ZEOLITES

By Robert L. Virta

Natural Zeolites

Zeolites are hydrated aluminosilicates of the alkaline and alkaline-earth metals. Approximately 40 natural zeolites have been identified over the past 200 years, the most common of which are analcime, chabazite, clinoptilolite, erionite, ferrierite, heulandite, laumontite, mordenite, and phillipsite. Zeolites are commercially valuable because of their unique ion-exchange, molecular sieving, and catalytic properties.

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 located 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 feldspar, montmorillonite, opal, quartz, and volcanic glass may be present in some deposits. The composition of these deposits was determined primarily by the temperature and pressure of formation and the chemistry of the altering fluids. If the alteration process has gone to completion, the zeolite content of portions of some deposits may approach 100%.

***Production.*—**Conventional mining techniques were used in the mining of natural zeolites. The overburden was removed to allow access to the ore and the ore was stripped for processing using front-end loaders or tractors equipped with ripper blades. Fractured ore was dried and then crushed using either jaw crushers or roller mills. The crushed ore was packaged directly for shipping or was screened to remove fine material when a granular product was required.

Eight companies mined or sold natural zeolites in the United States in 1994. Clinoptilolite was mined and/or processed in California, Nevada, New Mexico, Oregon, and Texas; chabazite was mined in Arizona. Total domestic production was 52,800 metric tons.

***Consumption.*—**Sales were 35,200 tons in 1994, a slight decrease from that of 1993. Natural zeolites were used for pet litter, animal feed supplement, fertilizer carrier, oil absorbent, odor control, aquaculture, horticultural applications, desiccants, gas absorbents, catalysts, and water purification, in decreasing order of consumption. As in previous years, over 50% of the natural zeolite was consumed as pet litter. Consumption patterns for most applications did not change. The only exception was with pet litter applications, where the reported consumption of zeolites declined. The properties that made natural zeolites commercially valuable included ammonium adsorption (aquaculture, aquarium filters, odor control applications, pet litter, and water purification), moisture adsorption (desiccants, odor control, and pet litter), and ion-exchange capabilities (wastewater cleanup and water purification).

Successful marketing of natural zeolites is dependent on selecting the proper zeolite for a specific application. A review paper discussed the properties of zeolites and recommended that information such as form, color, crystal structure, pore diameters, void volume, packing, etc. be determined for each zeolite product. This information will help the customer choose the proper zeolite for a specific application.[1]

***World Review.*—Australia.—**Zeolite Australia Ltd. worked with Global Soil Systems and Envirosciences Pty. Ltd. to market its natural zeolites. Their primary markets were animal feed supplements and acid mine drainage clean-up.[2]

Canada.—Princeton Zeolite Products Inc. and Princeton Industrial Mineral Joint Venture signed a letter of intent to sell their zeolite properties in British Columbia to I.M.P.A.C.T. Minerals Inc. I.M.P.A.C.T. Minerals will begin a bulk sampling program of the deposit and do market development.[3]

Cuba.—The International Marketing Firm for Industrial Minerals S.A. reported zeolite production of 600,000 tons per year in Cuba. Exports, primarily to Brazil, Colombia, Ecuador, France, Italy, Mexico, and Spain, were reported to be greater than in the previous 4 years combined.[4]

***Current Research and Technology.*—**The U.S. Bureau of Mines continued its work on using natural zeolites for treating acid mine drainage. As part of the study, the recycle characteristics of zeolites were determined. No decrease in the cation exchange capacities of the zeolites tested were detected after 40 loading and stripping cycles. Other work focussed on the removal of arsenic and other heavy metals from wastewaters. One study demonstrated that a calcium clinoptilolite removed low levels of cadmium, manganese, and zinc from mine wastewater, providing additional options for sludge disposal and lower costs for water treatment. Another study involved the pretreatment of natural zeolites with ferric sulfate solutions. The iron precipitates on the zeolites served as the collector for arsenic.

Synthetic Zeolites

Producers of synthetic zeolites announced plans to construct new plants and expand existing plants and introduced several new zeolites. Akzo Nobel began construction of a zeolite plant in Pasadena, TX and W. R. Grace announced plans to build a zeolite plant in Louisiana that will supply catalysts to its fluidized cracking catalyst plant. This activity is in response to growing demand for refinery catalysts in Asia.[5] United Catalysts Inc. introduced a new zeolite catalyst for use in manufacturing ethylbenzene from benzene and ethylene feedstock. The zeolite was developed jointly with Fina Technology. ABB Lummus Crest Inc. and Sinopec Technology Co. began work on commercializing its process for manufacturing ethylbenzene from benzene and dilute ethylene feedstock. The process uses a pentasil-type zeolite catalyst. The zeolite is not affected by impurities, such as H_2S, H_2O, CO, and CO_2, thereby reducing the need for feedstock pretreatment.[6] Engelhard Corp. introduced a zeolite catalyst for fluid catalytic cracking applications. The zeolite is more tolerant to nickel and vanadium and allows better control of the residual feedstock processing than other zeolite catalysts.[7] Crosfield introduced a new zeolite, A24, which was developed specifically for detergent use. The zeolite consists of smaller crystallites and has better calcium and magnesium exchange properties than other detergent-grade zeolites.[8]

Two companies announced plans to expand facilities that use synthetic zeolites. Georgia Gulf will upgrade its Pasadena, CA, cumene facility to use zeolite-based catalyst technology.[9] Lyondell Petrochemical Co. announced plans to add 2,000 to 3,000 barrels per day capacity to its zeolite-based methyl tert-butyl ether process line.[10]

Current Research and Technology.— Mobil Research and Development Corp. developed a new zeolite structure. The structure is composed of cages with dimensions of 0.71 by 0.71 by 1.82 nanometers and 10-ring apertures. Hexamethyleneimine was used as the template during the synthesis process. The zeolite may be synthesized as an aluminosilicate or a borosilicate.[11]

In other research, scientists at Perdue University synthesized oriented zeolite crystals. The crystals were grown on a gold coated silicon substrate which had been modified with an organophosphate. Oriented growth was largely attributed to the organophosphate coating. Possible uses for oriented zeolite crystals include catalytic membranes or chemical sensors for environmental monitoring.[12]

Surface modification improved the sorption characteristics of clinoptilolite for oxyanions. Clinoptilolite was treated with hexadecyltrimethylammonium (HDTMA). The surface-modified zeolite removed chromate, selenate, and sulfate from solution while the untreated zeolite did not remove these species. Anion retention was attributed to the formation of HDTMA-anion precipitates on the zeolite surface.[13]

The National Institute of Standards and Technology awarded a $2 million grant for a project to synthesize catalysts, including zeolites, on a microcrystalline scale. The objective is to synthesize crystals of uniform size and composition. These catalysts could exhibit unique properties that could improve reactivity and selectivity.[14]

Outlook

Mining and sales of natural zeolites increased from 12,000 tons in 1988 to 35,000 tons in 1994 with the peak year being 1993. Most of the sales increase resulted from the increased use of zeolites in animal feed and pet litter applications. Increases of the magnitude experienced between 1988 and 1993 are not anticipated to continue into the future. Domestic consumption for the next few years should be between 35,000 to 45,000 tons per year.

With regards to synthetic zeolites, the market with the largest growth potential are detergent applications, particularly in Asian markets. Another area for growth will be in environmental applications such as emission controls.

[1]Eyde, T. Using Zeolites in the Recovery of Heavy Metals From Mining Effluents. SME Preprint 94-16, 1994, 7 pp.

[2]Industrial Minerals (London). Zeolite Australia Marketing Drive. No. 320, May 1994, p. 9.

[3]Industrial Specialties News. I.M.P.A.C.T. Eyes Zeolite Deposit in British Columbia. V. 8, No. 16, Aug. 29, 1994, p. 3.

[4]Mining Journal. Cuban Zeolite Exports. V. 324, No. 8308, Jan. 6, 1995, p. 7.

[5]Chemical Week. Grace's $58 Million Expansion Targets Asia's Booming FCC Markets. V. 155, No. 17, p. 12.

[6]Chemical Week. UCI Makes Debut in EB Market with Zeolite Catalyst. V. 155, No. 119, Nov. 16, 1994, p. 16.

Chemical Engineering. A Zeolite Catalyst Eliminates the Need to Pretreat Ethylene Feed. V. 101, No. 12, Dec. 1994, p. 19.

[7]Chemical Marketing Reporter. Engelhard Introduces FCC Catalyst for Resid Feedstocks. V. 246, No. 16, Oct. 17, 1994, p. 24.

[8]———. Crosfield Claims Zeolite Breakthrough. V. 246, No. 1, July 4, 1994, p. 9.

[9]Chemical and Engineering News. Georgia Gulf to Upgrade Texas Cumene Facility. V. 72, No. 49, Dec. 5, 1994, p. 11.

[10]Chemical Engineering. Zeolite-Based Isomerization Cuts Cost of MTBE Production. V. 101, No. 1, Jan. 1994, p. 23.

[11]Haggin, J. Molecular Sieve with Unique Structural Features Synthesized. Chem. and Eng. News, v. 72, No. 27, July 4, 1994, p. 23.

[12]Haggin, J. Oriented Zeolite Growth on Surfaces Achieved. Chem. and Eng. News, v. 72, No. 18, May 2, 1994, p. 6.

[13]Haggerty, G. and R. Bowman. Sorption of Chromate and Other Inorganic Anions by Organo-Zeolite. Environ. Sci. Techno., v. 28, No. 3, 1994, pp. 452-458.

[14]Chemical and Engineering News. Project Targets Technology to Make Nanoscale Catalysts. V. 72, No. 48, Nov. 28, 1994, p. 32.

OTHER SOURCES OF INFORMATION

U.S. Bureau of Mines Publications

Minerals Yearbooks, annual (Also available by FAX by dialing 202-219-3644 and ordering document 860100).

Information Circular 9140.

Other Sources

Chemical and Engineering News, monthly.

Chemical Marketing Reporter, weekly.

Company annual reports.

European Chemical News, weekly.

Industrial Minerals (London), monthly.

Mining Engineering, monthly.

TABLE 1
DOMESTIC ZEOLITES PRODUCERS, 1994

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:	
Teague Mineral Products Co.	Do.
Texas:	
Zeotech Corp.	Do.