ZEOLITES

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Domestic survey data and tables were prepared by Linder Roberts, statistical assistant.

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 of which are analcime, chabazite, clinoptilolite, erionite, ferrierite, heulandite, laumontite, mordenite, and phillipsite. More than 150 zeolites have been synthesized. Some of the more common synthetic zeolites 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 saline, alkaline lake deposits and open hydrologic systems. The deposits are in Arizona, California, Idaho, Nevada, New Mexico, Oregon, Texas, Utah, and Wyoming. The major components of these deposits are chabazite, clinoptilolite, mordenite, and phillipsite. Erionite, orthoclase and plagioclase feldspars, montmorillonite, opal, quartz, and volcanic glass are present in some deposits.

Production..—Conventional 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. The ore is crushed, dried, and milled. The milled ore may be air-classified to size the product and 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.

Six companies mined natural zeolites in the United States in 1998. Three other producers did not mine zeolites during the year, but sold from stocks or purchased zeolites from other producers for resale (table 1). In addition, Moltan Co., a diatomite producer, mined a small amount of zeolite in Nevada to add to its agricultural products (Eyde, 1999). Clinoptilolite was mined and/or processed in Nevada, New Mexico, Oregon, Texas, and Wyoming; chabazite was mined in Arizona. Total domestic production of zeolites was 38,500 metric tons (t).

American Absorbents Natural Products, Inc., completed its mill in Hines, OR. Although capacity data are not available, the plant included drying, crushing, screening, and packaging equipment. The mill will process ore from the company's Harney, OR, mine. The company will focus its sales efforts on the absorbents market, particularly pet litter, and odor-control applications (North American Minerals News, 1998). American Absorbents also entered into an agreement with Mining Hard Rock Inc. to gain access to humates, which are salts of humic acid, for the production of zeolite and humate mixtures for horticultural applications (Industrial Specialty News, 1998a). Addwest Minerals International Ltd. continued with its feasibility study on the zeolite property that it acquired from U.S. Zeolites last year (Industrial Specialty News, 1998b). The sale of American Resource Corp. was not completed in 1998, although Badger Mining Co. was still proceeding with its purchase offer.

Consumption.—Approximately 31,200 t of natural zeolites was sold in 1998, a 4% increase compared with that of 1997. Natural zeolites were sold for, in decreasing order of consumption, pet litter, animal feed, horticultural applications (soil conditioners and growth media), wastewater cleanup, odor control, desiccant, gas absorbent, catalysts, oil absorbent, aquaculture, and water purification. Animal feed, horticultural, and pet litter applications dominated the zeolite business, accounting for more than 70% of the domestic sales. Sales for animal feed, aquaculture, fertilizer, horticultural, oil absorbents, and wastewater treatment increased, and sales for odor control, pet litter, water purification decreased. The largest increases were for horticultural applications and wastewater cleanup.

Prices.—Prices for natural zeolites vary 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 -40 to -325 mesh ground material. For consumer products, such as pet litter, fish-tank media, or deodorant applications, prices ranged from $0.50 to $4.50 per kilogram (Holmes, 1994). 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.—Imports of natural zeolites were estimated to be less than 200 t, and exports were estimated to be less than 1,000 t in 1998.

World Review.—Worldwide production of natural zeolites was estimated to be between 3 million and 4 million metric tons (Mt). Estimates for individual countries were China, 2.5 Mt; Cuba, 500,000 t to 600,000 t; Japan, 140,000 t to 160,000 t; the United States, 38,500 t; Hungary, 10,000 t to 20,000 t; Slovakia, 12,000 t; Georgia [republic of the former Soviet Union (FSU)], 6,000 t; Canada, Italy, and other republics of the FSU, 4,000 t each; Bulgaria, 2,000 t; and South Africa 1,000 t to 2,000 t. Small amounts of natural zeolites also were produced in Argentina, Australia, Germany, and Indonesia.

Mining has begun in the Jewish Autonomous Region in the Khabarovsk Territory of eastern Russia. Resources in the area are estimated to be 80 Mt, and mining is expected to approach 2,000 tons per month. The initial shipments were for water purification applications (Industrial Minerals, 1998b).

Current Research and Technology.—In 1998, research included horticultural (slow release fertilizers, soilless growth media), agricultural (poultry feed additives, controlling ammoniacal nitrogen in manure), catalysis (NO_x reduction, hexane isomerization), ion exchange, molecular sieving, and miscellaneous applications as plastics filler and a concrete additive.

Sorption is just one of the commercially exploited properties of zeolites. The reverse process, desorption, also is critical for many applications. Research was conducted at the New Mexico Institute of Mining and Technology on the desorption of chromate from surface-modified zeolite (SMZ) ions. The purpose was to determine if SMZ could be used as a permeable barrier for remediation of chromate-contaminated ground water. If the chromate could be readily extracted under normal ground-water conditions, then it would not be effective. Ten extraction methods were tested. Clinoptilolite from New Mexico was first treated with hexadecyltrimethylammonium complexes to form a surfactant bilayer on the surface of the zeolite. The SMZ was placed in solution with potassium chromate at various concentration levels and shaken. Various solvents then were used to extract the sorbed chromate. Most of the solvents extracted less than 20% of the sorbed chromate, suggesting that SMZ may be a viable option for remediation of chromate contaminated ground water (Li, 1998).

In a study at the University of Ankara in Turkey, the ability of a bentonite and clinoptilolite mixture to remove heavy metals from landfill effluent was tested. Usually, bentonite is used to seal landfills and prevent contamination of ground water from landfill effluent. The objective of this study was to determine if bentonite-amended zeolite beds also could effectively remove heavy metals from a landfill effluent and reduce leachate-based hazards. Clinoptilolite was ground to sand size and blended with bentonite. The bentonite-to-zeolite ratio of 0.04 was used for ion-exchange testing. The zeolite and bentonite mixture was found to have removed more than 90% of the lead, zinc, copper, and chromium and more than 80% of the arsenic and nickel from the landfill effluent through ion exchange (Kayabali and Kezer, 1998).

Clinoptilolite from South Dakota was tested as a single-use sorbent for metals found in water and waste streams. The sample was tested before and after acid washing to remove calcium carbonate. Synthetic and natural solutions containing copper, lead, and zinc were used. For the unwashed sample, 99.3%, 99.8%, and 96.5% of the copper, lead, and zinc, respectively, were rapidly removed from the synthetic solutions. Extraction was less efficient for the acid washed sample and for the natural solutions. Competition from other ions in solution may have affected the exchange process (Olin and Bricka, 1998).

On a more general note, three papers on different aspects of the zeolite industry were published. One was a bibliography of papers, published between 1993 and 1997, that discussed the occurrences, properties, and uses of zeolites from sedimentary deposits (Sheppard, 1998). A second paper reviewed research conducted in recent years on zeolite catalysis and prospects for the future; the bulk of the discussion was on synthetic zeolites (Hoelderich and Heinz, 1998). The third paper discussed the classification and nomenclature for natural zeolite minerals (Coombs, 1998).

Synthetic Zeolites

Catalysts.—W.R. Grace and Co. agreed to purchase Crosfield Group from ICI PLC for $455 million. Crosfield produced synthetic zeolites, silicates, silica, and hydroprocessing and specialty catalysts, which will complement Grace's current product line (Chemical & Engineering News, 1998a; Chemical Market Reporter, 1998b). PQ Corp. began construction on its pressure-synthesized zeolite plant in Kansas City, KS. The plant will be used by Zeolyst International, a joint venture between PQ Corp. and Shell Corp., for synthesizing zeolites for petrochemical processing (Chemical Week, 1998b).

Detergents.—In 1997, domestic sales of synthetic zeolites for detergents were estimated to be 350,000 t. Growth in 1998 was expected to be approximately 4%, similar to that of 1997. The growth in 1998 resulted more from manufacturers reformulating their products than market growth (Chemical Market Reporter, 1998a; Chemical Week, 1998a).

Molecular Sieves.—PQ Corp. began operating its 18,000 metric-ton-per-year (t/yr) capacity molecular sieve plant in Kansas in late 1997. The products initially will be marketed as sieves for two-pane insulated glass applications, a market that consumed 45,000 t/yr in 1998. Molecular sieves were a new market area for PQ Corp. (Chemical Market Reporter, 1998c).

UOP LLC purchased a 5,000-t/yr-capacity molecular sieve facility in Germany from Bayer AG (Industrial Minerals, 1998a).

Tricat Catalytic Products GmbH began construction of a $31.6 million plant in Bitterfeld, Germany, for synthesizing molecular sieves. Its initial capacity will be 2,000 t/yr. The plant will be constructed by Lurgi Oel Gas Chemie for Tricat (Chemical Week, 1998d; European Chemical News, 1998).

Current Research and Technology.—Researchers at Shell Chemicals, Zeolyst, and the University of Valencia in Spain developed a method to create thin zeolite sheets. By adjusting the chemistry and using sonic vibrations, the zeolite precursors are split into thin sheets, thereby exposing more reactive sites. Tests demonstrated that catalytic cracking of n-decane and diisopropylbenzene was more efficient than with conventional zeolite catalysts (Chemical Week, 1998c).

A method of incorporating organic molecules into the zeolite β structure was developed by researchers at the California Institute of Technology. The organic structures are derived from 2-phenyethyl-trimethoxysilane, which is added at the start of the synthesis process. Unwanted structures are removed chemically after synthesis is completed. The resulting zeolite acts as a molecular sieve, allowing reactants of specific sizes and shapes to enter the zeolite structure and be catalyzed by the organic molecules, which have been incorporated into the structure (Chemical & Engineering News, 1998b).

Outlook

Sales of natural zeolites have been around 30,000 t for the

past 4 years, fluctuating only slightly. This trend is not likely to change in the next 2 to 3 years. Sales for animal feed and fertilizer applications soon may surpass those for pet litter if the rapid growth exhibited by these two markets for the past few years continues.

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TABLE 1
DOMESTIC ZEOLITE PRODUCERS, 1998

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