ZEOLITES

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Natural zeolites were mined and processed by 11 companies in the United States in 2004. Mine production was 57,400 metric tons (t), and U.S. consumption was 49,100 t. Major markets were in animal feed, pet litter, and water purification applications, which accounted for more than 70% of domestic consumption. In 2004, exports were estimated to be between 500 and 1,500 t, and imports were mainly of gem-quality zeolite crystals.

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 clinoptilolite and chabazite. 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 absorption, 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 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 the zeolite or blend their zeolite products with other materials before sale to enhance 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 7 of the 11 companies accounted for 89% of the production and end-use data.

Ten companies mined natural zeolites in the United States in 2004. One other company did not mine zeolites during the year but sold from stocks or purchased zeolites from other producers for resale (table 1). Chabazite was mined in Arizona, and clinoptilolite was mined and processed in California, Idaho, Nevada, New Mexico, Texas, and Wyoming. New Mexico was the leading producer State. Domestic production of zeolites was 57,400 t compared with an estimated 45,400 t of production in 2003.

Bear River Zeolite Co. (BRZ) (a subsidiary of United States Antimony Corp., Thompson Falls, MT) reported that sales of clinoptilolite from its Idaho operation increased by 120% from 2002 to 2003, and sales in February 2004 were 55% greater than any single month's sales during the past 2½ years. Sales for water filtration accounted for more than 50% of sales, and more than 35% of sales were for animal nutrition and odor control applications. The company indicated that a second municipal water system in Canada has switched to using zeolite filtration instead of the traditional anthracite and sand filtration beds. The zeolite filtration unit reduced water turbidity by 50%, increased flow rates, and reduced the need to backwash the media as often as with anthracite and sand filtration beds. BRZ sells its products in Canada, China, Japan, Mexico, Peru, the United Kingdom, and the United States (Industrial Minerals, 2004; U.S. Antimony Corp., 2004§[1]).

Ash Meadows LLC, Bear River Zeolite Co., KMI Zeolites, St. Cloud Mining Co., Teague Mineral Co., and Zeotech Corp. mine clinoptilolite, which has the broadest use of the zeolites mined domestically. The two leading producers, St. Cloud and Zeotech, accounted for about 70% of the total U.S. zeolite production.

Uses for zeolites range from animal feed supplements to gas purification to wastewater treatment, but producers specialize in markets for which their zeolites are best suited. Thus, zeolite products containing significant amounts of smectite clay are sold mainly for a variety of absorbent applications, the clay content making it unsuitable for water filtration. The same absorbency properties, however, allow the zeolite to absorb such chemicals as potassium permanganate. Surface-modified zeolites (SMZ) can be used for gas purification and absorption of anions, such as chromate and selenate from water streams. Zeolites containing potassium permanganate in their framework can be used for removing such compounds as hydrogen sulfide, mercaptans, and ethylene from gas streams.

Growth within the zeolite industry lately has been driven by sales for water filtration applications. In 1999, sales of zeolites for this application were estimated to be 200 t. In 2004, sales were projected to be 2,500 t. For several years, swimming pool filtration applications dominated, but in recent years, an increased share of water filtration sales has been for industrial and municipal water filtration applications. Animal feed supplement applications also are gaining acceptance by nutritionists in the United States. Zeolites have been demonstrated through research to provide health and nutritional benefits, but they are sold only as a feed conditioning agent

[1]References that include a section mark (§) are found in the Internet References Cited section.

because of government regulations. Zeolites also are sold as soil amendments. These are either granular materials or zeolites amended with nutrients. Sales for this application were estimated to be about 5,000 metric tons per year (t/yr), although they are less than producer expectations in recent years (Peterson and Coufal, 2004).

Consumption.—Approximately 49,100 t of natural zeolite was sold in 2004 in the United States compared with an estimated 36,100 t in 2003. Domestic uses for natural zeolite were, in decreasing order by tonnage, animal feed, pet litter, water purification, horticultural applications (soil conditioners and growth media), odor control, fungicide or pesticide carrier, desiccant, oil absorbent, gas absorbent, wastewater cleanup, aquaculture, and catalyst. Animal feed, pet litter, and water purification applications accounted for more than 70% of the domestic sales tonnage. Sales in all except one end-use category increased. The largest increases in tonnage sales were for animal feed and water purification applications.

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 about $75 to $300 per metric ton. Most unit values were between $80 and $140 per ton. Holmes (1994, p. 1150-1151) reported that prices for industrial or agricultural applications ranged from $30 to $70 per ton for granular products down to 40 mesh and from $50 to $120 per 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 to $4.50 per kilogram. Prices for Asian and European zeolite (mainly clinoptilolite) were between $60 and $165 per ton (Geo.net Commodities GmbH, 2004§). 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 probably were between 500 and 1,500 t based on exports reported under Harmonized Tariff Schedule of the United States code 2530.90.8060 (a miscellaneous mineral export category). Exports of natural zeolites were likely to have been for high-value applications. Imports of natural zeolite were believed to be mainly in the form of gem-quality zeolite crystals. The bulk of the U.S. zeolite trade was in synthetic zeolite products.

World Industry Structure.—World production of natural zeolite was estimated to be between 2.5 and 3 million metric tons (Mt) based on reported production by some countries and production estimates published in trade journals. Estimates for individual countries were China, 1.5 to 2.0 Mt; the Republic of Korea, 150,000 t; Japan, 140,000 to 160,000 t; the United States, 57,400 t; Cuba, 37,500 t; Hungary and Turkey, 30,000 t each; Slovakia, 25,000 t; Bulgaria and South Africa, 15,000 t each; Australia, 7,000 t; Georgia, 6,000 t; New Zealand, 5,000 t; Canada, Italy, and the Commonwealth of Independent States, 4,000 t each; Greece, 3,000 t; and Ecuador, 2,070 t. Small amounts of natural zeolite also probably were produced in Indonesia.

In general, countries mining large tonnages of zeolite often have substituted zeolite-containing tuffs for various applications. Natural zeolites were used in large quantities for such applications as dimension stone (as an altered volcanic tuff), lightweight aggregate, pozzolanic cement, and soil conditioners. 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 ground or sawn volcanic tuff containing only a small amount of zeolite.

World Review.—**Australia.**—Envirozel Ltd. transferred 85% of its share of Zeolite Australia (a division of Envirozel Ltd.) to Mosaic Tile and Pottery Co. Pty. Ltd. Envirozel indicated that mining and marketing of zeolites did not reflect the company's focus on the development of new technologies for water treatment. Zeolite Australia marketed its zeolites for animal feed, soil amendments, and water treatment (Envirozel Ltd., 2004a, b; Zeolite Australia Pty. Ltd., 2004§).

Canada.—United Zeolite Products Ltd. (UZP) [a subsidiary of First American Scientific Corp. (FASC), Vancouver, British Columbia, Canada] announced that it had signed a $5 million contract with Halliburton Group Canada to supply a micronized zeolite product for use in gas- and oil-well cementing systems. FASC completed construction of the micronizing plant near UZP's Princeton, British Columbia, operation and was beginning trial runs of the equipment (C_2C Zeolite Corp., 2004; First American Scientific Corp., 2004).

Synthetic Zeolites

Consumption.—**Detergents.**—J.P. Morgan Partners, L.L.C. (a subsidiary of J.P. Morgan Chase & Co.) signed an agreement to purchase PQ Corp., Valley Forge, PA, pending stockholder approval. PQ is a supplier of synthetic zeolite to the detergent industry and produces other compounds used by the beverage, catalyst, chemical, petroleum, paper, and pulp industries (PQ Corp., 2004).

Current Research and Technology.—Researchers at The Ohio State University developed a sensor based on zeolite structures for the detection of nitrogen oxide and nitrogen dioxide [collectively known as nitrogen oxides (NOx)] in exhaust emissions. The exhaust gases are passed through a zeolite filter where carbon monoxide is removed from the gas stream and NOx gases pass through to the sensor electrode. By removing carbon monoxide interferences, NOx emissions above 100 parts per million were accurately determined, a level adequate for monitoring emissions in automobile and powerplant exhaust. The research team is testing various electrode metals and sensor designs to improve efficiency and allow monitoring for other pollutants (Azom.com, 2004§).

Scientists at Oak Ridge National Laboratory, Oak Ridge, TN, developed a portable cooling unit based on zeolite pressure-swing refrigeration technology. The unit employs a cartridge filled with zeolite. Water is passed through the zeolite cartridge, which is under vacuum. The water evaporates under the vacuum but then condenses on the zeolite, providing the cooling effect. Each cartridge can provide 30 to 45 minutes of cooling. The device is designed to be used by personnel exposed to high temperatures, such as fire fighters, and sports team mascots, who wear heat-retaining clothing (Oak Ridge National Laboratory, 2004).

Researchers at Polytechnic University of Valencia in Spain developed a new template for synthesizing zeolites. The organic

molecule used as the template is derived from quinolinium. The characteristics of the molecule permit the synthesis of zeolites with a high silicon-to-aluminum ratio in their structure. A high ratio is desirable for petroleum-processing applications because it improves the reactivity, hydrothermal stability, and hydrophobic properties of the synthetic zeolite (Chemical and Engineering News, 2004).

Outlook

Sales of natural zeolite have increased slowly as recognition of its versatility has increased. Sales for animal feed supplements, wastewater cleanup, and water purification applications continue to account for much of the growth in natural zeolite sales although other uses, such as for lightweight aggregate for specialty concrete products, are being commercialized. Based on recent trends, production of natural zeolites probably will increase to as much as 65,000 t/yr within 2 to 3 years. Sales of natural zeolite also will increase, possibly approaching 55,000 t/yr during the same time period.

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TABLE 1
DOMESTIC ZEOLITE PRODUCERS AND SUPPLIERS IN 2004

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.
Teague Mineral Products Co.	Do.
Nevada, Moltan Co.	Chabazite/mordenite.
New Mexico, St. Cloud Mining Co.	Clinoptilolite.
Texas, Zeotech Corp.	Do.
Wyoming, Addwest Minerals International Ltd.	Do.