

# ZEOLITES

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**Domestic survey data and tables were prepared by Raymond I. Eldridge III, 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 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 packaged in either 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 nine companies with responses accounting for approximately 90% of the production and consumption data.

Eight companies mined natural zeolites in the United States in 2000. 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 and Nevada; clinoptilolite was mined and processed in California, Idaho, Nevada, New Mexico, Oregon, Texas, and Wyoming; and mordenite was mined in Nevada. The largest producing State was New Mexico. Total domestic production of zeolites was estimated to be 41,800 metric tons (t) compared with an estimated 43,000 t in 1999.

GSA Resources, Inc., announced plans to acquire or collaborate with other suppliers of specialty minerals. The company's intent was to produce entire systems, rather than single products, that can be used for remediation of hazardous wastes, odor control, and other sorption applications (North

## Zeolites in the 20th Century

The mining of zeolites is a recent activity compared to many other mineral commodities. In 1900, there was no commercial mining of natural zeolites. Sustained mining of natural zeolites did not begin until the early 1970s. The delay in the start of zeolite mining can be attributed mainly to the fact that, prior to the 1950s, natural zeolites were originally considered to be mineralogical curiosities that filled vugs and fractures in igneous rocks, and commercial deposits were not known. In the late 1950s, large deposits of zeolite-rich volcanic tuffs were discovered in the western United States. Between 1950 and the mid-1980s, many large mining and petroleum companies conducted exploration programs. While these programs uncovered additional reserves, markets for natural zeolites did not develop as anticipated, and only a few hundred tons of zeolites were mined annually through the mid-1970s. By the mid-1980s, annual production and sales of natural zeolites were still below 10,000 metric tons, so the major companies withdrew from the industry. Companies better suited to small-scale mining then stepped in and have slowly developed the natural zeolite market into the small yet

sustainable industry that exists today.

In 2000, there were 41,800 tons of natural zeolites mined in several States in the Western United States. This is about triple the production and sales in the 1980s but less than the peak production and sales of 53,000 tons attained in 1994. Even with the short mining history, the industry has shifted its focus. Initially, zeolites were treated as bulk commodities, with producers seeking large volume markets. Pet litter applications, for which zeolites were well suited, became the mainstay of the industry, representing more than 50% of sales of natural zeolites annually in the mid-1980s. Producers, however, realized that low-value bulk sales of zeolites could not sustain the industry forever and began developing value-added applications. As a result, pet litter markets, while still important, commanded a far smaller share of the overall market in 2000, with the growth of horticultural (soil conditioners and fertilizer carriers), animal feed, waste water treatment, desiccant, water purification, and gas absorbent markets.

American Minerals News, 2000b). Centre Capital rescinded its purchase of American Absorbents Natural Products, Inc. (AANPI), from Equitable Assets Inc. The transaction was to have involved the exchange of one million shares of Centre Capital stock valued at more than \$11.3 million. AANPI, one of the larger producers of zeolite-based cat litter, still holds its zeolite deposit in Oregon (Moore, 2000; North American Minerals News, 2000c).

**Consumption.**—An estimated 30,900 t of natural zeolites was sold in 2000 in the United States compared with an estimated 35,000 t in 1999. 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, fungicide or pesticide carriers, desiccants, gas absorbents, catalysts, water purification, aquaculture, and oil absorbents. Pet litter, animal feed, and horticultural applications accounted for more than 70% of the domestic sales tonnage. Sales to individual markets did not change significantly compared with those of 1999.

**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 less than 100 t, and exports were estimated to be less than 200 t in 2000. The bulk of the international trade appears to be in synthetic zeolites.

**World Review.**—Worldwide production of natural zeolites was estimated to be between 3 million and 4 million metric tons (Mt) based on 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, 41,800 t; Hungary, 10,000 to 20,000 t; Slovakia, 12,000 t; Georgia, 6,000 t; New Zealand, 5,000 t; Greece, 4,750 t; Australia, Canada, Italy, and other republics of the former Soviet Union, 4,000 t each; 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.

**Australia.**—Talon Resources NL announced plans to develop horticultural and environmental products that were zeolite-based. The company has made its first sales to the agricultural market. The company also commissioned a zeolite production plant in Duarina, Queensland (Countryman, 2000).

**Canada.**—C<sub>2</sub>C Mining Corp. completed an animal feed study with Klok Feeds, which raises 40,000 feeder hogs annually. The zeolite was mixed with the feed ingredients, replacing the bentonite and lignite sulfinate binders normally used. The study revealed that the addition of zeolites in the feed reduced odors and increased feed conversion rates. C<sub>2</sub>C also worked with Amoco Canada Petroleum Co. Ltd. to conduct soil remediation tests using zeolites. Plans are to bring the C<sub>2</sub>C deposit into

production by the end of 2001. C<sub>2</sub>C also signed an agreement with Zeo-Tech Enviro Corp., which holds the rights to a zeolite deposit near Princeton, British Columbia. C<sub>2</sub>C will hold a 25% interest in the zeolite holdings and a new processing plant that is expected to be constructed by the end of 2001. In return, Zeo-Tech Enviro will have access to C<sub>2</sub>C's patented processing methods for specialty zeolite products and will receive a 25% share of C<sub>2</sub>C's zeolite properties near Kentville, Nova Scotia (North American Minerals News, 2000a).

**Ukraine.**—The Government of Ukraine has placed a 25% share of Zatissyansky Chemical Plant up for sale. The Government owned about 60% of the company. Zatissyansky Chemical is the only Ukrainian producer of zeolite powders (Industrial Minerals, 2000).

**Current Research and Technology.**—Researchers examined the exchange of sodium by cesium and strontium in analcime-bearing assemblages. The exchange was conducted at 250° C to 300° C and 39.7 to 85.8 bars of pressure in pure water and chloride solutions. A continuous solid solution between sodium and cesium and sodium and strontium did not occur. Thermodynamic calculations indicated that leaching would be minimized at about a pH of 8, suggesting that an analcime-albite-paragonite assemblage may act as a barrier to the migration of cesium and strontium from radionuclide-contaminated materials. This is an important consideration for underground storage of high-level radioactive wastes (Redkin and Hemley, 2000).

## Synthetic Zeolites

**Catalysts.**—Lurgi GmbH designed a fixed-bed catalytic cracker that can be incorporated into a naphtha steam cracker system. The fixed-bed system converts olefins into propylene and ethylene. The system is reported to convert 60 weight percent of C<sub>4</sub> and C<sub>5</sub> components from the steam cracker directly to propylene. Pilot plant studies are planned by Linde Division, Union Carbide Corp., who licensed the process from Lurgi. The catalytic cracker uses ZMS-5 zeolite in a fixed bed at 500° C and 1 to 2 bars to make the conversion. Coking and polymer formation are reduced through the introduction of steam. Cycle times are several weeks, and anticipated zeolite life is 15 months (European Chemical News, 2000b).

The Institut Francais du Petrole developed a new zeolite-based isomerization catalyst. The catalyst is reported to increase paraxylene yield to 93% compared with 88% with typical mordenite-based catalysts. Pilot plant testing has shown that paraxylene yield losses were reduced by 40% to 50%. The system also can operate under milder operating conditions, reducing operating and capital costs (European Chemical News, 2000a).

**Detergents.**—There was an estimated 1.04 Mt of synthetic zeolite used worldwide in detergents in 1998. This represents the largest volume segment of the synthetic zeolite market. In the United States, demand for powder detergents has declined. Liquid detergents surpassed powder detergents for the first time in 1998. Powders are still preferred in Europe but have lost some popularity with the consuming public. The declining demand, coupled with additional capacity that came online in the early 1990s, has resulted in overcapacity in Japan, North

America, and Western Europe; projected growth in detergent uses in these markets is -1%, -2%, and 0.4%, respectively (LePree, 2000). In Western Europe, zeolites were estimated to account for 75% of the builder market for home laundry detergents with phosphates making up the remaining 25%. Builders are used to reduce water hardness. The decision to allow phosphate-based detergents to carry the European Union's "eco-label" resulted in market gains in 1999. Despite gains in Asia, phosphate-based detergents may be threatened by new legislation to remedy lake eutrophication, the process of excess nutrients promoting plant growth at the expense of animal life, in some regions in China. If demand for zeolite builders grows in China, plants in Southeast Asia will supply that market (Chemical & Engineering News, 2000b).

**Molecular Sieves.**—PQ Corp. announced that it would withdraw from the molecular sieve adsorbent market in 2000. The company cited excess supplies and consequent marginal returns for the withdrawal. PQ will continue to supply synthetic zeolites for adsorption and separation, detergents, and chemical and petrochemical applications (Walsh, 2000).

Tricat Zeolites GmbH constructed a new plant in Bitterfeld, Germany, for manufacturing zeolites and sieves (European Chemical News, 2000d).

**Current Research and Technology.**—Demand for catalysts for petroleum refining is expected to increase at a rate of 1.9% per year between 1998 and 2003 as the demand for petroleum increases. One of the issues facing refiners is the reduction in the permissible sulfur content of gasoline. In 1999, the U.S. Environmental Protection Agency proposed reducing sulfur limits from 330 parts per million (ppm) to 30 ppm. Similarly, in Europe, proposed regulations will limit permissible sulfur content to 150 ppm in 2000 and 50 ppm in 2005. Emphasis is being placed on fluid catalytic cracking (FCC) units because FCC products contribute more than 90% of the sulfur in gasoline. Hydrocracking the FCC feed can reduce sulfur content but is expensive. Despite this, predictions were for growth in precious metals and zeolites for hydrocracking to increase. Another approach is to convert some of the sulfur species into forms that are more easily removed from gasoline. For example, catalysts that result in reaction pathways that lead to the formation of hydrogen sulfide would reduce sulfur in gasoline. Another approach is to develop catalysts that react with specific sulfur compounds that are difficult to remove from gasoline, such as benzothiophene. There also is a need to reduce olefin content of gasoline in response to new environmental regulations. Modified FCC catalysts and ZMS-5 zeolite have been used to control olefin content (European Chemical News, 2000c; Oil & Gas Journal, 2000a).

A mesoporous (large pore structure) zeolite catalyst has been developed by Haldor Topsoe Research Laboratories of Denmark for the epoxidation of cyclohexene. The zeolite structure contains titanium cations and, with the mesoporous structure, is chemically more active than conventional titanium-containing zeolite catalysts. The zeolite is prepared using an excess zeolite gel and a carbon matrix. The carbon is removed after synthesis by combustion (Chemical & Engineering News, 2000c).

A study was conducted on erosion of the FCC unit by FCC catalysts. FCC catalysts, typically composed of aluminum and

silica, can erode portions of the FCC unit not properly protected by linings. Attrition resistance was one characteristic that was considered critical. Attrition-resistant particles resulted in generation of fewer fine particles and fewer sharp-edged, irregular particles that are created when larger particles fracture. Attrition of the catalyst can result in particle losses in some FCC units, while those units designed to minimize fines loss will experience an increase in particle bulk density. Sharp, irregular particles erode the FCC unit more rapidly than spherical particles. The study also showed that increased cyclone velocity magnifies attrition rates and is influenced by particle density and size. In general, higher particle densities and smaller sizes tended to reduce erosion rates (Oil & Gas Journal, 2000b).

Scientists take advantage of the rigid structure and the pores and channels of zeolites to control the reactions. The pores and channels define the size of the molecules that can form and diffusion rates within the structure and even cause selective orientation of the molecules within the structure so that only one face of a molecule can react (Chemical & Engineering News, 2000a). For example, scientists at Tulane University in New Orleans working with researchers at the University of British Columbia in Vancouver created a stable chiral zeolite structure by loading an existing zeolite structure (zeolite Y) with chiral organic molecules. Previously, researchers had unsuccessfully attempted to synthesize the chirally modified zeolite structures. The use of the modified zeolite structure resulted in a high stereoselectivity during the reaction process. Sodium in the Y zeolite was found to be critical. When cesium, lithium, and potassium were exchanged for the sodium, enantiomeric excesses decreased. The chirally-modified zeolite structure will be used to synthesize molecules that are normally difficult to form and also to produce odd-shaped and highly strained chemical species (Chemical & Engineering News, 2000d).

Research continued on the use of zeolites to remove nitrogen oxides ( $\text{NO}_x$ ) from automobile exhaust. Chemists at the Catholic University of Leuven in Belgium, used the sodium variety of zeolite Y to absorb NO and  $\text{NO}_2$  as dinitrogen trioxide ( $\text{N}_2\text{O}_3$ ) from engines that use excess air to reduce carbon dioxide emissions. Barium oxides used in lean-burn engines work best with very low sulfur fuels. The zeolite Y adsorbent is not affected by the presence of sulfur oxides, and the absorption process can be reversed. This suggests the possibility of recirculated trapped  $\text{NO}_x$  into the intake air so it can be converted to nitrogen gas during the combustion process (Chemical & Engineering News, 2000e).

## Outlook

Market growth for natural zeolites will continue to be slow. Growth in the major market, pet litter, has been slight for the past few years and is not expected to increase significantly. Domestic sales of natural zeolites probably will be between 30,000 t to 35,000 t for the next few years. Pet litter probably will remain the largest market. As it has for the past few years, low-tonnage niche markets should offer opportunities for producers to introduce high-unit-value products, particularly for environmental applications. Markets for synthetic zeolites in the United States will slow. Detergents sales have stagnated

and possibly declined slightly in recent years. Sales in Europe also may slow as phosphate-based detergents regain acceptance. Possible growth can occur in China depending on the effectiveness of new legislation discouraging phosphate builder use. Projections for growth in the catalyst for petroleum refinery market are positive with the anticipated growth in demand for gasoline worldwide.

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TABLE 1  
DOMESTIC ZEOLITE PRODUCERS AND SUPPLIERS, 2000

State and company	Type of zeolite
Arizona:	
GSA Resources, Inc.	Chabazite.
UOP Inc.	Do.
California, KMI Zeolite, Inc.	Clinoptilolite.
Idaho, Steelhead Specialty Minerals, Inc.	Do.
Nevada:	
Ash Meadows Zeolite, LLC	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.