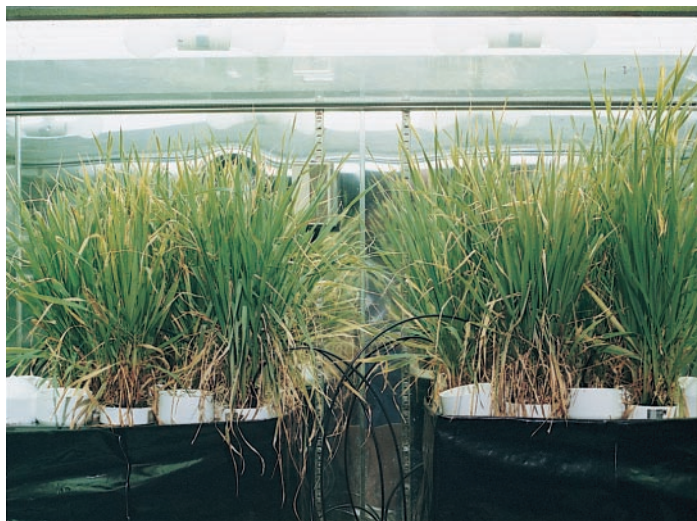

FIG. 7.   Wheat grown zeoponically for use in space flights and stations, Johnson Space Center, Houston, TX [Reproduced with permission from ref. 106 (Copyright 1997, AIMAT)]. Photograph by D. W. Ming.

FIG. 8.   Zeolite deodorization products from Itaya, Japan [Reproduced with permission from ref. 106 (Copyright 1997, AIMAT)].

ingly soluble phosphate minerals (e.g., apatite; refs. 80 and 81). The small amount of Ca in the soil solution in equilibrium with the apatite exchanges onto the zeolite, thereby disturbing the equilibrium and forcing more Ca into solution. The apatite is ultimately destroyed, releasing P to the solution, and the zeolite gives up its exchanged cations (e.g., K^+ or NH_4^+). Taking the zeolite–apatite reaction one step further, the National Aeronautics and Space Administration prepared a substrate consisting of a specially cation-exchanged clinoptilolite and a synthetic apatite containing essential trace nutrients for use as a plant-growth medium in Shuttle flights (Fig. 7). This formulation may well be the preferred substrate for vegetable production aboard all future space missions (82) and in commercial green houses.

Aquaculture. Natural zeolites can play three roles in aquaculture: (*i*) to remove ammonium from hatchery, transport, and aquarium waters; (*ii*) to generate oxygen for aeration systems in aquaria and transport; and (*iii*) to supplement fish rations. Zeolite cation exchange removes NH_4^+ from recirculating hatchery waters produced by the decomposition of excrement and/or unused food, much as NH_4^+ is removed from municipal sewage effluent (83–85). Phillipsite from the Neapolitan Yellow Tuff was used to remove NH_4^+ from the effluent from saline water in shrimp-culture tanks (86). Although zeolites are not as successful with saline-water as they are with freshwater effluents, these results suggest limited applications in seawater systems. The NH_3 content of tank-truck waters was reduced by such a system during the transport of live fish (87–89), and Jungle Laboratories (Comfort, TX) developed a technique of adding natural zeolites to plastic bags containing tropical fish to take up NH_3 generated during transport. In the U.S., at least four brands of granular clinoptilolite are currently on the market for use in filters in home aquaria, and fist-size blocks of zeolitic tuff have been sold as decorative (and ammonium-removing) additions to hobbyists' fish tanks.

The physiological similarity of fish and poultry suggests that the results achieved by feeding natural zeolites to chickens might be duplicated in fish at a considerable savings in cost. Several authors have reported that small additions of clinoptilolite (2%) in the rations of trout resulted in ≤10% improvement in biomass production, with no apparent ill effects on the fish (90–92).

Animal-Waste Treatment. Natural zeolites are potentially capable of (*i*) reducing the malodor and increasing the nitrogen retentivity of animal wastes, (*ii*) controlling the moisture content for ease of handling of excrement, and (*iii*) purifying the methane gas produced by the anaerobic digestion of manure. Several hundred tonnes of clinoptilolite is used each year in Japanese chicken houses; it is either mixed with the droppings or packed in boxes suspended from the ceilings (K. Torii, unpublished work). A zeolite-filled air scrubber was used to improve poultry-house environments by extracting NH_3 from the air without the loss of heat that accompanies ventilation in colder weather (93). Granular clinoptilolite added to a cattle feedlot (2.44 kg/m^2) significantly reduced NH_3 evolution and odor compared with untreated areas (94). As more and more animals and poultry are raised close to the markets to reduce transportation costs, the need to decrease

FIG. 9.   Footwear and garbage-can zeolite deodorization products [Reproduced with permission from ref. 106 (Copyright 1997, AIMAT)].

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air pollution in areas of large population becomes ever more apparent.

Other Applications

Consumer Products. Numerous natural zeolite-containing consumer products have come on the market in the U.S., Japan, Hungary, Cuba, and Germany, chiefly as deodorizing agents and as pet litters to take up water and odor-causing NH_3 from animal urine (Fig. 8). A horse-stall refreshener consisting solely of crushed clinoptilolite also has been sold in the U.S., and similar materials have been used for years at major livestock shows to decrease odors in barns and stalls. These applications depend mainly on the ability of clinoptilolite to exchange NH_4^+ from aqueous solution, thereby preventing the release of NH_3 into the atmosphere. Other natural zeolite deodorization products have been marketed to remove malodors from shoes, boots, and athletic footwear (e.g., Stinky Pinkys and Odor Zappers) and from garbage cans, refrigerators, and walk-in coolers (ref. 95 and 96; Fig. 9). The mechanism by which these products have achieved success is not well understood, but it is probably a surface-adsorption phenomena on the zeolite. In Russia, an unusual product (Zeo-Light) has been developed, consisting of zeolite-filled pillows and pads for funeral caskets to eliminate malodors.

Medical Applications. Natural phillipsite and certain synthetic zeolites were found to be effective filter media to remove NH_4^+ from the dialysate of kidney patients during hemodialysis, thereby allowing the cleansed saline solution to be used repeatedly in recirculating home and portable dialysis systems (97, 98). Zeolites, especially the natural varieties, are substantially less expensive than the zirconium phosphate ion exchanger currently used. In Cuba, inexpensive, indigenous natural zeolites are being studied as buffers to reduce stomach acidity and to treat stomach ulcers (99). External application of zeolite powder has been found to be effective in the treatment of athlete's foot (100) and to decrease the healing time of wounds and surgical incisions (101, 102). Although no systematic study has been made, anecdotal information from three mining operations in the United States indicates that the cuts and scrapes of mine and mill workers exposed to on-the-job zeolite dust heal remarkably quickly. In Cuba, it is common practice to dust the cuts of horses and cows with clinoptilolite to hasten the healing process. The bactericidal reactivity of natural zeolites is an untouched field.

ROLE OF MINERAL SCIENTISTS

Mineral scientists have played leading roles in the development of applications for natural zeolites, e.g., Ames (41) studied the cation-exchange properties of clinoptilolite and its use in treating municipal sewage and nuclear waste waters; Stojanovic (10) and Bush (11) studied the expansion properties of clinoptilolite; Filizova (57) developed zeolite pills and cookies to counteract Chernobyl fallout; White and Ohlrogge (60) developed rations for ruminants fed nonprotein-nitrogen-supplemented feeds; and U.S. Geological Survey (80) and National Aeronautics and Space Administration (82) mineral scientists used zeoponic substrate in space vehicles and greenhouse soils.

Although they brought to the table a broad base of scientific knowledge, most were less than expert in agriculture or animal science or in surface chemistry, colloid chemistry, or biochemistry, and they often had to prod or persuade agricultural, chemical, biological, and engineering colleagues to apply their expertise to these fascinating problems. In the future, mineral scientists investigating the use of natural zeolites (or of any of the industrial minerals mentioned above) must become more proficient in surface chemistry, cation exchange, biological reactivity, and colloid chemistry if they are to continue to contribute to the development of zeolite applications. In turn, the chemist, agronomist, animal scientist, biochemist, and engineer must become more knowledgeable about the mineral sciences. Multidisciplinary, cooperative efforts are essential if we are to understand, for example, how a zeolite functions in an animal's gastrointestinal system, how a zeolite gives rise to greater growth or healthier animals, the specific mechanism of surface adsorption of amine-treated zeolites with other organics in aqueous solution, or how untreated zeolites adsorb offending odors from footwear and other enclosed spaces. The adsorption, cation-exchange, dehydration, catalytic, and biotechnical properties of zeolitic materials must therefore become a major part of a mineral scientist's portfolio if he or she is to become a full partner in future investigations.

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