

# ZEOLITES

By Robert L. Virta

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, and 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, which is stripped for processing by using front-end loaders or tractors equipped with ripper blades. The ore is dried and then crushed by using either jaw crushers or roller mills. The milled ore is packaged directly for shipping or is screened to remove fine material when a granular product is required. In some cases, a pelletized product also is produced.

Six companies mined natural zeolites in the United States in 1996. (See table 1.) Although Steelhead Specialty Minerals did not mine in 1996, the company reported sales of natural zeolites. Clinoptilolite was mined and/or processed in Nevada, New Mexico, Oregon, and Texas; chabazite was mined in Arizona. Total domestic production was 39,300 metric tons.

**Consumption.**—About 28,500 tons of natural zeolites was sold in 1996, a 16% decrease from that of 1995. The various end uses for natural zeolites included in decreasing order of consumption, pet litter, animal feed, fertilizer carrier, odor control, oil absorbent, aquaculture, waste-water cleanup, catalysts, desiccant, gas absorbents, water purification, and paper applications. Pet litter and animal feed applications accounted for over 70% of the sales. Consumption increased for animal feed, aquaculture, catalyst, fertilizer carrier, gas absorbent, oil absorbent, paper, water purification, and waste-water cleanup applications. Sales for animal feed and fertilizer applications increased significantly, but in all other cases, the increases in sales were less than 200 tons. Consumption

declined for desiccant, odor control, and pet litter applications. The largest decrease was for pet litter applications.

The American Resources Corp. Inc. (ARC) continued its research into additional markets for clinoptilolite from its Ash Meadows, NV, deposit. In 1993, ARC had purchased the Ash Meadows deposit from East West Minerals Inc., as well as a mordenite deposit in Rome, OR, and a clinoptilolite-chabazite deposit in Bowie, AZ. The company currently markets zeolites for horticultural applications and odor control in nonagricultural and agricultural fields. ARC is looking to land-reclamation projects, hydroponics, aquaculture, and gas separation as some of the more lucrative future markets for their zeolites (North American Minerals News, 1996).

**Prices.**—Prices for natural zeolites vary with zeolite content and processing.

For industrial or agricultural applications, prices ranged from \$30 to \$70 per ton for granular products down to 40 mesh and from \$50 to \$120 per ton for -40 mesh to -325 mesh ground material. For consumer products, such as for 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.**—Less than 100 tons of natural zeolite was imported and from 400 to 500 tons was exported in 1996, according to the Journal of Commerce (JoC) Port Import/Export Reporting Service. Most of the zeolites imported into the United States in 1996 were either synthetic or mineral specimens, not bulk natural zeolites. The JoC data does not include zeolites imported from or exported to Canada and Mexico (Journal of Commerce, 1996).

**World Review.**—Worldwide production of natural zeolites was estimated to be more than 3 million tons. Estimates, in tons, for individual countries were Bulgaria, 45,000; Canada, 4,000; China, 2.5 million; Cuba, 500,000 to 600,000; Hungary, 10,000 to 20,000; Italy, 4,000; Japan, 140,000 to 160,000; Slovakia, 12,000; South Africa 1,000 to 2,000; the United States, 39,300; and the former U.S.S.R., 10,000. Small amounts of natural zeolites also were produced in Argentina, Australia, Germany, and Indonesia. Zeolites were used in Bulgaria in agricultural applications, such as animal feed additives, odor control, and soil amendments. Much of the zeolite production was used in pozzolanic cements and various other industrial and agricultural applications in China, and agricultural applications such as animal feeds and soil additives, and unspecified export markets in Cuba. In Japan, zeolites were used for water treatment, desiccants, agricultural applications (that is, animal feed and insecticide carrier) and as a paper filler.

Silver and Baryte Ores Mining Co. SA announced that it would begin mining and processing natural zeolites in northern Greece. The plant will produce five grades of clinoptilolite and have a capacity of 50,000 tons per year (Industrial Minerals, 1996).

**Current Research and Technology**—The U.S. Geological Survey tested the affinity of clinoptilolite-rich rocks (CRR) from six deposits in the western United States for nitrogen compounds in fertilizers. The objective was to determine the effectiveness of using CRR as fertilizer carriers; that is, would they would enhance the cation-exchange capacity of soils to which they were applied and would they slowly release fertilizers applied to the soil. Six low-sodium CRR's were exposed to potassium chloride, sodium chloride, and ammonium chloride solutions, rinsed, dried, and analyzed for potassium, calcium, and nitrogen content. The pH's of the solutions also were tested after the exchange procedure. Exchange capacities for ammonium ( $\text{NH}_4^+$ ) varied considerably. Amounts of nitrogen (in the form of  $\text{NH}_4^+$  and in soluble forms of ammonium and nitrate salts) after exposures to 57.1 weight percent ammonium nitrate solutions ranged from 94 to 164 pounds of nitrogen per ton of CRR. During the exchange process, calcium and potassium were lost from the clinoptilolite structure. The study concluded that CRR showed potential for increasing the cation-exchange capability of the soil by temporarily extracting  $\text{NH}_4^+$  when highly soluble  $\text{NH}_4^+$  rich fertilizers are applied to crop fields (Desborough, 1996).

Zeolite fines were pelletized by using a lignosulfonate as the binder. The lignosulfonate was burned off in an oxygen-reducing environment, leaving a carbon residue. The resulting pellets were durable, permeable, and insoluble in water. The agglomerated pellets had more ion-exchange capacity than untreated zeolites and were capable of removing high concentrations of lead (Peterson, 1996).

A 2-year trial of a zeolite-based heat-storage system began in the Munich, Germany, school system. The trial uses 7 tons of zeolite that is dried by a 130 °C steam-based heating system during off-peak hours. Moist air is drawn over the dried zeolite during the day, and the heat released by the zeolites (heat of adsorption) is used to warm the water in the building's conventional warm-water heating system. The energy stored in the zeolite beds ranges from 130 to 200 kilowatt-hours per cubic meter, which is two to three times that of warm-water storage systems (Chemical Engineering, 1996b).

## Synthetic Zeolites

**Absorbents**.—Crosfield Chemicals developed an absorbent that selectively absorbs water in the presence of small molecules. Its uptake of moisture is slower than other materials already in use, making its manufacture and storage easier. Potential uses are in zinc and aluminum anticorrosion paints (European Chemical News, 1996a). Corning Inc. developed a catalyst that uses a zeolite adsorber to reduce cold-start emissions. Cold exhaust is diverted through the zeolite adsorber until the catalytic converter reaches operating temperature.

Hydrocarbon emissions are reduced to 0.03 gram per mile, well below the U.S. standard set for 2000 (Chemical and Engineering News, 1996b).

**Catalysts**.—UOP Corp. installed a 66,000-ton-per-year cumene production unit for JLM Chemicals Inc. in Illinois. The unit produces a 99.95% pure cumene product and uses a zeolite catalyst instead of a solid phosphoric acid catalyst because the zeolite catalysts increases plant capacity (European Chemical News, 1996b).

Enichem S.p.A. also commissioned a zeolite-based cumene production plant near Porto Torres, Sardinia. Capacity will be increased by 30% to 40% with a reduction in operating costs by 20% to 30% (Chemical Engineering, 1996a).

**Detergents**.—PQ Corp. introduced a new zeolite for high-pressure-spray car-washing applications. The zeolite acts as a water softener and a cleaner and polisher (Chemical Market Reporter, 1996).

**Current Research and Technology**.—A high-silica zeolite with pore openings formed by 14, rather than 12 atoms, has been developed at the California Institute of Technology and the University of Texas. The new form reportedly is stable at 1,000 °C. The larger pore openings will enable the zeolite to catalyze a wide range of hydrocarbon reactions (Chemical Week, 1996). Silica-free zeolite  $\beta$  and aluminum-free, titanium-containing zeolite  $\beta$  have been synthesized without a need for zeolite seed crystals. The zeolites nucleated spontaneously and grew in a hydrothermal system containing tetraethylammonium and fluoride ions. Silica-free zeolite  $\beta$  has potential applications in acid-catalyzed reactions. Both varieties are hydrophobic and have improved thermal stability over conventionally crystallized forms (Chemical and Engineering News, 1996b). A new method of producing synthetic zeolite structures was developed at the Royal Institution and the University of Liverpool. With this technique, templates that are typically organic are added to the solution before hydrothermal synthesis begins. The catalyst framework condenses around the templates, which are later removed, and a structure with predetermined pores and channels remains. The method will allow researchers to synthesize zeolites with specific microporous structures (European Chemical News, 1996c).

## Outlook

The outlook for natural zeolites remains good. Producers are expanding their market lines and are working more closely with customers to cater to the customer's specific needs. Sales should continue to be in the 30,000- to 40,000-ton-per-year range.

With regard to synthetic zeolites, growth rates are expected to slow down compared with the past several years. Detergent markets in North America should show slow growth with the bulk of substitution of zeolites for phosphates completed. Although fluid cracking catalyst (FCC) markets declined in 1995 and 1996 owing to lower demand, FCC manufacturers believe that Asian markets will increase in the near future.

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TABLE 1  
DOMESTIC ZEOLITES PRODUCERS, 1996

State and company	Type of zeolite
Arizona:	
GSA Resources Inc.	Chabazite.
UOP Inc.	Do.
Nevada:	
American Resource Corp.	Clinoptilolite.
New Mexico:	
St. Cloud Mining Co.	Do.
Oregon:	
Teague Mineral Products Co.	Do.
Texas:	
Zeotech Corp.	Do.