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# ZEOLITES IN 1993

### 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%.

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.

Nine companies mined or sold natural zeolites in the United States in 1993. Clinoptilolite was mined and/or processed in Idaho, Nevada, New Mexico, Oregon, Texas, and Wyoming; chabazite was mined in Arizona. Total domestic production was 41,002 metric tons. Sales were 41,643 tons in 1993, an increase of 29% from that of 1992.

Prepared in the Branch of Industrial Minerals and Branch of Data Collection and Coordination, June 1, 1994.

(Printed on recycled paper)

Natural zeolites were used for pet litter, animal feed supplement, odor control, oil absorbent, water purification, fertilizer carrier, aquaculture, desiccants, gas absorbents, and waste water cleanup, in decreasing order of consumption. As in previous years, over 50% of the natural zeolite was consumed as pet litter. The tonnage of zeolite used in animal feed and odor control applications almost doubled while pet litter applications increased 36%. Less significant increases in terms of tonnage occurred for aquacultural applications, fertilizer carriers, gas and oil absorbency, and water purification applications. Consumption of natural zeolites for desiccants and waste water treatment 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 ionexchange capabilities (waste water cleanup and water purification).

American Resources Corp. announced plans to sell its Ash Meadows clinoptilolite operation in Nevada. The deposit contains approximately 20 million tons of proven and probable reserves.<sup>1</sup>

Ion-exchange studies were conducted by the U.S. Bureau of Mines on zeolite samples from Barstow and Hector, California and Buckhorn, New Mexico. Exchange capacities for cations commonly found in acid rock drainage were determined. Cation selectivity corresponded with the sodium content of the zeolite. The selectivities were  $Ca^{2+}>Cu^{2+}$  and  $Zn^{2+}>H^+>A1^{3+}>Fe^{2+}>Mg^{2+}$  for the Barstow sample;  $H^+>Cu^{2+}>Zn^{2+}>Fe^{2+}>A1^{3+}>Ca^{2+}>Mg^{2+}$  for the Buckhorn sample; and  $Zn^{2+}>Ca^{2+}>Cu^{2+}>Fe^{2+}>H^+>Mg^{2+}>A1^{3+}$  for the Hector sample. Loading capacities also corresponded with sodium content. Capacities for  $Cu^{2+}$  and  $Zn^{2+}$ , the cations of interest in acid rock runoff, ranged from 0.28 to 0.95 milliequivalents per gram (meq/g) for copper and 0.20 to 1.20 meq/g for zinc.<sup>2</sup>

The U.S. Bureau of Mines examined four clinoptilolite samples and one phillipsite sample to determine their effectiveness for treating acid mine drainage. The zeolites were from deposits in California, Nevada, and New Mexico. Ion-exchange tests showed that the cation selectivity was Pb > Ca >Zn > Mn > Cu > Cd > Al > Ni. After 48 hours, the loading values for zinc ranged from 0.65 to 0.90 meq/g. Those of copper ranged from 0.27 to 0.70meq/g. Wastewater from the Rio Tinto mine in Nevada was passed through exchange columns containing the same five zeolite samples. Approximately 370 grams of clinoptilolite from Hector, CA was required to process 1 liter of wastewater. This compares to 403 g of phillipsite from Pine Valley, NV and 493 g, 490 g, and 546 g of clinoptilolite from Buckhorn, NM, Barstow, CA, and Death Valley, CA, respectively. Copper, iron, manganese, and zinc were reduced below drinking water standards in all cases. The pH of the wastewater increased from 2.2 to approximately 6 during processing. All of the exchanged calcium and zinc was eluted during regeneration using a 20 percent NaCl solution. Only 73%, 42%, and 79% of the copper, magnesium, and manganese, respectively, were eluted during regeneration.<sup>5</sup>

The Bureau of Mines also initiated work on the use of zeolites for purifying drinking water (removal of copper and lead) and removal of arsenic from surface water. Preliminary studies gave positive results so work is continuing in these areas.

The Montana Bureau of Mines and Geology identified 15 deposits containing natural zeolites. These deposits were located in the western part of the State in altered volcanic deposits. Clinoptilolite was the predominant zeolite. Mordenite was found in trace amounts in two deposits. Other minerals present in minor to trace amounts were quartz, opal, feldspars, smectites, biotite, glass, gypsum, and kaolin. This work was part of a larger study investigating the use of natural zeolites for reducing heavy metal concentrations in water.<sup>4</sup>

# Synthetic Zeolites

Producers of synthetic zeolites announced several expansions, closures, and sales of plants. Engelhard Corp. purchased the fluid catalytic cracking facility in Savannah, GA from Katalistiks International.<sup>5</sup> Akzo Engineering Inc. awarded contracts for the expansion of its synthetic zeolite facilities in Pasadena, TX. The expansion is scheduled for completion in 1995.<sup>6</sup> Chemicals India installed a 10,000 ton-per-year facility for producing detergent-grade zeolites.<sup>7</sup> Crosfield Chemicals announced plans to build a 60,000 ton-per-year facility for detergent-grade zeolites in Warrenton, United Kingdom. The company also announced plans to expand its production facility in Eijsden, the Netherlands.<sup>8</sup> EniChem Augusta, based in Milan, Italy and the Turkish glass and chemical manufacturer, Sisecam, announced plans to build a synthetic zeolite plant in Turkey. The companies will manufacture detergentgrade zeolites for the Mid-East markets. The plant is scheduled for completion in 1996.<sup>9</sup>

The demand for phosphate-free laundry detergents resulted in increased sales of synthetic zeolites. Domestic consumption for detergent use in 1993 was estimated to be 350,000 tons. Consumption is expected to grow to 500,000 tons by the year 2000. This compares to an estimated production of approximately 50,000 tons in 1985. While the consumption of synthetic zeolites has grown rapidly in laundry detergents, they have been less successful at penetrating the dishwashing detergent and industrial cleaner markets.<sup>10</sup>

Fluid catalytic cracking (FCC) manufacturers continued to add capacity or plan expansions to meet growing demands for FCC (Akzo Chemicals, Catalysts & Chemicals Industries Co. Ltd., Engelhard Corp., and Grace Davison). Demand for FCC's is expected to be 4.8% on a worldwide basis. Manufacturers of FCC are working more closely with domestic refiners, whose products must comply with the Clean Air Act regulations on gasoline. The objective of this cooperation is to develop products and/or processes that will give refiners a greater control of the overall gasoline compositions, including olefin and aromatics yields and end-product vapor pressure.<sup>11</sup>

A new zeolite-based process for manufacturing cumene was developed. The process uses a zeolite-containing catalyst to selectively react benzene with propylene and inhibit the oligomerization of the propylene. Earlier zeolite-based technologies required complex reactor arrangements to prevent propylene-propylene reactions. The process results in higher yield and increased product purity at a lower capital investment.<sup>12</sup>

Two zeolites that possess structures intermediate to those of ZSM-5 and zeolite-ß were developed. The prominent features of these zeolites are the 10- and 12-ring pores that intersect to produce cages that are smaller than those of ZSM-5 and larger than those of zeolite- $\beta$ . These cages should allow improved shape-selective catalysis, such as with isomerization and alkylation processes.<sup>13</sup>

Research continued on the use of zeolites for reducing NO emissions from engines. A system based on fluidized bed technology using a copper-based ionexchanged zeolite was developed. In tests, preheated diesel exhaust containing 530 parts per million NO was passed through the fluidized bed. At gas velocities of 0.2 meters per second, 99% of the soot and 80% of the NO were removed from the exhaust.<sup>14</sup> Southwest Research Institute (SRI), San Antonio, TX, continued to investigate a zeolite-based catalyst for use in lean-burn engines. The institute previously showed that the catalyst could reduce emissions by 95% and will continue to study the effects of items such as aging, water poisoning, temperature, and exhaust composition on catalyst efficiency.<sup>15</sup> A metal-exchanged zeolite catalyst reduced NO<sub>2</sub> and NO into nitrogen, water, and CO<sub>2</sub> in the presence of methane and high levels of oxygen. The catalyst is stable over a wide temperature range and was designed for use with stationary engines.<sup>16</sup>

With stricter regulation of volatile organic compounds (VOC), new technologies are emerging for the paint industry. One system that has been developed consists of a rotor that is impregnated with zeolite. It is used to remove VOC's from spray booth exhaust. The VOC's are collected on the zeolite as the exhaust passes through the rotor. The cleaned exhaust is discharged into the atmosphere. A reverse flow of air recovers the VOC's from the zeolite and transports them to a thermal or catalytic oxidizer. The zeolite can effectively remove VOC's at temperatures of  $300^{\circ}$  F, is chemical stable, and nonflammable.<sup>17</sup>

<sup>1</sup>Industrial Minerals (London). Zeolite Operation Up for Sale. No. 314, Nov. 1993, p. 23.

<sup>2</sup>Bremner, P. and L. Schultze. Exchange Characteristics of Metal Cations Commonly Found in Acidic Drainage. Pres. at the 4th Int. Conf. on Zeolites, Boise, ID, Aug. 20-27, 1993.

<sup>3</sup>Zamzow, M. and L. Schultze. Treatment of Acid Mine Drainage Using Natural Zeolites. Pres. at the 4th Int. Conf. on Zeolites, Boise, ID, Aug. 20-27, 1993.

<sup>4</sup>Berg, R. and J. Lonn. Reconnaissance Survey of Bedded Zeolite Occurrences in Montana. Montana Bureau of Mines and Geology, Open File Report MBMG 267, 1993, pp. 25.

<sup>5</sup>Chemical Marketing Reporter. Engelhard Buys Katalistiks Unit. V. 243, No. 24, June 14, 1993, p. 4.

<sup>6</sup>Industrial Minerals (London). Akzo Expanding Zeolite Facilities. No. 314, Nov. 1993, p. 77.

<sup>7</sup>Chemical Week. New Zeolite Plant Starts Up. V. 153, No. 16, Nov. 3, 1993, p. 23.

<sup>8</sup>----. Crosfield Plans Zeolite Plant. V. 152, No. 14, Apr. 14, 1993, p. 28.

<sup>9</sup>Chemical Marketing Reporter. EniChem to Set Up Zeolites Plant in Turkey. V. 244, No. 25, Dec. 20, 1993, p. 22.

<sup>10</sup>Chemical Week. Green Detergents. V. 153, No. 15, Oct. 27, 1993, p. 37. ----. Zeolite Producers Claim Record Gains in 1992. V. 152, No. 3, Jan. 27, 1993, pp. 36-38.

<sup>11</sup>----. Refinery Catalysts: Some Recovery and Plenty of Future Promise. V. 152, No. 23, June 16, 1993, p. 46.

<sup>12</sup>----. Mobil/Badger to Market Zeolite-based Cumene Technology. V. 152, No. 7, Feb. 24, 1993, p. 9.

<sup>13</sup>Haggin, J. New Zeolite Structures Promising for Catalysis. Chemical and Engineering News. V. 71, No. 49, Dec. 6, 1993, p. 8.

<sup>14</sup>Chemical Engineering. A Zeolite Bed Cuts Soot and NO Emissions from Diesel Engines. V. 100, No. 12, Dec. 1993, p. 25.

<sup>15</sup>Chemical Week. SRI Studies Zeolíte NO<sub>x</sub> Control. V. 152, No. 12, Mar. 31, 1993, p. 40.

<sup>16</sup>Chemical Engineering Progress. New Catalysts Aim to Nix NO<sub>x</sub>. V. 89, No. 5, May 1993, p. 11.
<sup>17</sup>Drohan, Derrick. Eliminating Spray Booth VOCs. Paint and Coatings J. V.

"Drohan, Derrick. Eliminating Spray Booth VOCs. Paint and Coatings J. V. 9, No. 8, Sept. 1993, pp. 34-35.

#### OTHER SOURCES OF INFORMATION

### 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.

State and company	Type of zeolite
Arizona:	
GSA Resources Inc	Chabazite.
UOP Inc	Do.
Idaho:	
AIMCOR Corp	Clinoptilolite.
Steelhead Specialty Minerals	Do.
Nevada:	_
American Resource Corp	. Do.
New Mexico:	_
St. Cloud Mining Co	. Do.
Oregon:	_
Teague Mineral Products Co	Do.
Texas:	
Zeotech Corp	. Do.
Wyoming:	
U.S. Zeolites	Do.

TABLE 1DOMESTIC ZEOLITES PRODUCERS, 1993