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 are analcime, chabazite, clinoptilolite, erionite, ferrierite, heulandite, laumontite, mordenite, and phillipsite. The most commonly mined varieties of natural zeolites are chabazite and clinoptilolite. More than 150 zeolites have been synthesized; the most common are zeolites A, X, Y, and ZMS-5. Natural and synthetic zeolites are used commercially because of their unique adsorption, catalytic, ion exchange, and molecular sieve properties.

Natural Zeolites

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

Production.—Conventional open pit 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. In processing, the ore is crushed, dried, and milled. The milled ore may be air-classified as to particle size and shipped either packaged in bags or bulk. The crushed product may be screened to remove fine material when a granular product is required, and some pelletized products are produced from fine material. Producers also may modify the properties of or blend their zeolite products with other materials prior to sale to improve their performance.

Domestic data for natural zeolites were collected by means of a voluntary survey of the domestic mining industry. Survey forms were sent to 11 companies. Responses from 6 of the 11 companies accounted for more than 95% of the production and end use data.

Nine companies mined natural zeolites in the United States in 2003. Two other companies did not mine zeolites during the year but sold from stocks or purchased zeolites from other producers for resale. Chabazite was mined in Arizona and clinoptilolite was mined and processed in California, Idaho, Nevada, New Mexico, Oregon, Texas, and Wyoming (table 1). New Mexico was the leading producer State. Total domestic production of zeolites was 45,400 metric tons (t) compared with an estimated 44,400 t of production in 2002.

Bear River Zeolite Co. (BRZ) (a subsidiary of United States Antimony Corp.) obtained $250,000 in funding to construct three new buildings and purchase an augurs, crusher, generator, and silo, (Industrial Specialties News, 2003). BRZ indicated that sales of clinoptilolite in the first half of 2003 were three times greater than the first half of 2002. The company was producing 500 tons per month (t/mo) to 1,000 t/mo. BRZ exports more than 50% of its production, mainly to Canada. The largest market is animal feed supplement but zeolite also is sold for air filtration, odor control, soil amendment, and water filtration (Industrial Minerals, 2003c; Industrial Specialties News, 2003).

GSA Resources, Inc., a chabazite producer in Arizona, formed a new company—Cat Applied Technology, LLC—to market a new cat litter additive developed by GSA Resources. The litter box additive is formulated to change color under specific chemical conditions and is being marketed as a color indicator of a cat's health. The company also has continued its research on zeolite use in specialty cements. The work was being done in collaboration with C_2C Zeolite Corp., Calgary, Alberta, Canada, and Zeolite Australia Ltd., South Melbourne, Victoria, Australia. GSA Resources also began testing a modular wastewater treatment system, developed with New Earth Systems, Inc., St. George, UT, at poultry processing facilities. The system, using chabazite and New Earth Systems technology, acts as an ion exchanger and removes organics from wastewater (GSA Resources, Inc., 2003).

American Absorbents Natural Products, Inc. has placed its zeolite resources and processing facilities up for sale. This action resulted from the company's filing for Chapter 7 of the Federal Bankruptcy Code. The company, which stopped production of zeolites in 2001, owns the mineral rights to clinoptilolite deposits at Harney Lake and Sheaville, OR. Its plant has a capacity of 88,000 tons per year (t/yr) with an inventory of 6,500 t of unprocessed and 3,500 t of processed material (Industrial Minerals, 2003a).

Consumption.—Approximately 36,100 t of natural zeolite was sold in 2003 in the United States compared with an estimated 33,500 t in 2002. Domestic uses for natural zeolite were, in decreasing order by tonnage, pet litter, animal feed, water purification, horticultural applications (soil conditioners and growth media), oil absorbent, odor control, fungicide or pesticide carrier, miscellaneous applications, desiccant, gas absorbent, aquaculture, catalyst, and wastewater cleanup. Pet litter, animal feed, and water purification applications accounted for more than 70% of the domestic sales tonnage. The largest increases in tonnage sales were in animal feed and water purification. Declines occurred for sales of natural zeolite for fertilizer and oil absorbent applications. Sales to other markets did not change significantly from those of 2002.

Prices.—Prices for natural zeolite vary with zeolite content and processing. Unit values, obtained through the U.S. Geological Survey canvass of domestic zeolite producers, ranged from $85 per metric ton to $320 per metric ton. Most unit values were between $85 per metric ton and $140 per metric ton. Holmes (1994, p. 1150-1151) reported that prices

for industrial or agricultural applications ranged from $30 per metric ton to $70 per metric ton for granular products down to 40 mesh and from $50 per metric ton to $120 per metric ton for finer (-40 to +325 mesh) ground material. For such products as pet litter, fish tank media, or odor control applications, prices ranged from $0.50 per kilogram to $4.50 per kilogram. Prices for Asian and European zeolite (mainly clinoptilolite) were between $75 per metric ton and $172 per metric ton (Geo.net Commodities GmbH, 2003§[1]). 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.—Comprehensive trade data are not available for natural zeolite. Exports are thought to have increased, possibly to as much as 2,000 t, compared with those of prior years based on exports reported under Harmonized Tariff Schedule Code 2530.90.8060 (a generic export category) and increased interest in the use of zeolites in Canada for animal feed supplement and water filtration applications (Industrial Minerals, 2003c). Imports of natural zeolite were thought to be minimal. Most imported natural zeolites were in the form of gem-quality zeolite crystals. The bulk of the U.S. zeolite trade was in synthetic zeolite products.

World Review.—World production of natural zeolite was estimated to be between 2.5 million metric tons (Mt) and 3 Mt based on reported production by some countries and production estimates published in trade journals. Estimates for individual countries were China, 1.5 Mt to 2.0 Mt; Japan, 140,000 t to 160,000 t; the Republic of South Korea, 150,000 t; the United States, 45,400 t; Cuba, 37,500 t; Hungary and Turkey, 30,000 t each; Bulgaria, Slovakia, and South Africa, 15,000 t each; Australia, 7,000 t; Georgia, 6,000 t; New Zealand, 5,000 t; Canada, Greece, Italy, and other republics of the Commonwealth of Independent States, 4,000 t each. Small amounts of natural zeolite also probably were produced in Indonesia.

In general, countries mining large tonnages of zeolite often have substituted zeolite for other materials. Natural zeolites were used in large quantities for such applications as dimension stone (as an altered volcanic tuff), lightweight aggregate, pozzolanic cement, soil conditioners, etc. In these cases, the ready availability of zeolite-rich rock at low cost and the shortage of competing minerals and rocks are probably the most important factors for its large-scale use. Also, it is likely that a significant percentage of the material sold as zeolite in some countries is probably ground or sawn volcanic tuff containing only a small amount of zeolite.

Canada.—C_2C Zeolite Corp. licensed Halliburton Energy Services, Inc. to market an oil well cementing system developed by C_2C Zeolite. Zeolites are used to produce a lightweight cement product with high compressive strength (Industrial Minerals, 2003b).

Synthetic Zeolites

Catalysts.—Sud-Chemie AG, Munich, Germany, acquired the customer base, patents, and products of Alsi-Penta Zeolithe GmbH, Schwandorf, Germany. Alsi-Penta synthesized zeolites for use in environmental, petrochemical, and refining applications (Chemical Week, 2003).

Current Research and Technology.—Researchers at the University of Michigan introduced copper or silver into the sodium Y zeolite structure through ion exchange and found that the structure would absorb sulfur compounds at ambient temperature and pressure. A gram of the sorbent reduced the sulfur content of diesel fuel from 430 parts per million (ppm) to 0.2 ppm by weight. The Y zeolite had 40 times the sulfur removal capacity than previously developed sorbents. Improved sorbents could help refineries meet new U.S. air quality regulations that will be enforced in the next 3 years (Chemical and Engineering News, 2003b).

Researchers at the California Institute of Technology, Pasadena, CA, have developed a means in which organic templates that control the structures of synthetic zeolites may be disassembled and removed from the zeolite structure at relatively low temperatures and reassembled for reuse. Traditionally, organic templates are destroyed at high temperatures. Some templates are expensive and the high temperature firing sometimes affects the performance of the zeolite, particularly when thin zeolite films are required for molecular sieve applications (Dagani, 2003; Wood, 2003).

A new method for creating zeolite membranes was developed at the University of Massachusetts, Amherst, MA. The researchers used organic polycations to control the zeolite crystal shape and growth rate. The thin films were more efficient than other membranes when isolating xylene species. The straight channels extending across the thin film, the large crystal size within the film plane, and lack of cracks in the film were thought to contribute to the efficiency of the film (Chemical and Engineering News, 2003a).

Outlook

Sales of natural zeolite have rebounded from their sharp decline in 1996. Growth since 1996 has averaged 5.7% per year. Increased sales for animal feed supplements, wastewater cleanup, and water purification account for much of this growth. Horticultural and pet litter applications also have contributed to the growth, but to a lesser extent. As in the past few years, many companies continue to focus on the development of more value-added products. Given the limitations in growth and the returns of several zeolite markets, the focus on value-added products should allow companies to optimize their returns. Production of natural zeolites should be in the range of 45,000 t/yr and 50,000 t/yr, and sales of natural zeolite probably will reach 40,000 t/yr within a few years.

References Cited

Chemical and Engineering News, 2003a, Better zeolite membranes for separations: Chemical and Engineering News, v. 81, no. 10, March 10, p. 41.

Chemical and Engineering News, 2003b, Zeolites offer high selectivity, high capacity for sulfur removal: Chemical and Engineering News, v. 81, no. 27, July 7, p. 17.

Chemical Week, 2003, Sud-Chemie makes zeolites acquisition: Chemical Week, v. 165, no. 31, September 10, p. 6.

[1]A reference that includes a section mark (§) is found in the Internet Reference Cited section.

Dagani, Ron, 2003, Greener zeolites: Chemical and Engineering News, v. 81, no. 39, September 29, p. 7.
GSA Resources, Inc., 2003, In the news: GSA Resources Inc. Newsletter, v. 3, no. 1, April, 3 p.
Holmes, D.A., 1994, Zeolites, *in* Carr, D.D., ed., Industrial minerals and rocks (4th ed.): Littleton, CO, Society for Mining, Metallurgy, and Exploration, Inc., p. 1129-1158.
Industrial Minerals, 2003a, American Absorbents' zeolite for sale: Industrial Minerals, no. 429, June, p. 12.
Industrial Minerals, 2003b, C_2C/Halliburton zeolite tie-up: Industrial Minerals, no. 426, March, p. 19.
Industrial Minerals, 2003c, Zeolite sales boost to BRZ production: Industrial Minerals, no. 432, September, p. 16.
Industrial Specialties News, 2003, News in Brief: Blendon Information Services, v. 17, no. 15, August 11, p. 8.
Wood, Andrew, 2003, A novel route to zeolites: Chemical Week, v. 165, no. 36, October 8, p. 18.

Internet Reference Cited

Geo.net Commodities GmbH, 2003, Offers—Zeolites, accessed April 22, 2003, via URL http://www.geo.net.

GENERAL SOURCES OF INFORMATION

U.S. Geological Survey Publication

Zeolites in Sedimentary Rocks. Ch. in United States Mineral Resources, Professional Paper 820, 1973.

Other

British Zeolite Association.
International Committee on Natural Zeolites.
International Zeolite Association.
Mining Engineering.
Natural and Synthetic Zeolites. U.S. Bureau of Mines Information Circular 9140, 1987.
Economics of Zeolites, The. Roskill Information Services Ltd., 2003.

TABLE 1
DOMESTIC ZEOLITE PRODUCERS AND SUPPLIERS IN 2003

State and company	Type of zeolite
Arizona:	
GSA Resources, Inc.	Chabazite.
UOP Inc.	Do.
California:	
Ash Meadows Zeolite, LLC	Clinoptilolite.
KMI Zeolite, Inc.	Do.
Steelhead Specialty Minerals, Inc.	Do.
Idaho:	
Bear River Zeolite, LLC	Do.
Steelhead Specialty Minerals, Inc.	Do.
Nevada, Moltan Co.	Clinoptilolite/mordenite.
New Mexico, St. Cloud Mining Co.	Clinoptilolite.
Oregon, Teague Mineral Products Co.	Do.
Texas, Zeotech Corp.	Do.
Wyoming, Addwest Minerals International Ltd.	Do.