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. 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, 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 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 also are produced. 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 5 of the 11 companies accounted for more than 90% of the production data.

Nine companies mined natural zeolites in the United States in 2002. Two other companies 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, Oregon, Texas, and Wyoming. New Mexico was the leading producer State. Total domestic production of zeolites was estimated to be 46,000 metric tons (t) compared with an estimated 36,400 t in 2001.

Goldfield Corp. completed the sale of its mining assets to Imagin Minerals, Inc. in 2002. The sale included St. Cloud Mining Co., which is the largest zeolite producer in the United States. St. Cloud Mining also operates an aggregates operation. The aggregates and zeolite operations are in New Mexico. The company reported sales of 14,700 t of clinoptilolite in 2002. Markets for their clinoptilolite products included animal feed supplements, absorbents, air and water filtration, environmental products, odor control, and soil conditioners (Goldfield Corp., 2002; St. Cloud Mining Co, 2003§[1]).

Bear River Zeolite Co. (BRZ) (a subsidiary of United States Antimony Corp.) upgraded its facilities with the installation of a drier and a blending unit. The drier allowed year-round production at their facility, and the blending unit allowed the company to manufacture premixed products, consisting of ammonium, phosphate, and BRZ zeolite, for fertilizer applications. The company sold its zeolite for animal feed, fertilizer, odor control, soil amendment, and waste clean-up applications (United States Antimony Corp., 2002).

Victor Industries, Inc. announced that the U.S. Bureau of Land Management has approved its plan of operation for opening a zeolite mine in eastern Oregon. Victor Industries has been purchasing its zeolite but wanted an option to mine its own zeolite if the need arose. Victor Industries marketed several products for potting soils and soil amendments using zeolite (North American Minerals News, 2002; Victor Industries, Inc., 2002).

GSA Resources Inc., Tucson, AZ, and C_2C Zeolite Corp., Calgary, Alberta, Canada, have joined forces to produce ZeoFume, an alternative to silica fume. GSA Resources will supply the zeolite (chabazite) from which the product will be manufactured and C_2C Zeolite will supply the technology. The product is used in cement to increase performance for construction, oilfield cementing, and shotcrete applications. The chabazite is dried, heat treated, ground, and packaged. The zeolite's pozzolanic properties are enhanced through the heat treatment. The companies expect to manufacture 5,000 t in the United States and 4,000 t in Canada in 2003. GSA Resources mines chabazite from its deposit near Bowie, AZ. Reserves are estimated to be 590 million metric tons (Mt) of 90% chabazite content. C_2C Zeolite operates a clinoptilolite mine in British Columbia and has reserves in Nova Scotia that contain stilbite, mordenite, phillipsite, chabazite, and clinoptilolite (Industrial Minerals, 2002b).

Consumption.—An estimated 35,700 t of natural zeolite was sold in 2002 in the United States compared with an estimated 32,900 t in 2001. Domestic uses for natural zeolite were, in decreasing order by tonnage, pet litter, animal feed, horticultural applications (soil conditioners and growth media), miscellaneous applications, oil absorbent, odor control, desiccant, fungicide or pesticide carrier, water purification, aquaculture, wastewater cleanup, gas absorbent, and catalyst. Pet litter, animal feed, and horticultural applications accounted

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

for more than 65% of the domestic sales tonnage. The largest increases in tonnage sales were in animal feed and pet litter. Sales to other markets did not change significantly from those of 2001.

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 $60 per metric ton to $320 per ton. Most values were between $85 per ton and $160 per ton. Holmes (1994, p. 1150-1151) reported that prices for industrial or agricultural applications ranged from $30 per ton to $70 per ton for granular products down to 40 mesh and from $50 per ton 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 per kilogram to $4.50 per kilogram. Prices for Asian and European zeolite (mainly clinoptilolite) were between $69 per ton and $163 per ton (Geo.net Commodities GmbH, 2003§). 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. U.S. exports of natural zeolite were estimated to be between 100 t and 200 t. Imports of natural zeolite were believed to be minimal, most being in the form of gem-quality zeolite crystals. The bulk of the international trade was synthetic zeolite.

World Review.—Worldwide production of natural zeolite was estimated to be between 3 Mt and 4 Mt based on reported production by some countries and production estimates published in trade journals. Estimates for individual countries were China, 2.5 Mt; Japan, 140,000 t to 160,000 t; the United States, 46,000 t (reported); Cuba, 37,500 t; Hungary, 25,000 t; Slovakia, 15,000 t (reported); Georgia, 6,000 t (reported as 7,300 t in 1996); New Zealand, 5,000 t; Australia, Canada, Italy, and other republics of the former Soviet Union, 4,000 t each; Greece, 3,000 t; and South Africa 1,000 t to 2,000 t. Small amounts of natural zeolite also probably were produced in Bulgaria and Indonesia. Production capacity for Cuba (650,000 t) was reported in previous Minerals Yearbook publications because production data were not available prior to 2002. The reported production of 37,500 t for Cuba is more in line with traditional zeolite markets.

In general, countries mining large tonnages of zeolite often have substituted zeolite for other materials. The zeolite was used in large quantities for such applications as dimension stone, 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.

Australia.—Supersorb Environmental NL, with a zeolite mine in Australia, announced plans for trials of activated zeolite in wastewater treatment. The company believed that activated zeolite could offer higher filtration rates than traditional sand filtration systems while offering enhanced ammonium absorption and odor reduction (Industrial Minerals, 2002c).

Canada.—Zeo-Tech Enviro Corp. began mining at its Princeton, British Columbia, deposit. The company produced 4,000 t for shipment to C_2C Zeolite. The zeolite was processed for use in cement mixes for oil well cementing and construction applications. The product served as an alternative to fumed silica (Zeo-Tech Enviro Corp., 2002). C_2C Zeolite has an agreement with GSA Resources for similar applications in the United States.

Current Research and Technology.—The application of cellulose, clinoptilolite, and a combination of the two reduced the volatilization of ammonium nitrate (AN), ammonium sulfate (AS), and urea from calcareous sandy soil. Cellulose amendments reduced volatilization of AN, AS, and urea by 2.5, 2.1, and 0.9 times, respectively. Reductions achieved using only clinoptilolite amendments were 4.4, 2.9, and 3 times, respectively. A combination of cellulose and clinoptilolite amendments reduced AN, AS, and urea volatilization further than for either single amendment alone. The cellulose was believed to have increased microbial biomass, which can immobilize nitrogen, in the soil. The clinoptilolite decreased ammonia volatilization by retaining the ammonia in its pore structure. The leaching of nitrate and the loss of nitrogen through ammonia volatilization are two major avenues for the loss of nitrogen from agriculture soils (He and others, 2002).

Clinoptilolite and phosphate rock were applied to beds containing sunflowers to determine if the zeolite could enhance phosphorus uptake by the plants. The objective was to determine if the exchange of ammonia and potassium from the zeolite structure for calcium in the soil would enhance the dissolution of the phosphate rock. An ammonium-exchanged clinoptilolite mixed with a reactive phosphate rock provided the greatest benefits compared with a calcium- or potassium-exchanged clinoptilolite. Plant absorption of phosphorus was enhanced in the presence of the ammonia-exchanged clinoptilolite, although it was enhanced less than that by a soluble phosphorus source. The mixture, however, releases phosphorus in response to plant demand through exchange-induced dissolution, which may be an advantage over using soluble phosphorus sources (Pickering, Menzies, and Hunter, 2002).

Synthetic Zeolites

Detergents.—Zeolite usage in detergents increased in some regions and stagnated or declined in others. The world market was estimated to be more than 1 Mt. Europe consumed about 650,000 tons per year. Germany, followed by the United Kingdom, and then France are the largest European consumers. Markets in Western Europe generally have declined but, with a major producer of detergents switching its formulations to include zeolite, markets were expected to rebound slightly. Use also has increased in areas that have not yet banned phosphates in detergents. China, Eastern Europe, India, and Portugal were areas of potential growth for synthetic zeolite in the detergent market (Industrial Minerals, 2002a).

Current Research and Technology.—Researchers at Polytechnic University of Valencia (Spain) synthesized a modified faujasite zeolite structure. The modified structure contains larger cavities and channels than existing faujasite (zeolite Y) structures. The researchers used a large organic molecule as the basis for the synthesis process. The larger cavities and channels allow larger organic molecules to enter the structure for catalytic cracking. This is important for improving the efficiency of refinery catalyst operations. Laboratory tests showed that the new structure converted 72.5% of gasoil, a petroleum distillate, to smaller hydrocarbon molecules compared with 68% and 53.9% for two commercial catalysts (Scott, 2002).

Outlook

After declining sales for 2 years, sales of natural zeolite rebounded in 2002. Several companies focused on penetrating markets that were previously ignored, such as specialty concretes, and creating more innovative and possibly more marketable products, such as soil amendment blends. If these are successful, they may spur more interest in the use of zeolite as the commercial potential of these functional minerals is recognized. Sales of natural zeolite probably will remain in the range of 35,000 t to 40,000 t for the next few years.

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TABLE 1
DOMESTIC ZEOLITE PRODUCERS AND SUPPLIERS IN 2002

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