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INTRODUCTION

Zeolites, a family of natural and synthetic minerals, are composed of complex crystals of silicon, aluminum, and other elements. The minerals possess unique physical and chemical properties that are utilized in a variety of industrial, agricultural, and consumer-product applications. More than 40 species of natural zeolites have been identified by geologists, and over 100 species with no natural counterparts have been synthesized by chemists, making zeolites one of the largest of the known mineral groups.

Synthetic zeolites have dominated the market since their introduction in the 1950s, but industry analysts are confident that natural zeolites will play an increasingly important role in the future, as research and development activities reveal new areas of application and new techniques of chemical upgrading. Natural zeolites are presently mined in Japan, Italy, Hungary, Bulgaria, Yugoslavia, Mexico, Korea, Germany, and the United States.

Mississippi contains deposits of the zeolite species clinoptilolite. Clinoptilolite could be a resource of value to the state, as research indicates that it may be utilized in several of the more important industries in Mississippi. Although the deposits are extensive, very little information on the quality and characteristics of the resource base is available. Due to the number and diversity of potential applications and the exacting nature of the technical data and assistance that producers must be able to provide to customers, much more research on the properties of Mississippi's zeolite deposits must be conducted before commercial development can become a reality. As an illustration of the benefits that could be derived from such development, this report presents an overview of the zeolite industry, along with a brief description of some of the present and proposed uses for clinoptilolite.

THE MARKET FOR ZEOLITES

Zeolites have traditionally been marketed as highly specialized industrial mineral commodities designed for relatively sophisticated applications as catalysts and adsorbents. For example, synthetic zeolites have been used in the separation and purification of industrial process streams, and in the fluidized catalytic cracking process by which crude oil is converted into gasoline and other fuels. The traditional market segments are low volume in terms of demand, but prices are quite high, with some species selling for $6,000 per ton. In 1975, 29,000 tons of zeolite were consumed in the United States for these purposes.

In the 1970s, concern over the phosphates used as water softeners in detergents opened up an entirely new area of market interest for zeolites. Zeolites can remove calcium ions from water in much the same way as phosphates, but without their environmental dangers. Patents held by the established producers of synthetics were beginning to expire during this period, so that new producers were able to come on-line with plants designed to produce the first low-priced zeolites intended for a high-volume use. Detergent-grade zeolites were available for as little as $560-600 per ton, making them cost competitive with phosphates.

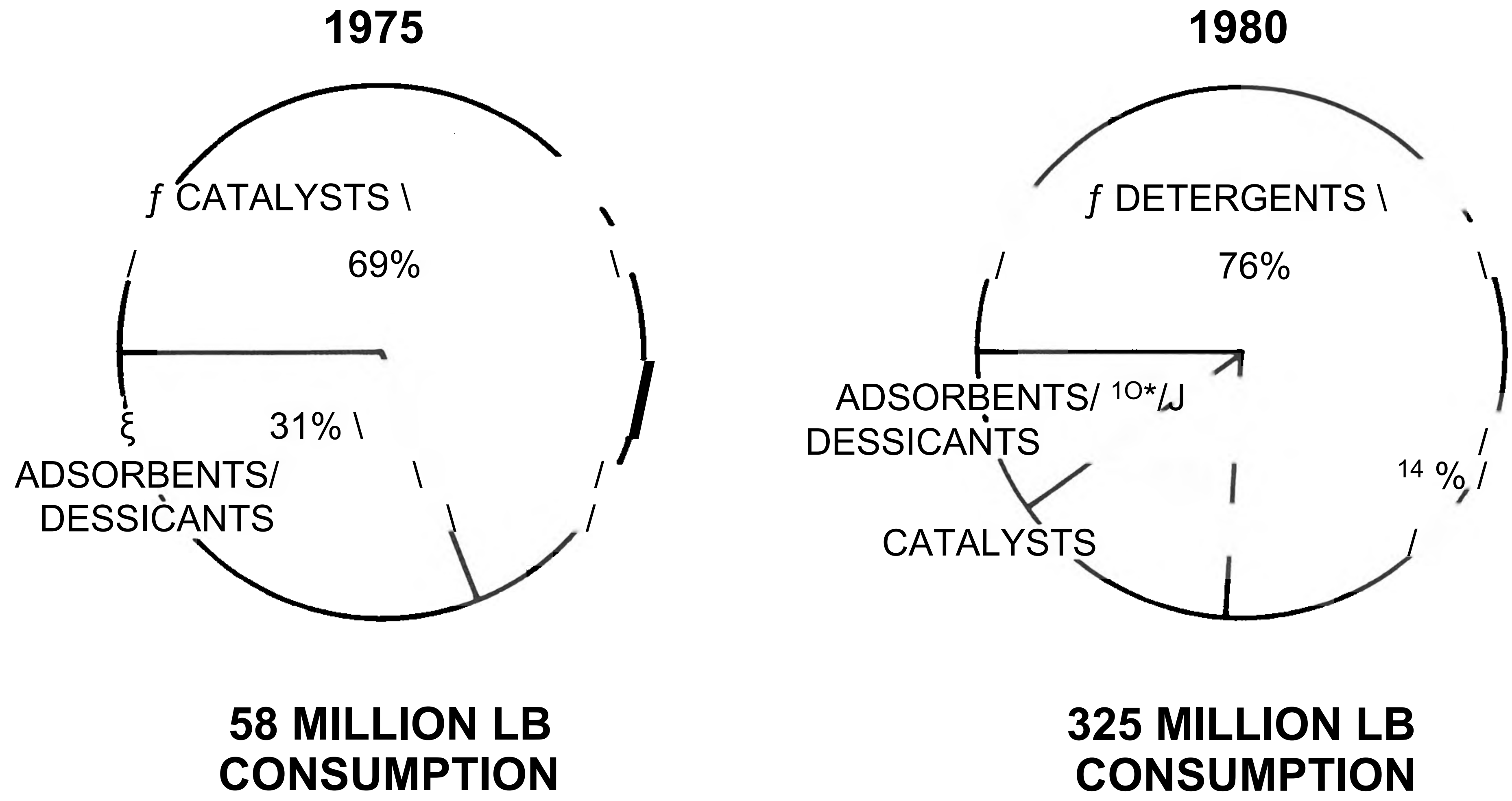
Detergent manufacturers quickly replaced phosphates with zeolites, with some brands consisting of 16-18 percent zeolite. As a result, consumption, which had been expected to increase by 25 percent over the 1975-80 interval, rose by more than 400 percent, to 162,500 tons (Figure 1). Industry analysts projected sales of 247,500 tons for 1985 as manufacturers continued to substitute zeolites for phosphates, and other applications based on the lower priced zeolites were developed.

In 1983, however, the detergent bubble began to burst, as major manufacturers removed zeolites from their best-selling brands due to problems with consumer acceptance. Briefly, zeolites did not perform as well as phosphates at lower wash temperatures, and did not rinse completely, leading to duller fabric finishes. Consumption fell rapidly after the loss of the detergent market, and with major plants having gone into operation in order to meet the detergent demand, there was overcapacity in the synthetic zeolite industry.

The ultimate impact of these developments on the natural zeolite industry is difficult to predict. The venture into detergents did lead to the development of low-cost synthetics, which could lead in turn to entirely new markets for zeolites; In the long term, this could be advantageous to natural zeolite producers, as natural zeolites are even less expensive than detergent grade zeolites. Prices of natural zeolites range from a low of $45 per ton to a maximum of $400 per ton. (Prices vary with the zeolite species, the application in question, the processing required, and other factors.) However, in the immediate term, the overcapacity in the industry will probably narrow the price differential between synthetic and natural zeolites, and the more variable natural product has always experienced some difficulty in competing with the tailor-made synthetics that are designed for a specific end use, for reasons outlined below.

Scientists and companies originally turned to synthesis because it was assumed that zeolites did not exist in nature in quantities feasible for economic development. The first synthetic, Zeolite A, was developed by Union Carbide in 1949. It was so successful —Zeolite A is still in use

FIGURE 1. Composition of the United States Zeolite Market



SOURCE: Patricia Layman, "Detergents Shift Focus of Zeolites Market," *Chemical and Engineering News* 60 (September 27, 1982): 11.

today —that producers rushed to develop and patent other synthetics. In this way, several new zeolites entered the market during the 1950s.

Another major event in the zeolite story occurred during the 1950s, when geologists began to discover that zeolites, rather than being extremely rare in nature, were one of the most common minerals. Zeolite is often difficult to distinguish in the field, so that exploitable deposits were not detected until advanced techniques such as the petrographic microscope and x-ray diffraction analysis were employed. With these methods available, geologists were surprised to discover that vast deposits of zeolites existed in the western and southeastern United States. Moreover, these deposits could be mined for a fraction of the selling price of synthetic zeolites, a fact that could not have delighted producers, given the substantial investment undertaken in synthesis of zeolites.

In spite of the lower prices, a natural zeolite industry has been slow to develop. Until recently, the zeolite market primarily consisted of the high-value, speciality fields of catalysis and adsorption. Generally speaking, natural zeolites are not competitive with synthetic zeolites in these technically exacting areas, due to their smaller pore sizes and lower adsorption capacities. Synthetic producers have also developed sophisticated marketing systems, an important factor in that suppliers must be able to furnish detailed product data that the customer can use to assess which type of zeolite is most appropriate. The large synthetic producers have been able to provide this service to potential customers, while the smaller natural producers have often been unable to do so.

Research on natural zeolites in certain applications has been underway for nearly twenty years, but results are still inconclusive, partially due to a certain incompleteness in the reporting of experimental results. As recently as 1982, a member of the U.S. Geological Survey warned that if zeolite agricultural researchers were not more rigorous in the characterizations of the zeolitic rocks used in their studies, the interpretation, reproducibility, and credibility of their experimental results could be questioned. The information reported should include mineral content and chemical composition, crystallite size, homogeneity, cation exchange and adsorption properties, and a description of any chemical modifications that were made. Only a part of this information is typically given.

Additional research is needed not only to determine whether zeolites are effective in certain applications but also to establish why they are effective. The biological and chemical mechanisms underlying the observed effects of zeolites in many areas of use are not well understood. If scientists are able to determine how zeolites induce certain phenomena, then they may be able to delineate conditions under which zeolites will or will not be effective, or to improve the performance of natural zeolites through chemical upgrading.

Although the zeolite industry is currently experiencing some difficulties due to the detergent setback, the foray into lower-cost, high-volume applications could ultimately work to the advantage of natural zeolite producers. The synthetics will probably maintain the markets in which they have become established, particularly the high-value speciality fields, but there are many other markets of huge potential in which there will be much greater competition from natural zeolites. Furthermore, it is expected that natural zeolites can soon be chemically upgraded to such an extent that they may be directly comparable to synthetic zeolites.

COMPOSITION AND PROPERTIES OF ZEOLITES

The commercial applications of zeolites are based on their physical structure and chemical composition. Zeolite molecules are rather unusual in that all their atoms are shared with each other in a three-dimensional cage structure, comprised of tetrahedral units of oxygen atoms surrounding an aluminum or a silicon atom. The units form microscopic channels and cavities within the zeolite crystals, and, as the tetrahedra connect with each other in a limited number of ways, the size of the pores and channels is exactly determined. Zeolites therefore possess an extremely regular crystal structure, which is honeycombed with channels that can trap molecules as a sieve does, or can bind up and selectively release large quantities of molecules through adsorption or ion exchange.

Adsorption refers to the extraction of molecules from a gas or a liquid onto a solid surface. After water has been removed from a zeolite particle by heating, its inner cavities are virtually empty, and the voids and channels of the zeolitic structure may be filled with a gas or liquid. Molecules in these substances that are small enough to pass through the channels will be adsorbed by the zeolite. Those with diameters that are too large to pass through the channels will be excluded.

Due to this sieving action, zeolites can be used to separate contaminants or other components from industrial process streams. Other agents may also be used as adsorbents, but zeolites are preferred when precise control over pore size is important. Zeolite crystals have an extremely narrow distribution of pore sizes, so that it is relatively easy to determine which species are capable of adsorbing molecules of the desired size.

The terms adsorption and molecular sieving refer to the same property, but involve differing volumes of separation. Molecular sieving refers to processes in which up to half of one component must be separated from another. Adsorption processes entail the removal of a component that is equal to 10 percent or less of the total volume of the stream involved.

Ion exchange is the reversible interchange of ions between a solid and a liquid, without permanently changing the structure of the solid. The exchangable cations (positively charged ions) are loosely bonded to the tetrahedral framework and may be exchanged easily by washing the zeolite particle with a strong solution of another ion. The synthetic zeolites in detergents soften water through ion exchange, by exchanging their sodium ions for the hard-water calcium ions. Zeolites are some of the most effective ion exchangers known to man, with cation exchange capacities (C.E.C.) of up to 3 to 4 milliequivalents per gram (Meq/gm).

Other important zeolitic properties are the silicious composition and the ability to gain and lose water reversibly. The former makes zeolites resistant to acids, which are used in some of the industrial processes involving zeolites. The latter is utilized in solar energy applications, and in a variety of processes in which moisture levels must be controlled.

Each species of zeolite has a unique crystal structure, and therefore a unique set of physical and chemical properties. That is, the species differ both as to their overall absorption and ion exchange capacities, and as to the types of molecules or ions that are adsorbed or exchanged. As a result, each species has its own area of potential applications and market interest. There are, however, some areas of overlap, so that there is room for competition between species in certain applications.

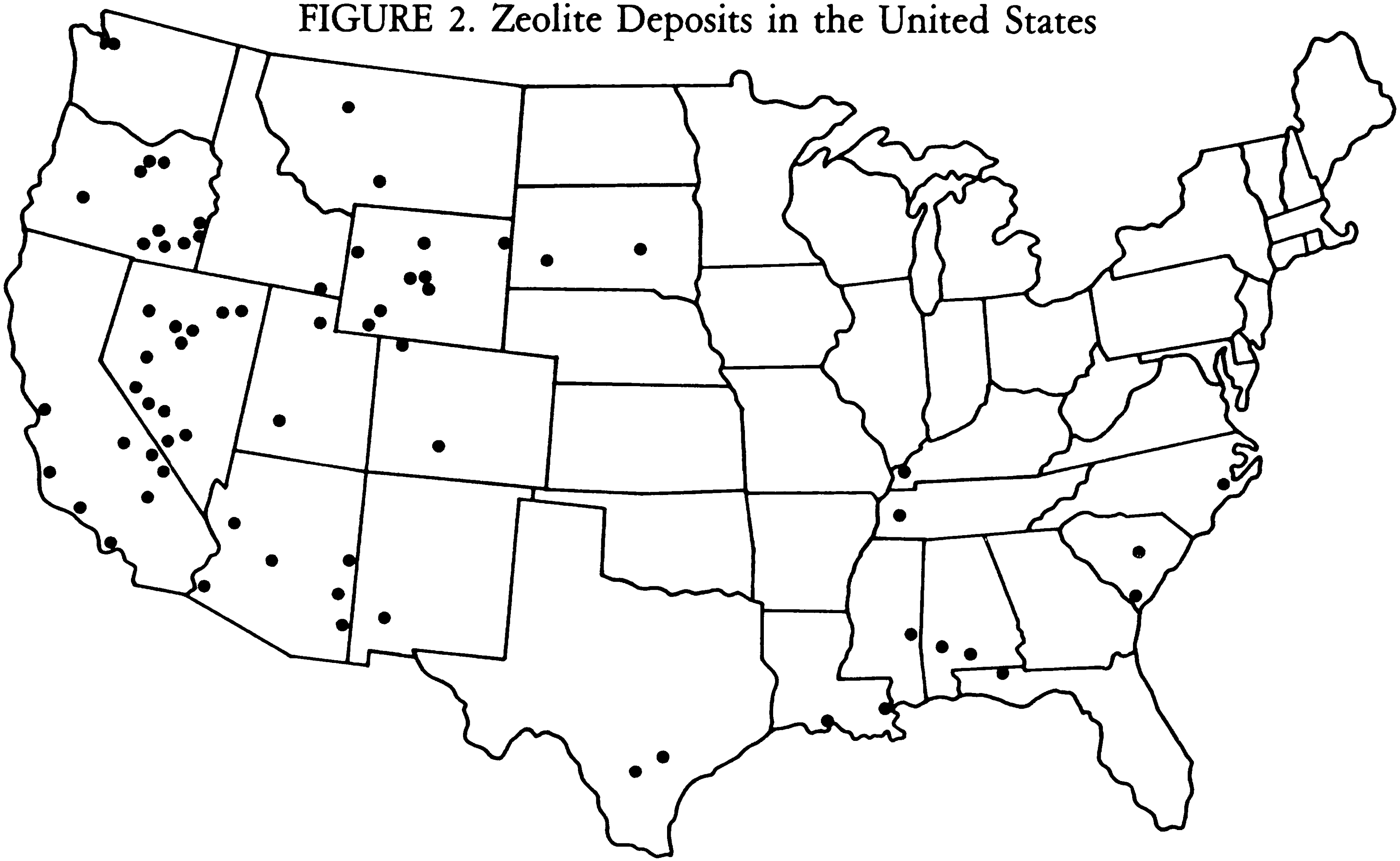
NATURAL ZEOLITES IN THE UNITED STATES

Six common zeolites are found in sedimentary deposits in the United States: analcime, chabazite, erionite, mordenite, phillipsite, and clinoptilolite. Currently, 23 states have reported deposits containing one or more of these species of zeolite. Most of the deposits are found in the western states; however, clinoptilolite is found in several southeastern states, including Mississippi. (See Figure 2.)

According to the U.S. Bureau of Mines, production of natural zeolites in the United States rose from several hundred tons in 1976 to approximately 5,000 tons in 1977, and has remained at that level. While market development activités and research have been extensive, sales are sporadic and to diverse markets. The largest single sale in recent years was made by the Phelps-Dodge Zeolite Company to British Nuclear Industries.

Mining has occurred primarily at three deposits—near Bowie in Arizona, near Hector in California, and in Jersey Valley in Nevada. Companies

FIGURE 2. Zeolite Deposits in the United States



SOURCE: Lenfond Stanley, ed,, *Industrial Minerals and Rocks,* 4th ed. (New York: American Institute of Mining, Metalurgical, and Petroleum Engineers, 1975): 1243, Figure 3.

that have engaged in the mining or marketing of natural zeolites include the Norton Company, Union Carbide, W. R. Grace, the Anaconda Copper Company, and the Phelps-Dodge Zeolite Company (formerly Occidental Petroleum).

NATURAL ZEOLITES IN MISSISSIPPI

The zeolite species clinoptilolite has been found in Mississippi in the Tallahatta Formation in Lauderdale and Clarke counties. Geologists are confident that further exploration will reveal other significant deposits of zeolite in the state. (See Figure 3.)

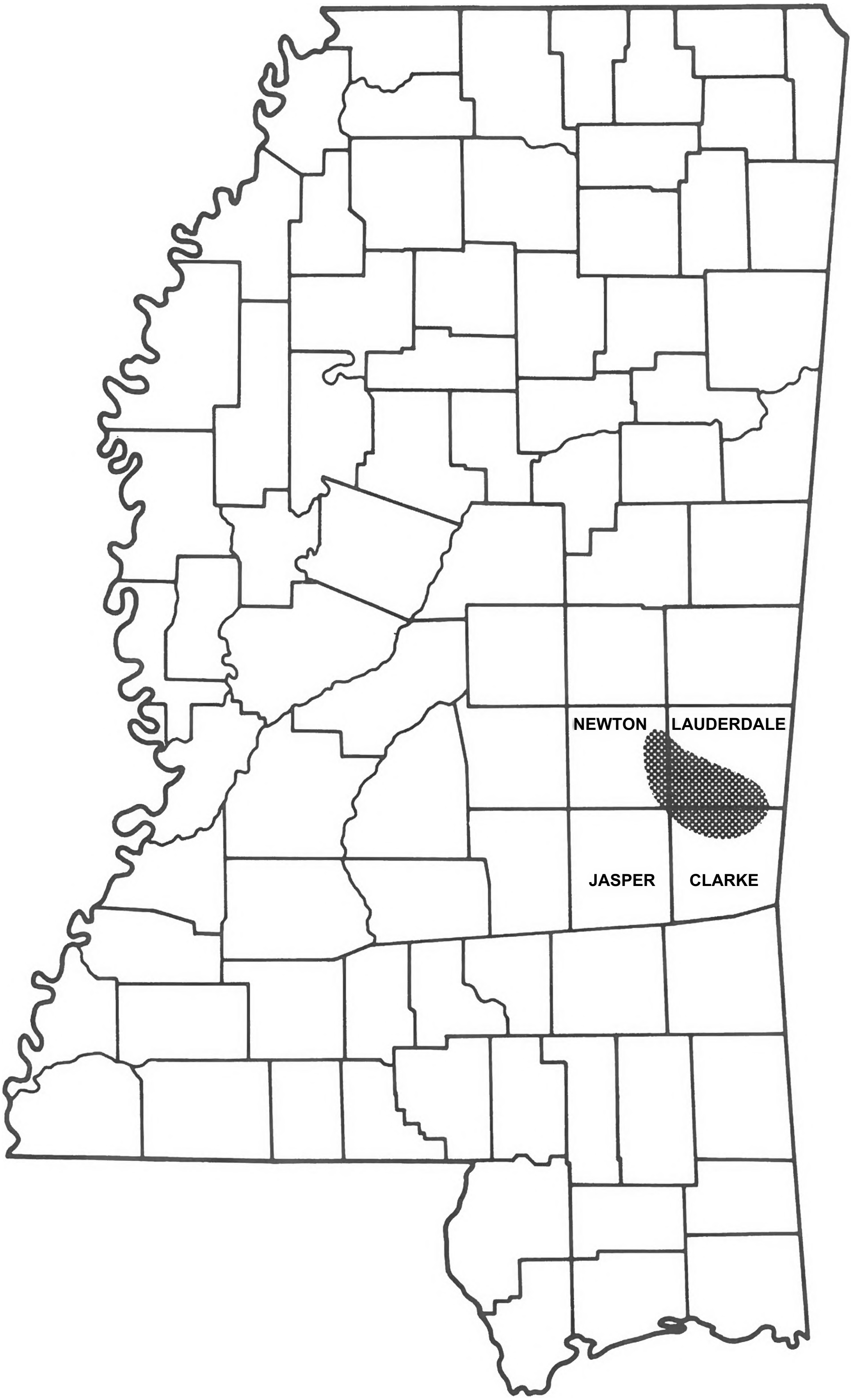
Two members of the Engineering School at the University of Mississippi independently collected and analyzed a total of 15 samples from the Tallahatta Formation in Mississippi. The amount of clinoptilolite in the samples varied, with one study reporting contents of 12 to 80 percent, and the other contents of 37 to 67 percent. Seven of the samples were also tested for their cation exchange capacity (C.E.C.). The C.E.C. ranged from .61 to .89 Meq/gm. This was somewhat lower than the average C.E.C. for western deposits of clinoptilolite, of 1.5 Meq/gm.

While the results of the few studies that have been conducted are not as encouraging as might be desired, much more study is needed before a final verdict on the properties of the state's zeolite deposits can be reached. As clinoptilolite could be utilized directly in many local industries, an investment in the acquisition of such knowledge could yield substantial returns, and is deserving of greater in-depth research.

POTENTIAL APPLICATIONS FOR NATURAL ZEOLITES

This section presents brief descriptions of some of the proposed uses for natural zeolite, particularly clinoptilolite. The applications discussed are by no means exhaustive — one company claims to have discovered 170 potential applications for zeolites —but do represent some of the major areas of research and market interest. The activities are also in varying stages of development. Natural zeolites have been utilized for some time in Europe and Asia, but are just beginning to be investigated by researchers and companies in the United States. Industry members are particularly interested in the agricultural market, as the volumes involved could approach or surpass those of the detergent market.

FIGURE 3. Zeolite Deposits in Mississippi



Agriculture

Soil Amendments. Due to their ion exchange capacity and water retentivity, zeolites are valuable soil additives. Japan has used natural zeolite (primarily clinoptilolite) as a soil conditioner and as a fertilizer for over a hundred years.

Zeolites improve the ability of soils to retain nitrogen by increasing their bulk ion exchange capacity. When zeolite is combined with fertilizer, nutrients are released gradually, thereby increasing their residence time in the soil. The result is enhanced crop yields. However, the effect varies with the type and origin of the soil involved as well as the crop to be grown. In particular, nitrogen retention efficiencies of clay-poor soils are drastically improved by the addition of zeolites, as the initial ion exchange capacity of such soils is quite low. Zeolites can also restore the pH balance of soils by neutralizing acids, and perform as a soil aerator.

Research on the effectiveness of zeolite as a soil additive is still underway, and is expanding into new directions. Scientists in Europe recently reported increases in vitamin C content as well as enhanced crop yields after a natural zeolite was added to tomato and strawberry fields.

Another benefit comes from the ability of zeolites to absorb moisture. When added to fertilizer, clinoptilolite reduces caking and hardening during storage.

Gamers. Their ion exchange and adsorption capacities render natural zeolites effective carriers of herbicides, fungicides, and pesticides. Zeolites are thought to extend the period of effectiveness after application by acting as a slow-release agent for the chemicals involved.

Animal Waste Treatment. Natural zeolites (clinoptilolite and chabazite) have been successfully used to reduce the odor, fumes, and moisture from animal wastes. Deodorizing of course reduces the nuisance value of animal wastes, but, more importantly, the adsorption of fumes may lessen the incidence of disease among animals in enclosures. Fumes emitted by chicken manure can give rise to respiratory diseases in poultry, resulting in smaller animals and decreased egg production. Zeolite also stabilizes waste compounds and retains nitrogen, thereby enhancing the value of animal wastes as a fertilizer.

For waste control purposes, zeolite can be directly applied to the enclosure or added to the animals' rations. When the latter method was employed, an unanticipated benefit opened up an entirely new area of interest in zeolites.

AnimalNutrition. Researchers who had added zeolite to chicken feed with the object of controlling the odor and moisture content of the waste noted that the chickens experienced faster weight gains. The implications of this finding ultimately led to a large body of research on zeolites in animal nutrition. Results published so far are inconclusive, but some research suggests that adding up to 10 percent zeolite to the diets of poultry, swine, and ruminants may have the following positive effects: increased average weight gains, a shorter period required to reach maturity, and improved feed conversion values (weight gain divided by nutritional feed intake). There was also some evidence of beneficial impacts on the animals' health —those in control groups had a lower incidence of death and disease, particularly with respect to diseases of the digestive system. However, other studies have found little evidence that zeolite has a significant impact on weight gains or feed conversion values. A final verdict on the effectiveness of zeolite as a feed additive must therefore await further research.

At the current state of knowledge, the process by which zeolites could induce biological or antibiotic phenomena in animals is not well understood. It is thought that the adsorption and ion exchange properties of zeolites either allow nutrient molecules to be retained in the digestive system longer, or bind up toxins that interfere with digestion. For ruminants, the most important effect seems to be that of ammonia removal. Zeolites are thought to enable poultry to use calcium more efficiently, resulting in stronger egg shells and less breakage.

A considerable amount of research on the effect of incorporating varying amounts of zeolite into the diets of different types of livestock is still underway, with the goal of determining the quantity of additive that is necessary to achieve maximum utilization of the feed on a consistent basis. If scientists are able to determine the conditions under which zeolites are effective nutritional supplements, then an attractive possibility of increasing the world's food supply exists.

Aquaculture. As the number of commercial fish farming operations continues to expand, aquaculture could become an important market for natural zeolites. The chemical and biological environment of aquacultural systems must be maintained within close limits at all times. Zeolites may be used to solve one of the major problems in maintaining this environment: that of controlling the ammonia released from fish wastes. In natural environments, the ammonia does not become a problem either due to circulation of the water or the unrestricted movement of the fish. In restricted environments such as hatcheries or farms, however, the ammonia can quickly reach toxic levels if not controlled. By adding zeolite to the water, ammonia levels in commercial fisheries may be reduced, and, with proper control of ammonia through zeolite, it is possible to increase the rate of feeding or raise the density of the population. There have also been reports that zeolites led to improved growth rates when added to the rations of fish.

Zeolites have successfully controlled the ammonia levels in tanks used to transport fish from one location to another, in some cases allowing as many as twice the number of fish to be moved in one tank.

Solar Energy

Zeolites' ability to attract and hold large quantities of liquid has been exploited in the construction of solar-powered refrigerators, space heaters, air conditioners, and water heaters. In the early 1970s experiments conducted at the University of Texas and the Massachusetts Institute of Technology met with considerable success in using natural zeolites (chabazite and clinoptilolite) as components of solar powered air conditioning and water heating units. One of the researchers, Dimiter Tchernov, was so impressed with the results of the experiments that he formed his own company, Zeopower, Inc., to manufacture solar powered refrigerators and heating and cooling units. He predicts that zeolite units will prove to be significantly less costly than conventional solar panels.

The specifics of each system vary according to the purpose, but all systems contain a zeolite solar panel and a water container or reservoir. At night as the zeolite panels cool, water is drawn into the zeolite pores so rapidly that evaporative cooling may cause ice to form. During the day as the zeolite is heated by the sun, water is desorbed from the panels and flows back into the reservoir. The cycle is repeated daily, and duration of the cooling is determined by the size of the reservoir.

Construction

Cement. Zeolites can be used as a source of pozzolans or as a lightweight aggregate in cement. Pozzolans are siliceous or siliceous and aluminous substances that react chemically with lime in the presence of moisture to produce a cementious compound. This is one of the oldest known uses of zeolites, dating back to the days of the ancient Romans, who used natural zeolites as pozzolanic raw materials in their highways, aqueducts, and public buildings. Zeolites have been extensively utilized in cement production throughout Europe, and are probably mined locally for this purpose in many other parts of the world, although the users may be unaware of the zeolitic content of the deposits.

Clinoptilolite, after being heated and expanded, may also serve as a lightweight aggregate. Zeolite products are significantly stronger and more resistant to abrasion than the volcanic glasses used as lightweight aggregates, although higher temperatures are required for expansion of zeolites.

Plywood. The glue used in lamination of plywood contains ammonia and water vapor which, if released, can lead to delamination, the major cause of product rejection in plywood manufacture. Due to their ability to adsorb moisture, zeolites may be used to prevent delamination. One firm has recently patented a natural zeolite for use as a filler in plywood glue for this purpose.

Pollution Control

Zeolites may soon play a role in solving one of the major problems facing society today. In the early 1960s, scientists at the U.S. Atomic Energy Commission demonstrated that clinoptilolite can remove radionuclides from the waste streams of nuclear facilities in much the same way that zeolites strip calcium ions from washwater. Clinoptilolite has been used at the Hanford, Washington, weapons production facility for this purpose, and a blend of natural and synthetic zeolites was recently used in the cleanup at Three Mile Island in Pennsylvania. Zeolites are less expensive than the organic ion exchange resins employed in nuclear waste treatment. Moreover, they react rapidly in glass and cement systems, leading to safer storage of the removed radioactive wastes.

Clinoptilolite has also been found to be an effective agent for the extraction of ammonium ions from sewage and agricultural effluents. Clinoptilolite-based systems are currently in operation in a small number of municipal wastewater treatment plants in the United States. Research on natural zeolites in industrial waste treatment is presently underway.

Other

Lastly, while space limitations preclude individual discussions of all the possible applications for natural zeolites, the ion exchange and adsorption properties of the minerals may also be used for the following purposes: to control sulfur emissions from stack gases of power plants; in oil-spill cleanups; in the production of oxygen-enriched gases; as a filler in paper; and in a wide variety of activities in which odor and moisture must be controlled. For example, zeolites can be used in carpet cleaners and in cat box fillers. They can also be packed between the frames of dual-pane insulating windows, to prevent discoloration from moisture released by the sealant. Clearly, zeolites are one of the most versatile of the minerals.

SUMMARY AND CONCLUSIONS

Although the zeolite industry is still recovering from the detergent setback, this exciting and useful mineral has been reborn in many new forms and applications since Zeolite A was placed on the market, and is still one of the most important of the industrial mineral commodities. Zeolite usage may also expand in the agricultural and consumer market segments, with the development of low-priced synthetics and continuing interest in the inexpensive natural zeolites.

Synthetic zeolites currently have a competitive edge over natural zeolites, but there are many steps that natural zeolite producers can take to enhance their competitive position. The properties of the deposits must be subjected to a rigorous analysis, and, based on the results, a market sphere of interest determined. A wide variety of uses may exist for a single species of zeolite, but the technical specifications of the applications can greatly differ. Producers of natural zeolites must determine which of these applications are best suited to the properties of their particular deposits, and develop a marketing program capable of furnishing interested parties with the information needed to assess the product.

At present, the state of knowledge on the zeolite deposits of Mississippi is far from that required for commercial development. However, if it is found that local clinoptilolite can be used in one or more of the state's industries, the acquisition of the knowledge would definitely be justified.

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The enclosed bulletin on the zeolite industry and Mississippi was prepared by M.M.R.I. to inform industry and other interested parties of the importance of zeolite as a mineral and of the potential role that Mississippi could play in the production of this mineral. It contains a non-technical description of the characteristics of zeolites and a discussion of some of the proposed and present uses. Many of the uses, such as those in agriculture and aquaculture, are of direct relevance to the economy of Mississippi.