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 (or) phillipsite. Other nonzeolitic 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.

Domestic data for natural zeolites were collected by means of a voluntary survey of the domestic mining industry. Survey forms were sent to nine companies with responses accounting for approximately 90% of the production and consumption data.

Eight companies mined natural zeolites in the United States in 1999. Three other producers 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/or processed in Idaho, Nevada, New Mexico, Oregon, Texas, and Wyoming; and mordenite was mined in Nevada. Total domestic production of zeolites was estimated to be 43,000 metric tons (t) compared with an estimated 40,000 t in 1998.

The sale of American Resource Corp. to Badger Mining Co. was finalized in 1999. American Resource Corp. will be operated as Ash Meadows Zeolite, LLC.

Consumption.—An estimated 35,000 t of natural zeolites was sold in 1999 in the United States compared with an estimated 33,000 t in 1998. Natural zeolites were sold for, in decreasing order by tonnage, pet litter, animal feed, horticultural applications (soil conditioners and growth media), wastewater cleanup, odor control, desiccant, fungicide or pesticide carrier, water purification, gas absorbent, catalysts, aquaculture, and oil absorbent. Pet litter, animal feed, and horticultural applications accounted for more than 70% of the domestic sales tonnage. Sales to most markets changed only slightly compared with those of 1998.

Prices.—Prices for natural zeolites varied with zeolite content and processing. For industrial or agricultural applications, prices ranged from $30 to $70 per metric ton for granular products down to 40 mesh and from $50 to $120 per ton for finer (-40 to -325 mesh) ground material (Holmes, 1994, p. 1150-1151). 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.—Although trade data for natural zeolites are not available, imports of natural zeolites were estimated to be, at most, several hundred tons, and exports were estimated to be less than 1,000 t in 1999.

World Review.—Worldwide production of natural zeolites was estimated to be between 3 million and 4 million metric tons (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, 43,000 t (reported); Hungary, 10,000 to 20,000 t; Slovakia, 12,000 t; Georgia [republic of the former Soviet Union (FSU)], 6,000 t; New Zealand, 5,000 t; Greece, 4,750 t (reported); Canada, Italy, and other republics of the FSU, 4,000 t each; Australia, 3,880 t (reported); Bulgaria, 2,000 t; and South Africa 1,000 to 2,000 t. Small amounts of natural zeolites also were produced in Argentina, Germany, and Indonesia.

C_2C Mining Corp. and Canadian Mining Co. Ltd. (CNC) announced a collaborative effort to process and market their zeolites. Both companies owned zeolite deposits in British Columbia; C_2C’s zeolites in Cache Creek are calcium- and sodium-rich, and those of CNC in Princeton are potassium-rich. By combining their resources, the companies will be able to serve more markets and to introduce new product lines (North American Minerals News, 1999a). Also, C_2C licensed its technology for encapsulating and stabilizing hazardous and radioactive wastes to Hytec Hydrocarbon Reclamation Ltd. The technology will be marketed to the petrochemical, mining, and nuclear industries (North American Minerals News, 1999b).

***Current Research and Technology.*—**The U.S. Environmental Protection Agency (EPA) considers arsenic to be a human carcinogen as a result of recent health studies. Consequently, it may lower the arsenic standard to 5 parts per billion or less from the current 50 parts per billion arsenic standard. Research to reduce arsenic levels in wastewater by using zeolites was conducted by the University of Florida and GSA Resources, Inc. The technology is based on the enhanced ability of chabazite to exchange arsenic when the chabazite is treated with a concentrated ferrous solution. By using the treated chabazite, levels of arsenic in drinking water were reduced to less than 8 to 10 parts per billion. The arsenic-exchanged zeolite passed the EPA Toxicity Characteristic Leaching Procedure and can be disposed of in a landfill. Testing to treat mine wastewater by mixing the chabazite with surface waters and allowing it to settle to the bottom of the holding ponds and to treat industrial wastewater using an upflow fluidized bed setup also is continuing (NuElectric, Inc., 1999; Pollution Engineering, 2000)

Synthetic Zeolites

***Catalysts.*—**Researchers are investigating ways to reduce hydrocarbon emissions during cold engine startups. In general, the catalyst temperature must reach about 300° C before catalytic reactions are initialized in automotive catalytic converters. One means of circumventing the problem is to trap the hydrocarbons in the engine exhaust in a zeolite catalyst. Engelhard Corp. developed a moderate silicon-to-aluminum ratio zeolite catalyst that was effective in trapping alkene and aromatic compounds at low temperatures. A 40% to 50% reduction in hydrocarbon emissions was reported (Chemical & Engineering News, 1999a).

Crosfield Group, which was a subsidiary of ICI PLC, ceased production of zeolite Y, which is used for refinery and chemical manufacturing processes. The closure of the 5,000-metric-ton-per-year (t/yr) plant in the United Kingdom was part of a plan to increase profitability of the company. By transferring production of catalysts to Synetix Group, which was ICI's new catalyst division, Crosfield will be able to focus on the synthesis of a variety of silicates, silicas, and zeolites for detergent applications. In 1998, W.R. Grace and Co. agreed to purchase Crosfield but the offer was concealed in 1999 (Alperowicz, 1999).

***Detergents.*—**Competition between zeolites and phosphates continues as producers sought ways to increase their share in the institutional and industrial (I&I) detergent market, which includes such products as high-pressure dishwashing detergents and cleaning agents. Sales of zeolites and phosphates have not increased significantly in the past few years, and the increased use of liquid laundry detergents has hurt zeolite sales growth in the United States. Sales of zeolites to the powder home laundry detergent market, however, have increased by 1% to 3% per year in recent years. In 1997, domestic use of zeolites in detergents was estimated to be 350,000 t/yr, and worldwide demand for detergent-grade zeolites was estimated to be 850,000 t/yr (Kemezis, 1999). Zeolites can compose up to 70% of a powder laundry detergent product (Chemical & Engineering News, 1999b).

Albermarle Corp., which was a U.S. supplier of detergent-grade zeolites, offered to purchase Albright & Wilson PLC (A&W), which was the world's largest supplier of sodium tripolyphosphate (STPP). Zeolites are used primarily in powder detergents, and STPP is used primarily in I&I cleaners and dishwasher applications. The purchase would improve A&W's marketing opportunities for its detergent builders (which soften the wash water by removing calcium and magnesium, thus resulting in enhanced surfactant performance) in the United States and Albermarle's marketing opportunities in Europe for its zeolite detergent builders (Scheraga, 1999).

***Molecular Sieves.*—**Tosh Corp. continued construction of a $26 million plant to manufacture a zeolite for high-performance oxygen pressure-swing-absorption applications. The plant is located in the Yamaguchi Prefecture, Japan. Its final capacity will be 2,000 t/yr, although only the first stage, a 1,000-t/yr-capacity unit, has been completed. The company will add additional capacity as markets dictate; increased sales are anticipated for iron blast and electric furnace, glass fusing, and waste incineration applications (European Chemical News, 1999).

***Current Research and Technology.*—**Researchers are using several different approaches to predict the outcome of zeolite synthesis processes. One method uses algorithms to predict mathematically potential zeolite structures that could form under specific chemical conditions. The algorithm has worked successfully on simple zeolite structures, but has not been extended to include more complex zeolite structures, such as ZMS-5. Work is underway to devise a method to determine the feasibility of synthesizing a predicted structure (Moore, 1999). Other methods took a more empirical approach. The Sintef Applied Chemistry Institute in Oslo, Norway, used a multisample autoclave to perform 100 simultaneous zeolite syntheses at temperatures up to 200° C. The multisample autoclave allowed rapid investigation of the effect of a wide range of variables at one time (Dagani, 1999). Researchers at the Max Planck Institute also used a multisample autoclave approach; 37 syntheses were performed at a time. Their method differed from the Sintef method in two ways—by using 2- microliter volumes, rather than 500-microliter volumes and by adhering the zeolite products to a silicon wafer that forms the bottom of the autoclave. The advantage of adhering the zeolite crystals to the silicon wafer was that they could be automatically analyzed by using x-ray microdiffraction without additional preparation (Dagani, 1999). Finally, researchers at Purdue University developed a third variation of the multisample synthesis. They worked with 6 sets of either 8 or 19 reaction chambers and 150- or 300-microliter samples. The synthetic zeolites were recovered by using centrifugation, and the samples were analyzed automatically by x-ray diffraction or manually by scanning electron microscopy. All these techniques reduced sample preparation time, decreased reagent demand, and rapidly provided a large amount of data on zeolite synthesis (Dagani, 1999).

Outlook

Market growth for natural zeolites has slowed considerably in the United States. Domestic sales of natural zeolites have fluctuated between 30,000 and 40,000 t/yr for the past few years but can be anticipated to be in the 35,000- to 40,000-t range in the near future. Pet litter probably will remain the largest market, although sales for animal feed and soil amendment applications are approaching similar levels. Low-tonnage niche markets should offer opportunities for producers to introduce high-unit-value products, particularly for environmental applications. Markets for synthetic zeolites have grown slowly, particularly for catalysts and detergents. This trend is expected to continue, particularly in western Europe and the United States. With the recovery underway in Southeast Asia from its economic downturn, markets there should start to rebound.

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TABLE 1
DOMESTIC ZEOLITE PRODUCERS AND SUPPLIERS, 1999

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