

ZEOLITES

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Zeolites are hydrated aluminosilicates of the alkaline and alkaline-earth metals. About 40 natural zeolites have been identified during the past 200 years, the most common of which are analcime, chabazite, clinoptilolite, erionite, ferrierite, heulandite, laumontite, mordenite, and phillipsite. More than 150 zeolites have been synthesized. Some of the more common synthetic zeolites are zeolites A, X, and Y and ZMS-5. Natural and synthetic zeolites are used commercially because of their unique adsorption, ion-exchange, molecular sieve, and catalytic properties.

Natural Zeolites

Commercial zeolite deposits in the United States are associated with the alteration of volcanic tuffs in saline, alkaline lake deposits, and open hydrologic systems. The deposits are in Arizona, California, Idaho, Nevada, New Mexico, Oregon, Texas, Utah, and Wyoming. The major components of these deposits are chabazite, clinoptilolite, mordenite, and phillipsite. Erionite, orthoclase and plagioclase feldspars, montmorillonite, opal, quartz, and volcanic glass are present in some deposits.

Production.—Conventional mining techniques are used to mine natural zeolites. The overburden is removed to allow access to the ore. The ore may be blasted or stripped for processing by using front-end loaders or tractors equipped with ripper blades. The ore is crushed, dried, and milled. The milled ore is packaged directly for shipping or may be screened to remove fine material when a granular product is required. In some cases, a pelletized product also is produced.

Eight companies mined natural zeolites in the United States in 1997. (See table 1.) In addition to the eight producing companies, Steelhead Mineral Resources Inc. also was a domestic supplier of clinoptilolite in 1997. Clinoptilolite was mined and/or processed in Nevada, New Mexico, Oregon, Texas, and Wyoming; chabazite was mined in Arizona. Total domestic production of zeolites was 30,100 metric tons.

American Absorbents Natural Products, Inc. obtained permanent mining permits for its clinoptilolite holdings in Harney County, OR and began full-scale production. The ore is processed at its mill in Hines, OR. The company sells its clinoptilolite for aquaculture, fertilizer mixtures, gas adsorption, odor control, landfill use, soil amendments, wastewater treatment, and water purification (American Absorbents Natural Products, Inc., AANPI general information, history, and chronology, accessed May 4, 1998, at URL <http://www.aanpi.com/brochpg3.htm>). Another company, Addwest Minerals International Ltd., entered the zeolite industry with its purchase of U.S. Zeolites, whose mine is located in Sweetwater County, WY.

Consumption.—Approximately 30,100 tons of natural zeolites was sold in 1997, a 6% increase from that of 1996. Natural zeolites were sold for, in decreasing order of consumption, pet litter, horticultural applications (soil conditioners and growth media),

animal feed, odor control, wastewater cleanup, desiccant, water purification, gas absorbents, catalysts, and aquaculture. Pet litter, horticultural, and animal feed applications dominated the zeolite business. These three applications accounted for over 70% of the domestic sales. The largest increases in sales were for horticultural applications and wastewater cleanup. Sales for desiccant and gas absorption increased slightly. Slight decreases in sales were observed for the remaining end-use markets.

Prices.—Prices for natural zeolites vary with zeolite content and processing. For industrial or agricultural applications, prices ranged from \$30 to \$70 per ton for granular products down to 40 mesh and from \$50 to \$120 per ton for -40 mesh to -325 mesh ground material. For consumer products, such as for pet litter, fish-tank media or deodorant applications, prices ranged from \$0.50 to \$4.50 per kilogram (Holmes, 1994). Quoted prices should be used only as a guideline because actual prices depend on the terms of the contract between seller and buyer.

Foreign Trade.—Less than 100 tons of natural zeolite was imported and between 350 tons and 450 tons was exported in 1997, according to the Journal of Commerce (JOC) Port Import/Export Reporting Service. Most of the zeolites imported into the United States in 1997 were either synthetic or mineral specimens, not bulk natural zeolites. The JOC data does not include zeolites imported from or exported to or through Canada and Mexico.

World Review.—Worldwide production of natural zeolites was estimated to be more than 3 million tons. Estimates, in tons, for individual countries were Bulgaria, 2,000; Canada, 4,000; China, 2.5 million; Cuba, 500,000 to 600,000; Hungary, 10,000 to 20,000; Italy, 4,000; Japan, 140,000 to 160,000; Slovakia, 12,000; South Africa 1,000 to 2,000; the United States, 30,100; and the former U.S.S.R., 10,000. Small amounts of natural zeolites also were produced in Argentina, Australia, Germany, and Indonesia.

Current Research and Technology.—The U.S. Geological Survey tested three clinoptilolite-rich rocks (CRR) for their ability to exchange copper, lead, and zinc in the presence of low concentrations of calcium and potassium, which compete with metal ions in the zeolite exchange process. The purpose of the study was to evaluate the potential use of CRR's for removing metal ions from adit and tunnel drainage waters at two sites in Colorado. The zeolites used in the study were calcium-rich, sodium-rich, and potassium-rich clinoptilolite samples from deposits in Texas, Wyoming, and Idaho, respectively. Samples were repeatedly exposed to acidified (pH of 2.1) solutions which contained 1.2 milligrams per liter copper, 1.3 milligrams per liter lead, 15 milligrams per liter zinc, and 2 milligrams per liter calcium. The sodium-rich CRR removed approximately 65% of the zinc, 55% of the copper, and 95% of the lead from solution and was more effective at removing copper and zinc from solution than the calcium- and potassium-rich CRR. All three zeolites were effective in removing lead. A second experiment was conducted using a solution with a pH of 2.6 and containing 100 milligrams per liter copper, 0.31 milligram per liter lead, 19

milligrams per liter zinc, 3.1 milligrams per liter calcium, 3.3 milligrams per liter potassium, and 15 milligrams per liter sodium. Again, the sodium-rich CRR from Wyoming removed more copper and zinc from solution than the calcium- and potassium-rich CRR (Desborough, 1997).

Chabazite was used in trial studies to test its potential for removing thallium from mine and process water discharges. Laboratory bench tests showed that the zeolite could reduce thallium levels from 0.9 part per million to less than 0.002 part per million at flow rates of 15 to 25 gallons per minute of effluent. Following the bench scale testing, a pilot plant was designed for a western mining operation. Using a three-column exchange system, thallium exchange was tested at flow rates of 5 to 25 gallons per minute. Thallium levels were reduced from 0.05 part per million to less than 0.002 part per million. The study also determined that thallium concentrations in the effluent could meet regulatory discharge standards despite calcium concentrations of 700 to 900 parts per million and sodium concentrations of 400 to 700 parts per million. The high calcium and sodium levels, however, affected the zeolite bed efficiency and life (Eyde, Johnson, and Hanley, 1998).

Synthetic Zeolites

Adsorbents.—TNO Institute of Environmental Services developed a method to dry and roast coffee, cocoa, and other beans in a single process. The beans are mixed with zeolite A that has been preheated to 100° C. The zeolite absorbs the moisture from the beans and releases its heat of adsorption, thereby increasing the temperature of the system. The zeolite and beans are separated by sieving and the zeolite is regenerated by heating between 300° C and 400° C. While capital cost is higher, operational costs and product quality are lower than using conventional methods (Chemical Engineering, 1997).

PQ Corp. announced plans to expand its zeolite plant in Kansas City, KS, to produce molecular sieves for the adsorbent and desiccant applications. The plant will have a capacity of approximately 18,000 tons per year (North American Minerals News, 1997). UOP Inc. began construction of a new production line for molecular sieve adsorbents at its Mobile, AL, plant.

The company also will add a production line for adsorbents to its plant in Italy. Both additions will have production capacities of 6,000 tons per year. UOP also expanded its adsorbent facility in China, doubling its capacity to 5,480 tons per year (European Chemical News, 1997b).

Catalysts.—Metal-enriched zeolites are known to effectively catalyze nitrous oxide in automobile exhaust. Most of these catalysts, however, break down in the presence of water, which can compose 5% to 10% of the exhaust gas. A reproducible method for producing iron-rich ZSM-5 zeolites that do not break down in the presence of water was developed. The iron-loading process involved exposing the acidic form of ZSM-5 to iron trichloride vapor. Iron dichloride formed in the zeolite cavities and hydrogen chloride gas was evolved. The remaining chlorine was removed by washing. The catalyst was effective at water vapor concentrations of 20% and exhibited maximum activity at 350° C (Chemical & Engineering News, 1997a).

Süd-Chemie began production of catalysts at its plant in Richards Bay, South Africa. The company will market the catalyst to the petrochemical and refining industry (Chemical Week, 1997c).

Detergents.—In 1996, approximately 343,000 tons of zeolite were used by U.S. detergent manufacturers, compared with 317,000 tons in 1995. Much of this increase was absorbed by existing product lines rather than new markets. European markets for zeolite builders, which remove calcium ions from the water, were estimated to be between 490,000 tons and 520,000 tons, with the market share of phosphate and zeolites in European detergents to be 25% and 75%, respectively.

U.S. capacity usage was estimated to be 80%. This is particularly encouraging because domestic manufacturers have been plagued with overcapacity problems for the past few years. This compares with a capacity usage in Europe and Asia of 50% to 60%. In general, worldwide growth of the detergent builder market was estimated to be 4% per year (Chemical Week, 1997a; European Chemical News, 1997a).

The debate continues, however, on the merits of using zeolite builders versus phosphates. Because phosphates are plant nutrients, they have received the blame for the eutrophication of lakes and streams. As a result, many States and municipalities have restricted the use of phosphates in detergents. Many other countries also have restrictions in place or are considering them. Phosphate builders, which remove calcium and magnesium ions from the water, continue to be used worldwide and sales are increasing in Latin America and Southeast Asia. Despite this, several zeolite producers view the Asian and Pacific regions as growth areas. Penetration into the Latin American market, however, was viewed as more difficult because of cost considerations (Kirschner, 1997).

Mizusawa Industrial Chemicals will decrease production of detergent-grade zeolite because of low profit margins. The plant capacity was reduced to 23,000 tons per year in 1997 and will be reduced to 12,000 tons per year in 1998 (Chemical Week, 1997b).

Current Research and Technology.—Researchers have developed a method for growing a thin continuous film of zeolite ZSM-5 on a gold substrate. A mercaptopropyltrimethoxysilane layer was first deposited on the gold substrate. The silane layer was then hydrolyzed under acidic conditions and its surface charge was reversed using a cationic polymer solution. This created a positively charged surface to which seed crystals of ZSM-5 were attracted. The silane and polymer layers then were removed by calcination, leaving the ZSM-5 seed crystals on the gold substrate. Finally, the substrate was exposed to a solution containing silicon dioxide and aluminum oxide resulting in the formation of a zeolite film from the seed crystals through a hydrothermal crystallization process. Potential uses for the zeolite films are in chemical sensors, microelectronics, and separation and catalysis processes (Chemical & Engineering News, 1997b).

Outlook

Sales of natural zeolites have increased from a few hundred tons in the early 1970's to the current 30,100 tons. This, while not impressive from a tonnage standpoint, actually represents an average annual growth of approximately 25%. Between the early 1970's and 1985, the markets were relatively flat (at several thousand tons) so growth after 1985 is even more impressive.

Sales will probably approach 40,000 tons by the year 2000 based on current trends. Pet litter will remain the mainstay of the industry. Sales for catalyst, desiccant, odor control, and water purification markets should increase slowly as these markets slowly expand. The

largest growth, however, should be in horticultural applications, where interest in zeolites for agriculture (growth media, soil conditioners, and so forth) is increasing, and wastewater cleanup, where water pollution issues continue to be a major concern.

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SOURCE OF INFORMATION

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TABLE 1
DOMESTIC ZEOLITES PRODUCERS, 1997

State and company	Type of zeolite
Arizona:	
GSA Resources, Inc.	Chabazite.
UOP Inc.	Do.
Nevada:	
American Resource Corp.	Clinoptilolite.
New Mexico:	
St. Cloud Mining Co.	Do.
Oregon:	
American Absorbents Natural Products, Inc.	Do.
Teague Mineral Products Co.	Do.
Texas:	
Zeotech Corp.	Do.
Wyoming:	
U.S. Zeolites	Do.