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INVESTIGATION OF INDUSTRIES WITH AGENTS WHICH ARE
NEWLY SUSPECTED AS OCCUPATIONAL HEALTH HAZARDS

Task I - Zeolites Report

Prepared by: Stan K. Futagaki
Project Leader for Zeolites

Flora H. Chang
Research Analyst

S. Thomas Golojuch
Research Analyst

Center for Occupational and
Environmental Safety and Health

Prepared for:

National Institute for Occupational
Safety and Health
Robert A. Taft Laboratories
4676 Columbia Parkway
Cincinnati, Ohio 45226

Attn: James L. Oser, Project Officer
Leo Sanders, Contract Officer

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1611 N. Kent Street • Arlington, Virginia 22209
(703) 524-2053 • Cable: SRI INTL WDC

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The production and use of natural zeolites are described. Chemical and physical properties, domestic sites of occurrence, mining quantities and processes, uses, potential biologic effects, and its presence as a contaminant in other ores are considered. The feasibility of conducting a cohort mortality study is addressed, and facilities for industrial hygiene or epidemiological study are recommended.

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ZEOLITES

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ABSTRACT

This Task I report on natural zeolites presents information on the limited production and use of this mineral group found throughout the western United States. The chemical and physical properties, biologic effects, and synthetic forms are also reviewed. It was determined that a cohort mortality study is not feasible because of the extremely small number of exposed workers during the required time period. Recommendations are made for sites to be visited during Task II to allow further characterization of the industry in terms of worker exposure and the specific zeolites involved.

I, INTRODUCTION

The National Institute for Occupational Safety and Health (NIOSH) has designated natural zeolites, a group of minerals in limited commercial use in the United States, as a newly suspected occupational health hazard. This designation has been made partly because of reports of mesothelioma (an invariably fatal neoplasm) arising in a foreign population residing in an area where these minerals are found in abundance. The objectives of this Task I report are to:

- Present information on naturally occurring zeolites
 - chemical and physical properties
 - sites of occurrence (United States)
 - mining quantities and processes
 - uses
 - potential biologic effects
 - presence as a contaminant of other ores
- Determine the feasibility of a cohort mortality study
- Recommend facilities for industrial hygiene or epidemiological study in Task II.

Information on the production and use of synthetic zeolites is also included in an appendix to give a better understanding of the development of the entire zeolite industry and especially to illustrate potential uses of the mineral and growth of this industry. For convenience, the term "zeolite" will refer only to the naturally occurring minerals

and not to the synthetics.

Specific information on mining sites, companies, quantities, processes, and uses and users is not readily available for this mineral group. This is probably due to the limited extent of mining and use currently, and because many of the involved companies consider information on this industry to be proprietary. The information presented in this report that is not referenced has been integrated from numerous contacts with involved individuals in government, academia, and industry. Grant Baugh, Bureau of Land Management; Robert A. Clifton, U. S. Bureau of Mines; Ted H. Eyde, Geological Services of Arizona; and Richard Sheppard, U. S. Geological Survey were of special help in accumulating information.

II. BACKGROUND

Zeolites are probably among the most common authigenic silicate minerals in sedimentary rocks. To date, there have been over 40 distinct species identified. These minerals are particularly abundant in deposits of saline, alkaline nonmarine environments and altered vitric tuffs, although they may occur in rock formations that differ widely in age, characteristics, and depositional environment (Hay, 1966; Mumpton, 1973; Sheppard, 1973).

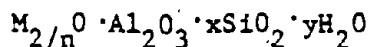
On the basis of depositional environment, sedimentary deposits of zeolites occur in saline, alkaline nonmarine deposits where their occurrence is widespread and relatively pure beds may be found, and in marine and fresh water deposits where they are most often found as alteration products of volcanic glass in thick accumulations of tuffaceous sediments (Hay, 1966). Zeolites are found in abundance most commonly throughout the western United States, especially in California, Nevada, Arizona, Colorado, Wyoming, and Oregon.

Chemical and Physical Characteristics

By definition, the zeolites are crystalline, hydrated aluminosilicates of alkali and alkaline earth elements (group I and group II), in particular sodium, potassium, magnesium, calcium, strontium, and barium (Breck, 1974; Flanigen, 1977). Zeolites have a framework structure made up of infinitely extended three-dimensional networks of aluminum tetroxide (AlO_4) and silicon tetroxide (SiO_4) tetrahedra linked by the sharing of all oxygens. This framework contains relatively large channels and

cavities occupied by the cations and water molecules. The mobile cations balance the net negative charge of the anionic framework and may be exchanged, to varying degrees, with other cations. The water molecules are also loosely bound and many types of natural zeolites may be reversibly dehydrated without disrupting the basic framework structure.

Zeolites may be represented by the empirical formula:



where M is the cation, n is the valence of that cation, x is a number from 2 to about 10, and y is a number from 2 to 7 (Mumpton, 1977a). The framework structures of zeolites are very open and void volumes of about 20-50% have been reported (Breck, 1974; Mumpton, 1973).

Most zeolites have a specific gravity of 2.0-2.3 and indices of refraction of 1.44-1.52 (Sheppard, 1973), whereas the specific gravities of quartz and feldspar, whose framework structures are dense and tightly packed, are about 2.6-2.7 (Mumpton, 1977a). The effective pore sizes of many zeolites are large enough to permit the entry of molecules up to several angstroms in diameter (Breck, 1974; Mumpton, 1973), depending on their size and shape.

The uniformity of the pores and channels in natural zeolites often make them more desirable for molecular sieving operations than adsorbents with widely random pore sizes, such as silica gel, activated carbon, and activated alumina.

Zeolites may be found in several structural forms in natural deposits, this being determined mainly by their basic crystalline structure. Most are nonfibrous in nature, such as clinoptilolite, which tends to occur in tabular form, and chabazite and analcime, which are equidimensional.

Erionite and mordenite are the only zeolites always occurring in a fibrous form in nature. Ferrierite and phillipsite are also sometimes fibrous, but do occur in other forms. There has been extensive work done on the crystal structures of the individual zeolites and this information can be found in several comprehensive references (Breck, 1974; Mumpton (ed.), 1977). There is also a discussion of the physical dimensions of some of the fibrous zeolites found in this report in Section VII, Biologic Effects.

Species Found in the United States

In the United States, the zeolites that are most common in zeolitic rock formations in decreasing order of abundance are:

	<u>Fibrous</u>	<u>Nonfibrous</u>
clinoptilolite (including heulandite)		X
analcime		X
mordenite	X	
erionite	X	
phillipsite	X	X
chabazite		X
laumontite		X
ferrierite	X	X

Oftentimes, more than one species occur together. For example, in the Bowie, Arizona area, the large deposits are mainly chabazite with erionite found in smaller amounts. Clinoptilolite and analcime are by far the most abundant zeolites found (Sheppard, 1973). The United States probably has the world's largest potential deposits of high-grade chabazite, erionite, and phillipsite, and the only high-grade

deposits of ferrierite in the world have been reported in central Nevada (Regis, 1970). The total identified, hypothetical, and speculative zeolite resources in the United States are conservatively estimated at 10 trillion tons (Sheppard, 1973). Indeed, if exploitation of natural zeolites on a large scale became desirable and feasible, the United States would likely be self-sufficient and a major exporter.

It was the discovery of these large, mineable deposits that opened the door for the potential commercial utilization of natural zeolites. The search for natural molecular sieve zeolites to compete with synthetic sieves began in the late 1950's and peaked in the early 1960's; it was carried out by several commercial organizations that explored and sampled deposits in Arizona, Colorado, Nevada, Oregon, Texas, and Wyoming (Sheppard, 1973). Exploration for zeolites again increased in the 1970's, specifically for mineable deposits suitable for use in pollution control, such as nitrogen removal from sewage wastewater, sour natural gas cleaners, and stack scrubbers. The known occurrences of the six most common zeolites in sedimentary deposits in the United States have been cataloged by Richard A. Sheppard (1971) of the U. S. Geological Survey (Olson, 1975) and the occurrences of the fibrous or potentially fibrous varieties, namely erionite, mordenite, and phillipsite, have been listed in Appendix A.

History

Zeolites were discovered by Cronstedt, a Swedish mineralogist, in 1756 (Breck, 1974). For 200 years zeolites were thought to occur typically as well-formed crystals in the cavities of basaltic and volcanic

rocks. Although more than 40 varieties of zeolites have been reported, these minerals were generally regarded as museum curiosities and very little geological study of their occurrences was undertaken. In the meantime, however, much work was devoted to the study of the chemical properties of zeolites. Many papers appeared in the literature describing the adsorption, ion-exchange, and dehydration properties of these remarkably open-structured framework aluminosilicates.

It was not until the late 1950's and early 1960's that reports of nonigneous occurrences of zeolitic mineral deposits began to appear in the literature (Deffeyes, 1959; Hay, 1966; Sheppard, 1973). It is now known that zeolitic minerals occur widely and abundantly in sedimentary formations and as alteration products of volcanic ash and other pyroclastic materials.

During the 1950's, Union Carbide and other industrial laboratories devoted considerable effort towards the production of synthetic zeolites to be used in a growing zeolite molecular sieve market, and, to date, more than 90 varieties have been synthesized. Information on synthetic zeolites is presented in Appendix C.

Glossary

- authigenic - minerals which are formed in situ before burial and consolidation of the sediment to rocks.
- basalt - volcanic rock, dark colored and fine-grained, occurring as a lava and composed primarily of calcium feldspar and pyroxene.
- detrital - refers to minerals occurring in sedimentary rocks which were derived from pre-existing igneous, sedimentary, or metamorphic rocks.
- igneous - formed by volcanic action or intense heat, such as rocks solidified from molten magma at or below the surface of the earth.
- metamorphic - formed by change in the mineralogical, structural or textural composition, such as rocks acted on by pressure, heat, chemical action or similar forces.
- overburden - soil overlying bedrock, or soil, rock, or other naturally occurring material overlying a useful deposit.
- pozzolan - any of a variety of natural and artificial substances, such as volcanic rock, added to cement to lend particular properties.
- pyroclastic - general term applied to detrital volcanic materials that have been explosively or aerially ejected from a volcanic vent and which also applies to rocks made up of these materials.
- sedimentary - a rock formed by the deposit of mechanical, chemical or organic sediment.
- tuff - a rock composed of the finer kinds of volcanic detritus (generally less than 4 mm in diameter) usually more or less stratified and in various states of consolidation.
- vitric - having the nature or quality of glass, as in color, composition, brittleness or luster.

III. MINING AND PROCESSING

It is generally acknowledged that accurate production figures for natural zeolites in the United States and worldwide are unavailable. However, estimates of annual world production in recent years have been as high as 300,000 tons (Eyde, 1976), with the United States contributing only a very small portion of this figure.

Zeolites have been mined commercially in this country on a very small scale since the early 1960's on an intermittent basis. Although, many mineable deposits of zeolites exist throughout the western United States, claims that are held by many companies are in anticipation of increased future uses. Only a total of about 5,300 tons of mainly chabazite (with a little erionite) from Bowie, and clinoptilolite probably mainly from two other sites were reported to have been mined and marketed in 1977. Something over 1,000 tons of ore in 1976 were reported to have been shipped from Bowie, Arizona, which is the most active site for zeolite mining in the United States. This general trend in active mining sites and amounts of minerals removed is not expected to change considerably for at least the next few years.

Mining Sites

Of a total of more than 300 individual occurrences of analcime, phillipsite, chabazite, erionite, mordenite, and clinoptilolite known in 25 states, only about 12 are reported to have produced more than experimental quantities of ore (Mumpton, 1973). There are at least 15 companies holding 500 zeolite claims in 7 western states. Of the other zeo-

litic tuff occurrences that have been claimed, most are controlled by small mining companies and speculators in anticipation of development of large-scale uses for zeolites in the United States.

Table III-1 shows the various locations of zeolite deposits that are known to be mined or have been mined (usually to a limited extent) and the particular species and physical form.

Table III - 1
Mining Locations

Fibrous:

Union Pass, Arizona--mordenite
Shoshone, California--erionite
Jersey Valley, Nevada--erionite
Rome, Oregon--erionite, mordenite

Nonfibrous:

Horseshoe Dam, Arizona--clinoptilolite
Hector, California--clinoptilolite
Creede (Ft. Collins), Colorado--clinoptilolite
Castle Creek, Idaho--clinoptilolite
Fish Creek Mountains, Nevada--clinoptilolite
Buckhorn, New Mexico--clinoptilolite

Mixed:

Bowie, Arizona--chabazite, erionite
Wickieup, Arizona--analclime, chabazite, clinoptilolite, erionite, phillipsite
Lake Tecopa, California--analclime, chabazite, clinoptilolite, erionite, phillipsite
Lovelock, Nevada--mordenite, clinoptilolite
East Gate, Nevada--erionite, clinoptilolite
Pine Valley, Nevada--erionite, phillipsite

The zeolite deposits near Bowie, Arizona, were the first to be commercially exploited, and probably have been and continue to be the primary site for the mining of natural zeolites in the United States. Chabazite from this deposit was the first natural zeolite mineral to be marketed in this country; the Union Carbide Corporation removed about 50 tons from this site in 1961-1962, and added it to their product line of molecular sieves (Eyde, 1976).

The deposits at Bowie are made up primarily of chabazite with small amounts of erionite that occur in a 1.5-m thick zone of thinly bedded zeolitic tuff overlying a 20-cm thick, massive blocky unit.

It is the 20-cm thick unit of higher grade ore that is generally selectively mined at this site. The beds outcrop over a 10-square mile area close to the surface and several million tons of chabazite/erionite ore appear to be present (Mumpton, 1973). The Bowie chabazite is an analog of the 5A Calcium synthetic zeolites, although it tends to have a better acid resistance than any zeolites synthesized to date. A major use of this mineral is thought to be in the drying and purification of slightly acidic gas streams.

The zeolitic ore at the Union Pass, Arizona, deposit is a hard, dense, altered-flow tuff, about 50-75 m thick. It consists of 50-75% mordenite, with some clinoptilolite and cristobalite (Mumpton, 1973). There are at least 12 large, mineable clinoptilolite deposits in the United States, including those at Hector, California, and Tehachapi, California, which have been mined for uses in ion-exchange processes for radioactive and sewage wastewater treatment and for use in pozzolanic cements (Mumpton, 1973). Information indicates that several of these deposits have not been mined recently.

The erionite deposits near Rome, Oregon, were quarried until recently. Although several companies, including The Anaconda Company, Norton Company, and Occidental Mining Corporation have mining claims in the Rome area (Malheur County), large-scale mining operations have been suspended pending the outcome of hearings involving the mining companies and various environmental groups. Opponents of mining operations in the area contend that such activities would detract from the recreational value of the area and endanger certain plant and animal species. Mining company representatives (Occidental Mining Corporation) say that their activities would only involve 2 or 3 people working for 4 months of the year, and would not result in the types of problems cited by environmentalists.

Before mining of these deposits was halted, operations were probably intermittent, although details of the operations there are sketchy. Approximately 12 stone buildings, some more than 50 years old, in nearby Jordan Valley are constructed from zeolites found in this area. Zeolites have been used as building or dimension stones to a limited extent in scattered areas throughout the western United States, and in many countries around the world, because of their availability and desirable physical characteristics. More detailed information regarding the use of zeolites in building is lacking in the United States, because they are generally used in small quantities and without prior mineralogical identification.

More detailed information concerning the particular types and approximate amounts of zeolites mined will be presented in relation to the companies involved in these operations.

Process Description

Although mining of zeolites has taken place in areas throughout the west, especially in Arizona, Nevada, California, and Oregon, it tends to be a very intermittent operation based largely on a market with a very erratic demand schedule. As an example, the Bowie, Arizona, site may be worked 60-100 days from one year to the next, depending on the amount of material needed for a particular year, based on orders and projected usage.

There is probably some isolated quarrying for use of zeolites as dimension stones, although this would tend to be for very small amounts and would generally be completed in a matter of days. This type of mining would probably be done on an as-needed basis when the mineral was readily available in a particular area. It is doubtful that this type of quarrying is done anywhere on a regular basis.

Mining of zeolites for other commercial uses is done at more or less established claim-sites, but it is still subject to the erratic demand for these minerals. Virtually all zeolite mining operations are of an open-pit surface mining variety, similar to the type done in sand and gravel excavating and perhaps most like the operations carried out for clay production, except that zeolite mining tends to be a more exact, careful process aimed at getting a very pure ore.

The Bowie, Arizona site is probably a typical example of a zeolite mining operation and mining operations at other sites will be similar. This site has typically been mined for about three months out of the year; usually during the cooler seasons. Essentially all work at the

site is performed outdoors. The area to be mined is explored, sampled, and blocked off in preparation for mining. Generally, a series of small contractors will perform the work. Various types of machinery, including bulldozers, trucks, earth movers, backhoes and front end loaders may be necessary, depending on the characteristics of the site and the operations being performed. If necessary, overburden must be removed (stripped) and stored, replaced, or otherwise disposed of. High grade ore is removed by one contractor in a stripping operation that requires the use of highly specialized machinery. There is usually an attempt to remove ore that is mostly high grade chabazite. Because of the uses for which ore from the Bowie site is marketed, erionite is generally considered a contaminant which should be avoided as much as possible. After the chabazite/erionite ore is stripped, another one or two contractors will break up the ore into pieces with back hoes and other machinery and attempt to separate and clean up the mineral. Clay and other impurities are sometimes removed from the desired zeolitic mineral by hand. The mined zeolites are then stockpiled in ground piles, silos, bins, or sheds. At the Bowie site, front-end loaders and trucks are used to remove the mineral to storage sheds. The zeolites are allowed to dry in these sheds, and stockpiles may sometimes be held for a year or more, with the moisture content of the chabazite/erionite from the Bowie site typically being reduced from about 17% to about 5%. Generally little other processing is performed at the mining sites. A hammer mill for grinding or pulverizing may be used at mining sites as WR Grace apparently does at its Bowie site. Since there is very low demand for natural zeolites at this time, it has not generally been considered economically justifiable

to carry out more complex processing operations at mining sites.

Double Eagle Petroleum and Minings Company's clinoptilolite mining operations briefly consist of ripping overburden, ripping clinoptilolite, and stockpiling the mined mineral. This company operates a crushing and wet screening plant at its Buckhorn, New Mexico clinoptilolite deposit. Wet screening is necessary to produce a product which will meet the turbidity standards for advanced wastewater treatment plants.

Other processing operations are generally performed at locations other than the mining sites. Minerals may be crushed, pulverized, ground, and screened in order to segregate particle sizes. Natural zeolites are sometimes mixed with a binder (such as clay or lignin), calcined, extruded, or otherwise processed. These types of processes are basically the same as those used for synthetic zeolites. As an example, Norton Company purifies its high grade chabazite/erionite from Bowie, bonds it with acid resistant materials, and then extrudes it as 1/8 inch or 1/16 inch pellets or beads.

Although limited specific process information was available from industry, it appears that potential worker exposure to natural zeolites exists in the mining and processing of zeolites as a result of personal contact, dispersion by wind, and mechanical or physical manipulation of the minerals. It is also fairly certain that because of the limited production scale, there are a small number of workers involved in zeolite mining and processing.

Although there was at least one dissenting viewpoint, it appeared to be generally thought that the basic structure of a particular zeolite would not be altered as a result of processing; e.g., as a result of crushing, a fibrous zeolite would produce fibers and an equidimensional

zeolite would fracture equidimensionally.

Mining Companies

Companies and organizations that are or have been engaged in mining or research concerning natural zeolites include:

The Anaconda Company
Atomic Energy Commission
U. S. Bureau of Mines
Colienco
Double Eagle Petroleum and Mining Company
Filtrol Corporation
U. S. Geological Survey
WR Grace and Company
Harrison Western Corporation
Leonard Resources
Letcher and Associates
Mine Safety and Health Administration
Mobil Oil Corporation
NL Industries
Norton Company
NRG Nu-Fuel Company
The Pennsylvania State University
Reserve Synthetic Fuels Incorporated
Union Carbide Corporation
Yuma Zeolite Corporation

Details concerning the companies mining and using zeolites and the amounts used are sparse and often speculative because of the small amounts of the minerals involved, the intermittent nature of the mining activities, the lack of reporting requirements, and the proprietary nature of such information. Based on published information and conversations with persons in government and industry, a general outline of the extent of mining and use of natural zeolites in the United States has been made.

Although essentially none has been shipped to date, the Double Eagle Petroleum and Mining Corporation has stockpiled 50,000 tons of clinoptilolite in anticipation of use primarily in sewage and radioactive wastewater treatment processes and as a deoderant in poultry houses. This clinoptilolite has been removed from deposits in Buckhorn, New Mexico, Fish Creek Mountain, Nevada, and Castle Creek, Idaho. This company has apparently shipped quantities suitable for research and development only at this time. Double Eagle has also mined some phillipsite for experimental purposes from a deposit in Pine Valley, Nevada. This mining has primarily all been done in the last few years.

WR Grace and Company owns claims on at least two zeolite deposits; one is near Lovelock, Nevada, although the mordenite and clinoptilolite that apparently occur in that area have not been mined by WR Grace to any appreciable extent, and the other is at the Bowie, Arizona, deposit. The chabazite taken from Bowie is used primarily as an acid resistant purifier for sour natural gas and has been removed at the rate of about 10 tons per year for the last 3 years.

Union Carbide appears to have one of the larger zeolite mining programs in the United States. This company is the most active in mining at the Bowie deposit and probably accounts for most of the estimated 1,800 tons taken from there in 1977. The first commercial mining of natural zeolites in this country occurred at Bowie in the early 1960's when Union Carbide removed about 50 tons of primarily high grade chabazite ore, containing small amounts of erionite, in their first year of production. The Linde Division of Union Carbide markets this mineral (AW-500) along with their synthetic molecular sieve zeolites, primarily for use as a dessicant and gas dryer. During the early 1960's Union Carbide mined small amounts of erionite-containing ore from a deposit near Pine Valley, Nevada. There were few uses for this mineral, and only a few hundred tons were taken. Claims were also made in 1958 on erionite deposits near Jersey Valley, Nevada, although it is unclear whether any ore was ever mined. Union Carbide has mined small amounts of mordenite in northwest Arizona, near Union Pass.

Chabazite ore containing small amounts of erionite is mined and marketed by the Norton Company. This mineral is taken from the Bowie deposit, where Norton Company has claims, and is mainly used as a dessicant, especially for petroleum products. The amounts mined and length of time Norton has worked the Bowie deposit is unknown. Small amounts of mordenite are reported to have been mined by Norton near Rome, Oregon, although details are lacking. The Norton Company also offers natural clinoptilolite and ferrierite on special request, although the source of these minerals is unknown.

It is thought that The Anaconda Company has four main zeolite mines, including ones near Ash Meadows, Nevada; East Gate, Nevada; and Tecopa, California; from which are obtained clinoptilolite, erionite, phillipsite, and mordenite. Erionite may be mined near Shoshone, California (this may be East Gate, Nevada). The Anaconda Company recently supplied 430 tons of clinoptilolite to the Upper Occoquan Sewage Authority in Northern Virginia for a tertiary water treatment plant. This material is used to remove nitrogen wastes in the form of ammonia from sewage wastewater. It is likely that Anaconda also supplied the clinoptilolite for the twin Tahoe-Truckee Sanitation District treatment plant. It has been reported that Anaconda mined 2,000 tons of clinoptilolite in 1977 possibly from a site in California.

It is thought that Mobil Oil Corporation mines erionite in central Nevada, probably near Jersey Valley, by open pit and possibly underground methods for internal use as a petroleum catalyst or molecular sieve for use in hydrocarbon separations.

About 1,500 tons of clinoptilolite, probably from the Creede (Ft. Collins), Colorado area, were mined and marketed in 1977 by Colienco. It has been reported (Eyde, 1976) that NL Industries supplied clinoptilolite from its Hector, California, site for use at a wastewater treatment plant in Rosemount, Minnesota.

IV. USES

Even though it is generally agreed that the extent to which natural zeolites are used domestically is quite limited, specific information in this area is not well documented and very difficult to obtain. Much of the use and process information is considered proprietary at this time. From what is known, it is believed that the number of occupationally exposed workers is small and the degree of the exposure to these zeolites is generally minimal (not including mining and processing operations). Since it is very important to retain their selective adsorption and ion-exchange properties, these zeolites are carefully packaged, transported, and handled to avoid contact with contaminants in industrial environments. In addition, zeolite-packed reactors or reacting vessels are enclosed systems and the expected occupational exposure during installation and maintenance may involve only a small number of employees.

When zeolites are processed with a special binder, e.g., clay, they are often extruded to form pellets or beads. This particular process may reduce the amount of respirable particles of zeolites for the workers involved in the zeolites installation or maintenance of reacting vessels.

The current and potential uses of zeolites are based on the following physical and chemical characteristics (See Table I):

1. Selective adsorption capabilities caused by molecular sieve action and/or dipole charge of molecules.
2. Hydrophilic nature of zeolites after water molecules are driven off by heating to 300-400°C.
3. Ion-exchange capabilities of the loosely bound resident cations.

Table I

Uses Determined by the Physical and Chemical
Properties of the Natural Zeolites

Uses	Properties		
	Molecular Sieve/ Dipole Charge	Hydrophyilic Nature	Ion- Exchange
1. Separation and Drying of Industrial Streams	X	X	X
2. Petroleum Cracking Catalysis	X		X
3. Production of Synthetic Fuels	X	X	-
4. Wastewater Treatment			X

Separation, Drying, or Purification of Industrial Streams

In petrochemical industries, the natural zeolites are useful as adsorbents in separating, drying, or purifying chemical products in various processes (Eyde, 1976, Norton, 1978). The selective adsorption capabilities (e.g., molecular sieve action) are determined by the size of pores or cavities of the zeolites, effective diameters of molecules of absorbates, and strength of dipole moment. Examples of their use are:

1. In an oil field, raw gas is separated from crude oil during the casing process. Oil is fed through a zeolite-packed column where the raw gas is adsorbed and removed.
2. Water molecules are adsorbed by the zeolites and removed from streams in drying processes for hydrochloric acid, chlorine, reformer hydrogen, and petroleum solvents.
3. In the purification processes, hydrochloric acid is adsorbed and removed from streams of reformer hydrogen, chlorine, and chlorinated hydrocarbons by the selective adsorption capability of zeolites packed in the reacting vessels.

Petroleum Cracking Catalysis

Some of the natural zeolites, especially, chabazite, have proven useful as catalysts or catalyst carriers in reactions such as hydrocracking, hydroisomerization, alkylation, and reforming in petroleum industries (Union Carbide, Norton Company, 1978). The zeolites are usually first processed either by combining with a clay base or activated with other catalysts before introduction into the reacting systems. When the processed zeolites are packed in a catalytic reactor, e.g., a reforming reactor, the zeolites provide more active sites for reactants during the cracking reaction. The zeolites may be regenerated; however, this may not be econo-

mically feasible. In addition, the capabilities of zeolites may be reduced by the process of regeneration which usually involves high temperatures.

Production of Synthetic Fuels

In the area of expansion of fuel supply, chabazite is currently used in a methane-recovery system by Reserve Synthetic Fuel, Inc. Gases produced from decomposed organic matter at the Palos Verde Landfill in Southern California are processed using the technique of pressure-swing adsorption. The raw gas is fed through processed chabazite-packed columns which remove carbon dioxide, water, hydrogen sulfide, and other contaminants yielding purified methane.

Wastewater Treatment

In wastewater treatment, clinoptilolite is currently used to bring ammonia nitrogen to the level permitted by local regulations. Clinoptilolite has been singled out among other natural zeolites to be considered for such purposes because of its occurrence in high purity forms (Sheppard, 1971), its high affinity for ammonium ions in the ion-exchange process, and its adsorptive capacity. The Rosemount plant in Minnesota was the first one of two on-going wastewater treatment plants. The system requires approximately 41 tons of clinoptilolite (supplied from NL Industries' deposit at Hector, California) for operating at design capacity of 600,000 gallons per day (gpd) (Eyde, 1976). The Tahoe-Truckee Sanitation District Plant in California is operating at a capacity of 6 million gpd (Eyde, 1976). The Upper Occoquan Sewage Authority of Fairfax County, Virginia, Tahoe's sister plant, will be in operation soon. In the Upper Occoquan plant, approximately 430 tons of clinoptilolite (supplied by Anaconda

Company) are required for eight clinoptilolites beds for operating at design capacity of 116,000 gpd. The Alexandria Sanitation Authority of Alexandria, Virginia is constructing a wastewater treatment plant that can operate at a design capacity of 54,000,000 gpd. There is concern over the accumulation of removed ammonia nitrogen from this natural zeolite ion-exchange process. Investigations have shown that fertilizer can be produced by chemically combining the ammonia nitrogen with sulfate. This particular method of managing the removed ammonia nitrogen will contribute to the increasing acceptance of the use of natural zeolites in wastewater treatment.

Current Suppliers of Natural Zeolites

1. W. R. Grace & Co.
Davison Chemical Division
Baltimore, Maryland
2. Norton Company
Chemical Process Products Division
Akron, Ohio
3. Union Carbide Corp.
Linde Division
Tarrytown, New York
4. NL Industries
Tallmadge, Ohio
5. Anaconda Company
Denver, Colorado

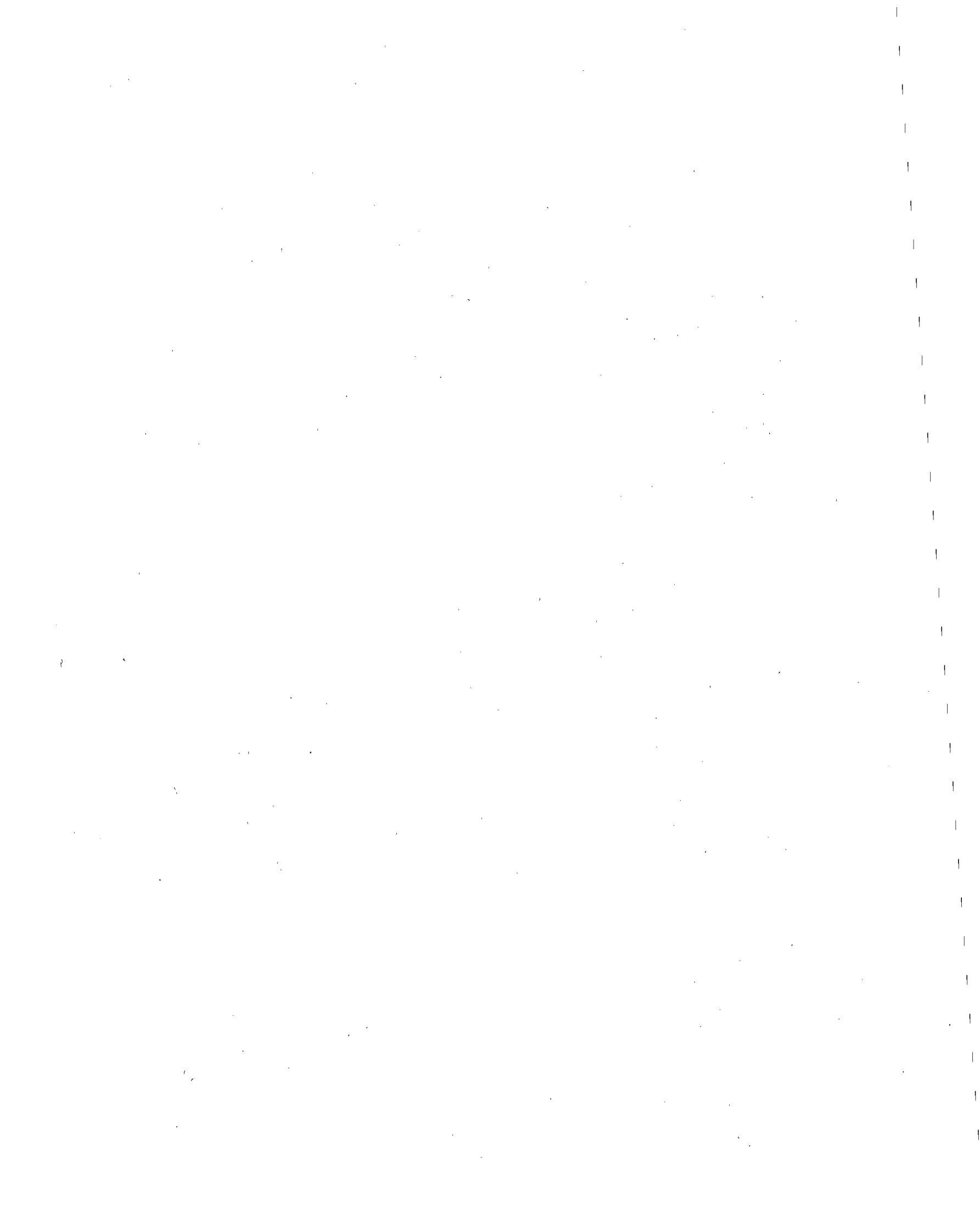
Current Users of Natural Zeolites

1. Union Carbide Corp.
Tarrytown, New York
2. Shell Oil Company
Shell Chemical
Houston, Texas
3. Mobile Oil Corp.
New York, New York

4. Exxon Chemical Company, USA
Houston, Texas
5. Reserve Synthetic Fuel, Inc.
Signal Hill, California
6. The Rosemount Plant of Minnesota
7. The Tahoe-Truckee Sanitation District Plant of California
8. The Occoquan Sewage Authority of Fairfax County, Virginia

Although not specifically identified, it is believed that limited quantities of natural zeolites are presently being used by other chemical, petrochemical, and petroleum refining companies.

A mineral termed "green sand" has been mined and marketed for at least the past 15 years in the New Jersey area, and mistakenly referred to as zeolite. This "green sand" has been used for various purposes including as a water softener. Analysis by x-ray diffraction recently showed that this material was definitely not any form of zeolite.



V. POTENTIAL USES

There are numerous applications of zeolites other than those mentioned in the previous chapter. These include those being used in other countries as well as those currently being researched in this country. The following applications are important when considering the potential of the zeolite industry; however, these applications are not currently being used domestically to any significant extent.

Husbandry and Fishery

In Japan, clinoptilolite has been used as a dietary supplement for swine and poultry (Mumpton, 1977b). Nakaue and colleagues at Oregon State University also conducted similar experiments on chickens (Nakaue, 1978). However, Nakaue's group reported that the increased growth rate of chickens placed on the diet containing clinoptilolite was not as significant as reported by Japanese researchers. In the same study, the average amount of dietary intake in chickens fed clinoptilolite was found to be higher than in the controls. It was concluded that these chickens required more feed because fewer calories were provided by clinoptilolite-containing diets.

Clinoptilolite is also being used in Japan to adsorb and control odors, and to aid in the disposal of sewage in swine raising (Honda and Koizumi, 1976). Nakaue and colleagues currently are involved in applying clinoptilolite to the bedding of chicken cages within confined areas (Nakaue, 1978). They report that the concentration of ammonia and the litter moisture levels are decreased by using clinoptilolite.

In the United States, one company has developed a water filtration system containing disposable filters packed with clinoptilolite. The clinoptilolite undergoes an ion-exchange process adsorbing ammonia nitrogen. This process would be beneficial in the fishery industry and transportation of live fish, shellfish or lobsters.

Radioactive Waste Treatment

Zeolites have been used in the treatment of radioactive wastewater produced as a result of increasing nuclear operations (Weinstein et al, 1964). Clinoptilolite, mordenite, erionite and chabazite have been studied for this purpose because of their high ion-exchange selectivity and resistance to radiolytic degradation (Mercer and Ames, 1976). These calcinated zeolites, and especially clinoptilolite, were found useful in separating and purifying cesium-137 from the radioactive wastewater by ion exchange. A small-scale process was described in which the radioactive wastewater is fed through columns of packed clinoptilolite, and the major portion of cesium-137 is removed by the ion-exchange process. The removed and purified cesium may be used in fuel reprocessing in the nuclear industry (Stroller and Richard, 1961).

Coal-Gasification Process

Some zeolites are under investigation for their potential use in the process of converting coal to synthetic gas. These zeolites act as adsorbents to remove ammonia and sulfur dioxide from the raw gas (Hayhurst, 1976). A current problem for this application concerns the competitive

adsorption by zeolites of both water and ammonia within the same process.

Production of Oxygen and Nitrogen Gases

A study from Japan indicates that, when air is fed through pre-treatment columns of silica gel and granulated clinoptilolite, water, sulfur dioxide, and carbon dioxide are removed. A high percentage of oxygen in air is then generated by feeding this purified airstream through a column packed with mordenite for the removal of nitrogen gas. The nitrogen-saturated mordenite column can be treated to obtain the purified nitrogen gas (Minato and Tamara, 1976).

Pozzolans in Cements and Concretes

It is reported that in 1912, clinoptilolite-rich pozzolans were used to partially replace cement required in the construction of the Los Angeles Aqueduct (Mumpton, 1973). There is no further information on the more recent domestic use of zeolites for this type of application. In Bulgaria, tuff containing a high content of clinoptilolite is mined for use as a pozzolan (Mumpton, 1973). In the United States, zeolites are currently being tested for possible use as a pozzolan in the construction of water-containing structures, such as dams and aqueducts.

Other Uses

At atmospheric pressure, zeolites have demonstrated a selective adsorption capacity for methane. This has possible application in the storing or transporting of methane gas in zeolite-lined tanks (Munson, 1976).

Clinoptilolite has been used in Japan for conditioning acidic soil by delaying the release of ammonium ions or other important cations from fertilizer. Also in Japan, a major amount of mined clinoptilolite is extensively used as a filler for paper in the paper manufacturing industry (Torii, 1976).

VI. BIOLOGIC EFFECTS

Toxicologic information on natural zeolites is virtually nonexistent. However, exposure to at least one of the fibrous zeolites, erionite, has been implicated in an unusually high incidence of what was diagnosed as malignant pleural mesothelioma (determined by electron microscopy), calcified pleural plaques, and chronic fibrosing pleuritis in some of the residents of Karain, a village in Turkey (Baris et al, 1978a). In the study year of 1974, when the village population was 604, 14 (2.3% of the total population) died of mesothelioma (Baris et al, 1975). The incidence of mesothelioma in this village in 1975 was found to be 1.3% (Baris et al, 1975); in 1975/1976 the incidence was 1.9% (Baris et al, 1978b). Asbestos-induced mesothelioma was found by the same primary investigator in many regions of Turkey at the same time (Baris, 1975), but, in the locale in question, there were no known asbestos deposits. However, a study of Karain's various water supplies showed small quantities of asbestiform fiber (particle length, 5-70 μ) clumps in the water piped from a nearby spring and from one of the old wells (Baris et al, 1978b). The water from the spring had been used for drinking, washing, and cooking for over 100 years. The source of these fibers was not indicated; the piping systems were not made of asbestos (Baris et al, 1978b).

At the time of the initial study (Baris et al, 1975), the investigators speculated that the diseases in this village might have been caused by silicates of volcanic origin found in the soil. In 1978, the investigators speculated that the diseases might have been caused by exposure to

the undefined but small amounts of asbestos in the village drinking water supply because asbestiform fibers were found at autopsy in the pleura of two of five persons who died of mesothelioma (Baris et al, 1978b). However, in their latest report (Baris et al, 1978a), the investigators attributed the diseases to exposure to erionite. The authors discounted asbestos in the water as the cause of the mesotheliomas in this area because of the small amounts present and because of the abundance of erionite of unstated but "respirable" dimensions in the soil of the area (Baris et al, 1978a). The unusual cultural practice of the people in this farming community of sieving the soil mixed with natural fertilizer in April of each year resulted in an unusually high exposure to the dust. The authors (Baris et al, 1978a) believed that fibers of materials having the same dimensions as that of asbestos had a similar carcinogenic potential.

This report (Baris et al, 1978a) of mesothelioma formation in humans attributed to exposure to erionite, one of the fibrous zeolites, does not prove that the carcinogenic relationship is real, especially in light of the absence of studies of the carcinogenic potential in laboratory animals. Furthermore, the finding of asbestiform fibers in the water (Baris et al, 1978a, 1978b) should not be totally dismissed as having been a causative agent, since the amount of exposure was not known and could have been significant. A relevant study of asbestos-linked cancers can be found in the NIOSH Revised Recommended Asbestos Standard (NIOSH, 1976).

Even though exposure to one or more zeolites could not be linked positively to the development of malignant mesothelioma, the investigators (Baris et al, 1978a) raised a valid doubt of the safety of erionite based on its physical similarities to asbestos fibers. Wagner et al (1976)

showed that glass fibers, when produced with similar size dimensions, caused mesothelioma in rats when intrapleurally injected, but not when the fiber diameter was increased considerably ($0.12\ \mu$ vs $1.8\ \mu$). Stanton (1973) also maintained that fibers other than asbestos could cause mesothelioma, but only when the fiber diameter was of the same order as that of asbestos. It is stated in the revised recommended standard for asbestos (NIOSH, 1976) that asbestos fibers having a diameter of less than $0.5\ \mu$ are the most active in producing tumors.

The length of a fiber is also an important consideration in the potential carcinogenicity of the material in question. For an asbestos fiber to produce carcinogenic effects, it is thought that the fiber length-to-diameter ratio must be 3:1 or greater (NIOSH, 1976). In addition, fibers that are $20\ \mu$ or more in length apparently do not migrate once in the body, but fibers less than $20\ \mu$ move at a rate that is inversely proportional to their length (Karacharova et al, 1969; Friedrichs et al, 1971). Although movement of asbestos through the gastrointestinal tract has, as yet, not been adequately demonstrated (NIOSH, 1976), ingestion should be considered a potential route of exposure.

Another consideration is the size of the particle when it is inhaled. It has been shown with asbestos (Timbrell, 1965; Timbrell, 1972) that fibers having dimensions greater than $3\ \mu$ in diameter and $100\ \mu$ in length are not considered respirable in that they will be removed from the lungs by ciliary action or they will not even reach the lungs.

Considering the above-mentioned factors that may be necessary for carcinogenic action with asbestos, erionite and mordenite are the most similar zeolites in physical dimensions to asbestos. Erionite is needle-shaped, and the needles are $10\text{--}20\ \mu$ in length and about $0.5\text{--}1\ \mu$ wide

(Mumpton, 1977a). Mordenite needles are from 5 to 20 μ in length and 0.5-1 μ in diameter (Mumpton, 1977a). Since there is a report (Baris et al, 1978a) that associates mesothelioma formation with exposure to erionite, and because fibers other than asbestos, e.g., fiberglass (Wagner et al, 1976) can cause mesothelioma in animals, the zeolites most closely resembling asbestos physically, e.g., erionite and mordenite, should be further investigated to determine if there is a carcinogenic potential.

The only toxicity information found on nonfibrous zeolites was an animal experiment testing clinoptilolite (Timar et al, 1966). The investigators injected rats intratracheally with clinoptilolite a single time and determined the effects by necropsy at selected intervals over 1 year. They reported that 10 days after injection a typical foreign-body reaction developed, with granuloma formation, the presence of which did not change over the 1-year period.

VII. RECOMMENDATIONS OF STUDY POPULATION AND PLANT VISITS

Although there is abundant information on the mineralogy, chemical and physical properties of zeolites, the specific information necessary to assess the feasibility of a cohort mortality study and to select plant visit sites for a Task II study is more difficult to obtain, and in some cases unavailable during the timeframe of preparing this Task I report. Despite this, it is felt that an accurate overall view has been obtained of the mining and use of zeolites in this country enabling definite suggestions and recommendations on the usefulness, feasibility, and protocol of additional studies.

Mortality Study

A cohort mortality study investigating mesothelioma formation and zeolite exposure does not appear feasible at this time because there was not a sufficient work population exposed to zeolites during the required time period. In considering work populations in the mining, processing, and use categories, the latency period of mesothelioma must be considered. This latency period ranges from about 15 to 25 years or longer (Levine, 1978). Discounting the sporadic and very limited use of zeolites as a building stone and its apparent one-time use as a pozzolan in the Los Angeles Aqueduct in 1912, commercial mining of zeolites did not start in this country until 1961 by Union Carbide in the Bowie, Arizona area. Because of the latency period for mesothelioma, only workers exposed between 1961 and 1965 were considered for the study population.

The first-year production of zeolites at Bowie was very small,

approximately 50 tons or one railcar load. Even though production has slowly increased, even in 1977 the total production from Bowie, which is and has been the major mining site, is estimated at only approximately 2,000 tons or 40 carloads. It is believed that other companies did not start their mining operations to any major extent at Bowie or any other location by 1965. The mining and limited milling performed at each site involved only a small number of workers (approximately 6). Based on this and the limited scale during these early years, an estimate of less than 50 workers were involved in the mining and milling operations between 1961 and 1965. Even without considering the availability of the required records, this starting group appears inadequate for a study population.

It is also very doubtful that there were sufficient numbers for a suitable study population exposed during these years in the processing and application phases of zeolites. The zeolites were used to a limited extent as a catalyst, adsorbent, and ion exchange resin in process industries; however, significant proportions of the total produced during 1961-1965 were probably used in research. The number of workers involved and the degree of exposure were probably very small and because of this, documentation by personnel records is very questionable.

Despite the lack of a suitable study population for a cohort mortality study, there are other alternatives that are within the scope of this project to further assess the carcinogenic potential of zeolites.

1. Survey mesothelioma and lung cancer rates by county comparing geographical locations where fibrous, nonfibrous, and no zeolites are found. If fibrous zeolites are similar to asbestos in carcinogenic activity, increased lung cancer rates should also be expected in the

exposed population. In this survey, it would be vital to recognize areas where asbestos deposits are known.

2. Identify a suitable study population exposed to zeolites by considering mining and milling operations where zeolite is a contaminant of other ores. There appears to be a number of other mining operations in most of the areas where zeolite deposits are known. Appendix B discusses this further and lists by location other typical mining activity. It can be determined if zeolites are contaminants in these other mining operations by instituting a limited schedule of bulk and air sampling. The Mine Safety and Health Administration (MSHA) recently initiated a project which is directly related. They are attempting to identify all mining operations where zeolites occur even as contaminants and do plan a sampling program. A combined effort with MSHA seems the most effective approach for further study in this area.

3. Try to obtain as much information as possible from Japan where zeolites and especially fibrous mordenite has been extensively used.

Plant Visits

This Task I study has revealed that there is a general lack of specific information on the zeolite industry in this country, both in production and application phases. A Task II industrial hygiene study would be very useful to characterize the various aspects of this industry and evaluate if a potential health hazard exists. This Task I study also indicates that the current extent of production and use domestically is

quite limited; however, if foreign use and the extent of domestic research and available quantities are indicators, the potential for rapid expansion of this industry should not be ignored. Several members of this mineral group are fibrous with physical characteristics similar to asbestos and this is further reason why this industry should be investigated. The types of information that can be accumulated in a Task II study include:

- specific types of zeolites being mined
 - composition of ores
 - structural characterization
- processes
 - mining and milling
 - processing, e.g., addition of clay binders
 - application or use
- qualitative and some quantitative assessment of worker exposure
- other hazards in processes
- existing control technology
- possible structural change of fibrous or nonfibrous types during processing
- availability of work records

Some of this information can be obtained by increased cooperation by the involved companies. However, a limited schedule of Task II plant visits which would include walk through surveys with limited sampling (bulk and air), should provide much information. In order to characterize the total industry, mining, processing, and use should be covered by these visits. Plant visit recommendations for Task II include:

- A. Mining and Milling - A site visit to several mining operations in the Bowie, Arizona area would allow a comprehensive study of the major commercial mining deposit in the country. Several

companies such as Union Carbide, Norton Company, W. R. Grace, as well as the local contractors could be visited on the same trip.

- B. Processing - Union Carbide and Norton Company appear to be the two major processors of natural zeolites for use as adsorbents and catalysts. A visit to one is recommended. Specific plant location is not known at this time.
- C. Use - Both Union Carbide and Mobil Oil have been doing research on zeolite applications, particularly in process industries. Also, they are probably users of natural zeolites in limited quantities. A visit to one company is recommended.

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Appendix A
ERIONITE (E), MORDENITE (M), AND PHILLIPSITE (P)
OCCURRENCES IN SEDIMENTARY ROCKS

<u>Location</u>	<u>Zeolite</u>
<u>Oregon</u>	
Near Bearbones Mountain, Lane County	M
Vicinity of Stein's Pillar, Crook County	M
Near Durkee, Baker County	E
Near Rome, Malheur County	E, M, P
West face of Hart Mountain, Lake County	M, P
Near Harney Lake, Harney County	E, P
<u>Wyoming</u>	
Beaver Rim, Fremont County	E, P
Near Split Rock, Natrona County	P
Near Green River, Sweetwater County	M
<u>South Dakota</u>	
Near Mud Buttes, Butte County	P
Sheep Mountain Table, Shannon County	E
<u>Colorado</u>	
Near Creede, Mineral County	M
<u>Nevada</u>	
Pine Valley, Eureka County	E, P
West flank of the Shoshone Range, Lander County	E
Reese River, Lander County	E
Jersey Valley, Pershing County	E, P
Near Lovelock, Pershing County	M
Near Copper Valley, Churchill County	M

<u>Location</u>	<u>Zeolite</u>
<u>Nevada</u> (cont.)	
Near Eastgate, Churchill County	E
Teels Marsh, Mineral Co.	P
Near Silver Peak, Esmeralda County	M, P
Nevada Test Site, Nye County	M
<u>California</u>	
Owens Lake, Inyo County	E, P
Lake Tecopa, Inyo County	E, P
Searles Lake, San Bernardino County	P
Mojave Desert, eastern Kern County and San Bernardino County	E, M, P
Near Nipomo, San Luis Obispo County	M
<u>Arizona</u>	
Union Pass, Mohave County	M
Near Wikieup, Mohave County	E, P
Near Horseshoe Reservoir, Maricopa County	E, P
Near Morenci, Greenlee County	M
Near Bear Springs, Graham County	E, P
Along San Simon Creek, Cochise and Graham County (near Bowie, Arizona)	E

Adapted from information compiled by R. Sheppard, United States Geological Survey, 1971, and published in Olson, 1975.

Appendix B
ZEOLITES AS A CONTAMINANT OF OTHER MINING OPERATIONS

Although there has been little, if any, sustained, long-term worker involvement in zeolite mining operations in the United States, it may be possible to study worker exposure to zeolites as contaminants in other mining operations. Zeolites have been found in a number of different types of sedimentary rocks, including limestone, phosphorite, coal, bauxite, and ironstone (Hay, 1966). They may be present in varying amounts in pozzolans and clays. Bentonite clays, which are found in large amounts in Montana, have been associated with deposits of zeolites. Zeolitic minerals are known to occur with copper deposits in northern Michigan, and U. S. Geological Survey papers dating back to the early 1900's are reported to describe this area. Zeolites may also occur as alteration products associated with sedimentary deposits of gold and silver in the western United States.

Although many zeolite deposits are not considered to be mineable because of the overburden characteristics, the low grade of the ore, and for other reasons, they are known to occur widely and abundantly throughout the western United States. Thus, it is possible that zeolitic minerals may occur as contaminants in many types of surface mining operations.

The Mine Safety and Health Administration (MSHA) in Phoenix is aware of only intermittent production of zeolites, especially in Arizona, Nevada, California, and Oregon. The only recent (since 1973) commercial production that MSHA is aware of is that carried out at the Bowie, Ari-

zona site. Although MSHA attempts to monitor production of even very small amounts of zeolites, it is possible that short-term mining operations may not be detected. Recently, a large scale screening program concerning zeolites has been established. Part of this program will include sampling for zeolites at all operations where zeolites are mined or are potentially mined. This will include virtually all surface-type mining operations including sand, gravel, and various types of metal and mineral production. All types of zeolites will be sampled, and special attention will undoubtedly be focused on fibrous varieties.

The following is a listing of mining and processing operations, along with the material handled, that are located in several selected counties where deposits of zeolites have been reported. These companies are examples of operations in which workers may possibly be exposed on a regular, sustained basis to zeolites as contaminants occurring along with other minerals and rocks. It would be necessary to do more detailed surveys and sampling at operations such as these to determine if there actually is potential for exposure to zeolites. Information on when these operations began would also be necessary to determine if suitable study populations of workers exposed to zeolites as a contaminant exist. This list is intended to present a brief sampling of the types of mining and milling operations existing in areas where deposits of zeolites have been reported to occur. It is not intended to imply that zeolites are necessarily found as contaminants in these operations and it is not meant to give a complete and comprehensive account of the mining industry in these areas.

Sources for the material compiled in this table include:

E/MJ International Directory of Mining and Mineral Processing Operations, 1978.

Pit and Quarry Directory of the Non-Metallic Minerals Industries, 1970.

World Mines Register, 1975-1976.

Arizona

Cochise County

Cyprus Johnson Copper Co.--copper

Cochise Sand and Rock Co.--sand and gravel, crushed rock

Warren Redi-Mix--sand and gravel, crushed gravel

Maddux and Son--sand and gravel

Paul Lime Plant Inc.--ground limestone, crushed limestone, limestone

Graham County

Inspiration Consolidated Copper Co.--copper oxides and silicates

Gila Valley Concrete Co. Inc.--sand and gravel

Maricopa County

Ari-Zonolite Co.--lightweight aggregates

Superlite Builders Supply--pumice products

Arizona Gypsum Corp.--gypsum, bentonite, diatomite

Arizona Portland Cement Co.--Portland cement

Concrete Industries Inc.--volcanic ash, tuff

AC Haigler--pumice, pumice products

Mohave County

Duval Corp.--copper, molybdenum, silver

Red Dog Mining Inc.--gold

Arizona (continued)

Yuma

Desert Gold Ltd.--gold ore, manganese ore

California

Inyo County

Bishop Building Materials--pumice

Huntley Mines--pyrophyllite, clay, talc

Insulating Aggregates--pumice

Sierra Talc Co.--clay

United Sierra Division--clay

Kern County

Pacific Western Industries Inc.--Portland cement

Phoenix Constr. Co.--Portland cement

California Portland Cement Co.--Portland cement, pozzolan

San Bernadino County

Owl Services Rock Co.--sand and gravel

Island Empire Milling and Mining Corp.--gold, silver, platinum minerals

Desert Minerals Inc.--talc, clay

NL Industries Inc.--bentonite

Pfizer Inc. Minerals, Pigments, and Metals Div.--limestone, talc, clay

Molycorp Inc.--rare earths

Vinnell Mining and Minerals Corp.--silica

Hi Desert Concrete Products--rock, sand

RT Vanderbilt Co. Inc.--talc, refractories clay, bentonite

Southwestern Portland Cement Co.--Portland cement

California (continued)

San Bernardino County (continued)

Kasler Corp.—sand and gravel

Dana Materials Co.--concrete aggregates

Ridgelite Products Co.—lightweight aggregates

California Portland cement Co.—Portland cement, limestone

Kleen-Gro. Co.--volcanic ash, pumice

Colorado

Mineral County

Ft. Collins Ready Mix--sand, base

Pete Lien and Sons Inc., (Colorado Lien Co.)—ground calcium, filler

Sterling Sand and Gravel Co.--sand and gravel, crushed gravel

Nevada

Churchill County

Dodge Construction Inc.—sand and gravel

Silver State Construction Co.--sand and gravel, crushed stone, bituminous aggregates

Eureka County

Carlin Gold Mining Co.--gold, mercury

Idaho Mining Corp.—gold, silver

NL Industries Inc. (Baroid Div.)—barite

Pershing County

Tungsten Properties Ltd.—tungsten

The Wolfran Co.—perlite, gypsum, marl

Nevada (continued)

Nye County

Cind-R-Lite Co.--lightweight aggregate

Oregon

Malheur County

Ready-to-Pour Concrete Co.--sand and gravel

Snake River Sand and Gravel--sand and gravel

Appendix C SYNTHETIC ZEOLITES

Background

Currently, the production, use, and importance of synthetic zeolites domestically is much greater than the naturally occurring zeolitic minerals. As mentioned earlier, natural zeolites have been recognized for at least 200 years and were originally used as building materials and then later for their unique adsorptive properties (Breck, 1975; McBain, 1932). Synthetic zeolite development began in 1948 when Union Carbide investigated various adsorbents that could be used in the separation and purification of atmospheric gases and for other industrial processes (Union Carbide). Natural zeolites were tested in this study and showed favorable results. However, the two main disadvantages that were realized before with natural zeolites, i.e., the necessity to locate high-grade natural deposits and the variability and unpredictability of these minerals, became apparent. Because of this, Union Carbide soon started a successful venture in the synthesis of these materials and by 1953 had produced over 30 separate types (Union Carbide).

As a mechanism for rapidly identifying commercial applications, Union Carbide in 1954 distributed samples of synthetic zeolites to approximately 100 companies in the chemical, petrochemical, and petroleum refining industries. A large percentage of these companies reported favorable results, especially in dehydration and gas purification processes, and

requested that larger quantities be made available. Union Carbide started the synthetic zeolite market in November 1954 by making their products commercially available (Breck, 1975; Union Carbide). Since then, as the number of industrial applications and demand has increased, several other companies have gone into the synthetic zeolite manufacturing business (Norton Company, 1978; SRI International, 1978).

Today synthetic zeolites are used widely in the chemical and petrochemical industries (Breck, 1975; Collins, 1968; Lee, 1973). The unique attributes found in the natural zeolites have been duplicated and improved in an easily manufactured synthetic. Because of this, synthetic zeolites have become an important tool as an adsorbent, catalyst or catalyst carrier, and ion exchange resin used in many of the process industries such as the chemical, petrochemical and petroleum refining. They have also found application in the production of natural gas as well as in water treatment plants (Lee, 1973).

Manufacturing Processes

There are three basic processes used in synthesizing zeolites (Breck, 1975; Union Carbide):

- 1) Synthesis of high purity zeolites from reactive aluminosilicate gels; this is referred to as the hydrogel process;
- 2) Use of clay group minerals, e.g., kaolin, as a starting material; and
- 3) Use of other naturally occurring minerals, e.g., natural silicas, amorphous minerals, and volcanic glass.

Process No. 1 or the hydrogel process is similar to the original synthesizing process and is still the important commercial process for producing synthetic zeolite adsorbents and catalysts. In this process, alumina trihydrate is dissolved in hot caustic and mixed with sodium silicate solution to form a homogeneous gel. The gel is then transferred to a separate tank where crystallization occurs by increasing the temperature to 200°F.

The zeolite crystals are often mixed with various types of inorganic clay binders to form agglomerates that increase the physical strength. These agglomerates are then extruded to form beads or pellets and then calcined (Norton Company, 1978; Union Carbide).

Structure and Types

Like the natural zeolites, synthetic zeolites are crystalline aluminosilicates that are honeycombed with spaces connected by pores ranging in size from about 3 to 10 angstrom in diameter. There are approximately 90 different synthetic zeolites commercially available (Breck, 1975). Some of these are related to the natural zeolites but many have structures that are not similar. Unlike other adsorbents, synthetic zeolite molecular sieves have very uniform pore sizes.

Manufacturers and Production

Although actual production figures are not included for each company listed in Table 1, there is an indication of some of the plant's annual capacity limits. Based on these figures and information received from various contacts, a rough estimate of at least 200,000 tons of syn-

thetic zeolites are being produced annually.

Current Synthetic Zeolite Manufacturers

1. W. R. Grace & Co.
Davison Chemical Division
Baltimore, Maryland
2. Norton Company
Chemical Process Products Division
Tallmadge, Ohio
3. Union Carbide Corporation
Linde Division
Chicasaw, Alabama
4. Culligan International Company
Culligan USA. division
San Bernardino, California
5. J. M. Huber Corporation
Havre de Grace, Maryland

Potential Synthetic Zeolite Manufacturers

1. Ethyl Corporation
2. FMC Corporation
3. Philadelphia Quartz Company

Uses and Users

Since 1954, when synthetic zeolites became commercially available, they have found a wide variety of applications in industry. They have become particularly important in the chemical, petrochemical, and petroleum refining industries. For purposes of discussion, the wide variety of uses can be put into three classifications: in industrial adsorption processes, as a catalyst, and as an ion-exchange resin (Lee, 1973).

Adsorbent

1. Hydrocarbon Separation Processes

A. n-Paraffin Separation

A particular synthetic zeolite (CaA molecular sieve) with a specific pore size of 5 angstrom is used to separate n-paraffins from mixtures of 150 paraffins and aromatics. This is applicable primarily to the petrochemical industry.

B. p-Xylene Separation

Because of its increased use as a raw material in polyester products, p-xylene demand has also increased. Synthetic zeolites are used to separate p-xylene from a C8 aromatic mixture containing xylenes and ethylbenzene.

C. Olefin Separation

Used to separate olefins, such as n-butylenes from a feed stock containing olefins and paraffins.

2. Drying Gases and Liquids

A. Cracked Gas Drying

Used in the manufacturing processes for producing ethylene and propylene. The removal of water is an important step in the separation and purification of these important petrochemicals.

B. Other Liquid and Gas Drying

Zeolites are all very hydrophilic and effective dessicants. They are used extensively to dry numerous chemicals such as solvents and synthetic gases.

3. Separation and Purification of Industrial Streams

A. Purification of Air Prior to Liquefaction

Used to remove water vapor and carbon dioxide before liquefying air.

B. Natural Gas Purification

Water vapor, sulfur compounds, and carbon dioxide are removed effectively.

C. Oxygen Enrichment of Air

Water is aerated by passing through zeolite beds.

D. Pollution Control

Used to remove SO_2 , H_2S , and NO_x from industrial off-gas streams.

4. Nonregenerative Applications

Used in dessicant cartridges to dry Freon-type refrigerants and in the manufacture of dual-pane windows.

Catalysts and Catalyst Carriers

Synthetic zeolites are active crystalline catalysts used for hydrocracking, hydroisomerization, alkylation, reforming, and cracking.

These reactions proceed through carbonium ion intermediates, which the synthetic zeolites provide. Catalytic sites are located probably at cation sites or vacated cation sites. Synthetic zeolites are effective catalysts because of several reasons including the silica:alumina ratio, pore size, type of cation present and number of cation deficient sites.

Also, synthetic zeolites can serve as catalyst supports for metal

or metal compound cocatalysts. These applications are especially useful in the rubber, plastics, adhesive, and paint and coatings industries.

Ion Exchange

Zeolites readily undergo ion exchange of their resident cations such as sodium, hydrogen, etc. with a large variety of other ions. These include the alkaline and rare earths plus the noble and transition metals. They have also been used for recovering and storing radioactive cesium.

Because of their ion exchange capabilities, they have been used as water softening resins in water treatment plants and for cleaning up radioactive wastes in nuclear power plants. They are also being used in detergents to replace phosphates.

Identified Users

Continental Oil Company
Exxon Chemical Company, USA
Shell Chemical Company
Union Carbide Corporation
Allied Chemical Corporation
Chevron Chemical Company
Mobil Oil Company
Shell Oil Company
Proctor and Gamble

Appendix D
SEARCH STRATEGY

A literature search of reference sources on the natural zeolites provided information on the occurrences and mining, production and processes, the uses and applications, and the health effects of the natural zeolites including the toxicity and carcinogenicity in animals and humans.

The reference sources are as follows:

I. Computerized search of data bases

1. Toxline, Medline, Chemline and Cancerline of the National Library of Medicine
2. Dialog of Lockheed Information Systems
3. Orbit of System Development Corporation (SDC) Search Service
4. NIOSHTIC of the National Institute for Occupational Safety and Health (provided by NIOSH)

II. Inhouse references

1. Kirk-Othmer Encyclopedia of Chemical Technology, ed 2 rev. New York, Interscience Publishers, 1966, vol 11
2. Lowenheim FA, Moran MK: Faith, Keyes, and Clark's Industrial Chemicals, ed 4. New York, John Wiley and Sons, 1975
3. Chemical Economic Handbook. Menlo Park, Calif, SRI International, 1977 and 1978
4. Patty FA (ed.): Industrial Hygiene and Toxicology, ed 2 rev. New York, Interscience Publishers, 1963, vol 2
5. Hawley GG (ed.): The Condensed Chemical Dictionary, ed 8. New York, Van Nostrand Reinhold Co, 1971
6. Sax NI: Dangerous Properties of Industrial Materials, ed 4. New York, Van Nostrand Reinhold Co, 1968
7. Sittig M: Pollution Control in the Asbestos, Cement, Glass and Allied Mineral Industries. Park Ridge, NJ, Noyes Data Corp, 1975

8. Key MM, Henschel AF, Butler J, Ligo RN, Tabershaw IR (eds.): Occupational Diseases — A Guide to Their Recognition, DHEW (NIOSH) Publication No. 77-181. US Department of Health, Education, and Welfare, Public Health Service, Center for Disease Control, National Institute for Occupational Safety and Health, 1977
9. Thomas Register, ed 67. New York, Thomas Publishing Co, 1977
10. Engineering and Mining Journal—International Directory of Mining and Mineral Processing Operations, 1978
11. Pit and Quarry Directory of the Non-Metallic Minerals Industries, 1970
12. World Mines Register, 1975-1976

III. Retrieved Literature

Literature was obtained from local libraries including Library of Congress, George Washington University Library, and National Library of Medicine.

IV. Tree search

The bibliographies of all received literature were screened for additional references.

