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 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 with responses accounting for more than 95% of the production and consumption data. Nine companies mined natural zeolites in the United States in 2001. Three 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; clinoptilolite was mined and processed in California, Idaho, Nevada, New Mexico, Oregon, and Texas; and mordenite was mined in Nevada. The largest production was in New Mexico. Total domestic production of zeolites was estimated to be 36,000 metric tons (t) compared with an estimated 41,800 t in 2000.

Goldfield Corp. announced its intent to exit the mining industry and sell its mining assets. The sale will include St. Cloud Mining Co., which is the largest zeolite producer in the United States. St. Cloud Mining operates aggregate quarries and a zeolite mine and mill processing facility in New Mexico. The company reported sales of 16,000 t of clinoptilolite in 2001. Markets for their clinoptilolite products include absorbents, air and water filtration, animal feed supplements, environmental products, odor control, and soil conditioners (Goldfield Corp., 2002a, p. 4-5; 2002b).

United States Antimony Corp. (USAC) began mining a zeolite deposit near Preston, ID. The deposit is 245 meters thick and contains reserves exceeding 220 million metric tons (Mt) of clinoptilolite. Bear River Zeolite, LLC (which is 75% owned by USAC), will operate the mine and mill. The company is anticipating production capacity of 200 metric tons per day. The company plans to sell zeolite as an anticaking agent, feed additive, oil absorbent, soil amendment, and for water filtration. Bear River Zeolite also is developing a fertilizer product consisting of ammoniated zeolite and phosphate for use on fruit, vegetable, and potato crops and in potting soils (Mining Engineering, 2001; United States Antimony Corp., 2002).

GSA Resources, Inc., Tucson, AZ, and C_2C Zeolite Corp., Calgary, Canada, signed a 2-year agreement to promote each other's zeolites products. The objective is to draw upon the patented technologies and proprietary applications of each company and allow the companies to market a broader range of products across North America. GSA Resources developed technologies for removing ammonia contaminants, arsenites and arsenates, chrome, radioactive cations, and thallium from liquids. C_2C developed its technology for encapsulating hazardous waste, making lightweight building materials, and soil remediation. GSA Resources believes that arsenic remediation will become a particularly important market for zeolites in the coming years because U.S. water utilities will have to meet the U.S. Environmental Protection Agency's (EPA) new drinking water standard of 10 parts per billion for arsenic by January 23, 2006. The previous EPA standard was 50 parts per billion (North American Minerals News, 2001c; U.S. Environmental Protection Agency, undated§[1]).

American Absorbents Natural Products, Inc. (AANPI) announced that it would withdraw from the natural zeolite market. Shareholders voted to change the company name and refocus its attention to other industries. AANPI has retained Barso Global Management, Ltd. to sell its zeolite assets, consisting of a mine and mill in south-central Oregon. The company marketed its zeolite products for odor control, gas or liquid absorption, horticultural applications, and animal feed supplements (American Absorbents Natural Products, Inc., 2001).

Consumption.—An estimated 32,900 t of natural zeolites was sold in 2001 in the United States compared with an estimated

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

30,900 t in 2000. Domestic uses for natural zeolites were, in decreasing order by tonnage, pet litter, animal feed, horticultural applications (soil conditioners and growth media), odor control, oil absorbent, desiccant, water purification, fungicide or pesticide carrier, wastewater cleanup, aquaculture, gas absorbent, and catalyst. Pet litter, animal feed, and horticultural applications accounted for more than 65% of the domestic sales tonnage. From a tonnage standpoint, sales to individual markets did not change significantly compared with those of 2000.

***Prices.*—**Prices for natural zeolites vary with zeolite content and processing. Unit values, obtained through the U.S. Geological Survey canvass of domestic zeolite producers, ranged from $70 to $300 per metric ton. Little information is published on prices for specific products or product applications. The latest prices were given in 1994 when 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. 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 zeolites. Exports of natural zeolites were estimated to be between 100 t and 200 t. Imports were believed to be less than 100 t in 2001. The bulk of the international trade was synthetic zeolites.

***World Review.*—**Worldwide production of natural zeolites was estimated to be between 3 and 4 Mt on the basis of reported production by some countries and production estimates published in trade journals. Estimates for individual countries were China, 2.5 Mt; Cuba, 500,000 to 600,000 t; Japan, 140,000 to 160,000 t; the United States, 36,000 t (reported); Hungary, 10,000 to 20,000 t; Slovakia, 9,000 t (reported as 8,640 t in 1999); Georgia, 6,000 t (reported as 7,300 t in 1996); New Zealand, 5,000 t; Greece, 3,000 t; Australia, Canada, Italy, and republics of the former Soviet Union, except Georgia and Slovakia, 4,000 t each; Bulgaria, 2,000 t; South Africa 1,000 to 2,000 t; and Argentina, 150 t. Small amounts of natural zeolites also probably were produced in Germany and Indonesia.

In general, countries mining large tonnages of zeolites often have substituted zeolites for other materials. These zeolites are used in large quantities for such applications as pozzolanic cement, lightweight aggregate, dimension stone, and soil conditioners. In these cases, the ready availability of zeolites 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 more realistically ground or sawn volcanic tuff containing only a small amount of zeolites. If that is so, then that would greatly reduce the estimated world production of natural zeolites.

Australia.—Talon Resources NL, the leading Australian producer of absorbent minerals, sought to strengthen its position through a pro rata share issue. The company hoped to raise $1.9 million in capital, which would permit the company to pursue further growth in the field of environmental technologies, notably using activated zeolites (Industrial Minerals, 2001b).

Canada.—C_2C Mining Corp. acquired 10 mineral claims east of Kamloops, British Columbia. The deposits in this area may contain millions of tons of reserves and contain chabazite, thompsonite, and stilbite in varying amounts. This will supplement the 35 Mt from C_2C Mining's Cache Creek reserves. The company also obtained governmental approval to develop its deposit in Nova Scotia. Reserves were estimated to be 2 Mt (Industrial Minerals, 2001a; North American Minerals News, 2001b).

C_2C Mining and Zeo-Tech Enviro Corp. have developed a lightweight zeolite concrete that meets the American Society for Testing of Materials C90 standard for load-bearing masonry units. The material is reported to be 40% lighter than traditional products. C_2C Mining mines the zeolite used for the lightweight concrete from its Princeton quarry in British Columbia (Zeo-Tech Enviro Corp., 2001). The company also began testing its lightweight concrete for down-hole cementing of gas and oil wells. The work is part of a joint project between C_2C Mining, the National Research Council of Canada, and the University of British Columbia (North American Minerals News, 2001a).

Kazakhstan.—Jt. St. Co. Yrystas began production in its Shankhanai deposit in Almaty oblast. The material was processed in the nearby 2,500-metric-ton-per-year (t/yr) plant. The zeolite is marketed to the domestic oil and gas industries. Previously, the Kazakhstan oil and gas industries used imported zeolites (Industrial Minerals, 2001c).

***Current Research and Technology.*—**A reconnaissance study of volcaniclastic rocks in western Montana found that samples from 14 of 37 localities contained zeolites. The predominant zeolite observed was clinoptilolite although analcime and mordenite also were identified in a few deposits. Most of the deposits were of Tertiary age and were noneconomic. One Cretaceous age deposit along Grasshopper Creek, southwest of Dillon, MT, was potentially economic. The deposit contained more than 90% clinoptilolite and up to 20% mordenite in various portions of the deposit. The most economically viable portion of the deposit contained about 90,000 t of zeolitic tuff, grading from 60% to 70% zeolite. Ammonia exchange capacities of samples from Grasshopper Creek ranged from 0.68 to 1.29 milliequivalents per gram. Exchange capacities for other locales ranged from 0.08 to 1.86 milliequivalents per gram (Berg and Cox, 2001, p. 6-7).

A wide variety of research was conducted in 2001. Research covered such topics as copper and lead adsorption (Gomonaj and others, 2001; Makurin and others, 2001), catalytic reduction of polystyrene using clinoptilolite (Lee and others, 2001), radioactive waste treatment (Dyer and others, 2001), pretreatment of clinoptilolite in laboratory-scale ion exchange beds (Inglezakis and others, 2001), and arsenite and arsenate uptake by clinoptilolite-rich tuffs (Elizalde-Gonzalez and others, 2001).

Synthetic Zeolites

***Catalysts.*—**The catalyst market represents the largest share of the domestic synthetic zeolite market. The synthetic zeolites are used for fluid catalytic cracking (FCC) of crude petroleum. Faujasite-type, also called zeolite Y, and ZMS-5 zeolites are the most commonly used synthetic zeolites. Two forms of zeolite Y may be used—one containing rare-earth elements in the exchangeable cation sites and one being ultrastable Y. FCC processing has been made more efficient through the use of synthetic zeolites, improving to a yield of about 75.7 liters (20 gallons) of gasoline per barrel with ultrastable Y in the late 1980s from a yield of about 53 liters (14 gallons) per barrel of gasoline in the 1960s with amorphous aluminosilicate catalysts (Katz, 2001).

AgipPetroli SpA reported decreased sulfur content, increased gasoline selectivity, and reduced gas and coke yields at its refinery in Priolo, Italy. The refinery began using a recently developed catalyst consisting of a proprietary zeolite in an alumina-sol matrix. The catalyst uses hydrogen transfer to transform sulfur species into molecules that are easier to crack in the reaction process. The sulfur is removed from the gasoline as di-hydrogen sulfide. The company reported a 35% decrease in gasoline sulfur, 20% lower catalyst consumption, 1.4 weight percent higher conversion, lower coke and dry gas yields, and increased gasoline selectivity and octane barrels (Genco and others, 2001).

Detergents.—With vast overcapacity in the detergent-grade zeolite industry, Degussa-Hüls AG withdrew from the detergent zeolite market in 2001. Degussa closed its plants in Wesseling, Germany, and Taipei, Taiwan, and sold its plant in Zubillaga-Lantarón, Spain, to FMC Foret (a subsidiary of FMC Corp.). Degussa's three plants had a capacity of 215,000 t/yr but sold only 120,000 t of zeolites in 2000 (Chemical and Engineering News, 2001; Chemical Week, 2001a).

The closure of Degussa's two plants eliminated about 165,000 t/yr of world capacity (the company's plant in Spain had a capacity of 50,000 t/yr) and should improve the competitive position of the remaining producers. In 2001, production overcapacity was estimated to be about 100% in Asia, 30% to 40% in Europe, and 10% to 20% in North America. With Degussa's exit from the market and the idling of some plants in Europe, production overcapacity was predicted to decrease to 80% in Asia and 10% in Europe. The prolonged overcapacity situation has been detrimental to zeolite producers because detergent manufacturers used it as leverage to demand price reductions. Prices are believed to have fallen by 70% since 1992. The increased use of detergent concentrates, which consume smaller amounts of zeolites, and liquid detergents have contributed to the downturn in demand for detergent-grade zeolites (Chemical Market Reporter, 2001; Chemical Week, 2001c).

Industrial Zeolite Ltd. continued construction of its synthetic zeolite production facility in Alexandria, LA. The company is a new entrant into the U.S. synthetic zeolite market and will produce detergent-grade zeolites for Procter and Gamble Co. (Chemical Week, 2001b).

Outlook

Sales of natural zeolites have vacillated between 28,000 t and 35,000 t for the past 7 years. The peak sales occurred in 1993 when 41,600 t of zeolites were sold or used. Current sales are 10,000 t below this mark. While innovation continues, markets for natural zeolites still seem to remain static. For the next 2 years, production and sales are not anticipated to increase significantly. The industry, however, is waiting to see how two major environmental concerns play out. The first is arsenic in drinking water. In experiments, modified zeolites have been shown to remove arsenic to levels below the EPA's new 10-parts-per-billion arsenic standard. While companies have 3 years to come into compliance, the EPA predicted that more than 6,000 water companies would not be able to comply with even a 20-parts-per-billion standard (North American Minerals News, 2001c; U.S. Environmental Protection Agency, undated§). If this proves true, then the potential for a large demand for modified zeolites could occur. Another issue concerns large animal stockyards. Animal waste runoff from these stockyards contributes to local stream pollution and, with the advent of "supersized" dairy and hog farms, has become a major environmental concern. Zeolites already have proven their mettle at controlling odors and helping to solidify animal waste in small farming situations. If large-scale animal stockyards are required more tightly to control animal runoff, then this could represent a considerable market for natural zeolites.

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TABLE 1
DOMESTIC ZEOLITE PRODUCERS AND SUPPLIERS, 2001

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.	Clinoptilolite/mordenite.
New Mexico, St. Cloud Mining Co.	Clinoptilolite.
Oregon:	
American Absorbents Natural Products, Inc. 1/	Do.
Teague Mineral Products Co.	Do.
Texas, Zeotech Corp.	Do.
Wyoming, Addwest Minerals International Ltd.	Do.

1/ Withdrew from zeolite industry in 2001.