MINING SURVEILLANCE INVESTIGATION
NATURAL ZEOLITES

FINAL REPORT

ANNE ALBERS

ENVIRONMENTAL INVESTIGATIONS BRANCH
DIVISION OF RESPIRATORY DISEASE STUDIES
NATIONAL INSTITUTE FOR OCCUPATIONAL SAFETY AND HEALTH
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LIST OF CONTENTS

PREFACE

Section 101(a)(6)(B) of the Federal Mine Safety and Health Act of 1977 states that the Secretary of Health and Human Services "...shall, for each toxic material or harmful physical agent which is used or found in a mine, determine whether such material or agent is potentially toxic at the concentrations in which it is used or found in a mine." The Act designates the National Institute for Occupational Safety and Health (NIOSH) as the agency in the Department of Health and Human Services responsible for activities in the field of mine health.

Part of the NIOSH effort in this field has been a surveillance program which conducts preliminary investigations into specific agents found or used in mines which are of concern with respect to their potential as an occupational health hazard. These investigations are limited in scope to literature reviews and preliminary industrial hygiene field surveys. The findings of these preliminary investigations are used to plan future NIOSH research efforts in the field of mine health.

INTRODUCTION

A fibrous variety of the mineral zeolite has been correlated with a high incidence (22 cases/10,000 people) of pleural mesothelioma among the inhabitants of two small villages in central Turkey.(1-2) The report generated concern due to the widespread use of synthetic zeolites and the potential for natural analogues to be mined on a large scale.(3)

In a subsequent geological study of the area in central Turkey, it was found that the geological data collected suggested that a negative correlation existed between the occurrence of zeolites and the incidence of pleural mesothelioma.(4) The only ubiquituous mineralogical parameter found was an abundance of volcanic glass and cristobalite.

Under contract to NIOSH, SRI International performed a review of available information on zeolites.(5) NIOSH contacted a number of producers and users of zeolites (natural and synthetic) in order to obtain samples for microscopic analyses and to assess the extent of the production and use of zeolites. NIOSH also conducted an industrial hygiene survey of the most active commercial mining site located near Bowie, Arizona. The survey found that workers were not exposed to fibrous zeolite or to total or respirable particulate material in excess of existing or recommended exposure limits.(6)

The purpose of this report is to provide background information on the zeolite industry in the United States; describe the mineral family of zeolites; how they are mined and processed; identify the principal industrial uses of zeolites, the principal areas where they are mined, and the number of mines and miners involved; report on findings from NIOSH industrial hygiene surveys at zeolite mines and deposits; and review the scientific literature concerning the toxic effects to animals and humans associated with exposure to specific varieties of zeolites.

HISTORICAL BACKGROUND

The word zeolite was coined by Baron Cronstedt, a Swedish mineralogist who recognized them as a new group of minerals in the 1750's. The first analysis of their crystal structure was made in 1930. In the late 1940's research workers at Union Carbide began a program of zeolite synthesis and study.(3)

The development of high capacity, selective adsorbent zeolites from this research has been declared as a major research achievement.(7) Since the late 1950's there has been exploration and sampling of zeolite deposits by commercial organizations and private parties in the western United States. The exploration peaked in the early 1960's when the search concentrated on natural zeolites that might compete with the synthetic zeolites as molecular sieves. In the early 1970's exploration increased again only with the emphasis on the location of zeolite deposits suitable for pollution control technology.(8) Synthetic zeolites for use as detergent builders have recently gained an estimated market of 300 million pounds per year.

MINERAL COMPOSITION AND STRUCTURE

Zeolites are crystalline, hydrated aluminosilicates of the alkalies and alkaline earth cations. They can be viewed as hydrated equivalents of the feldspars. They have an infinitely extended three-dimensional anion framework with an atomic ratio (Al + Si):O=2. The trivalent aluminum requires the presence of additional positive charges in order to maintain electrical neutrality. The cations generally are Ca^{+2}, Na^{+},or K^{+}.(9) The basic framework arrangement consists of SiO_4 and AlO_4 tetrahedra in a geometric form which results in open structures. The framework encloses networks of channels, or pores, which lead to sizeable central cavities. In the hydrated form the cavities are filled with mono and divalent cations surrounded by water molecules. When dehydrated the cations become coordinated with oxygen on the inner surface of the cavities.(10)

The dimensions of many zeolites are large enough to allow molecules up to several angstroms in diameter to enter and to become adsorbed in the vacant cavities. Certain zeolites with a high percentage of vacant cavities (void volume) are therefore useful as commercial adsorbents. Molecules with diameters larger than the channels are unable to enter the cavities and consequently are not adsorbed by the zeolite. This is the reason for the well known molecular sieve action of many zeolites.(10) These two properties of zeolites - their ability to separate molecules based upon molecular size and configuration and to adsorb molecules with a selectivity that is not found with conventional adsorbents - are responsible for the current interest in them.

ZEOLITE VARIETIES

Zeolite minerals have diverse origins with respect to age, lithology, and geologic setting. Only nine zeolite species (analcime, chabazite, clinoptilolite, erionite, ferrierite, heulandite, laumontite, mordenite, and phillipsite) commonly occur in zeolite deposits. Analcime and clinoptilolite are the most abundant zeolites in sedimentary rocks. Nearly monominerallic beds are known, but most deposits consist of two or more zeolites as well as clay minerals, silica minerals, and feldspars.(8)

The zeolites of concern, with respect to occurring in a fibrous mineral habit, of producing mineral particles with aspect ratios of 3 to 1 or greater, are given below along with their chemical formula and crystal system.(8)

SPECIES	FORMULA	CRYSTAL SYSTEM	COMMENTS
Erionite	$(Na,K,Ca)_9(Al_9Si_{27}O_{72}).27H_2O$	Hexagonal	Abundant in sedimentary rocks
Mordenite	$Na_8(Al_8Si_{40}O_{96}).24H_2O$	Orthorhombic	Abundant in sedimentary rocks
Ferrierite	$(Na_2Mg_2)(Al_6Si_{30}O_{72}).18H_2O$	Orthorhombic	Rare in sedimentary rocks
Phillipsite	$(Na,K)_{10}(Al_{10}Si_{22}O_{64}).20H_2O$	Orthorhombic	Abundant in sedimentary rocks

Sedimentary erionite occurs as rod- or needle-shaped crystals. Mordenite occurs as long, delicate fibers, as cottony aggregates, and as short, stubby crystals.(9) Chabazite is not a fibrous variety of zeolite and has been reported to occur with erionite. The Bowie, Arizona, deposits consists of several million tons of chabazite/erionite ore.(10) Ferrierite and phillipsite are also reported to sometimes occur as fibers. The U. S. has the largest potential deposits of high grade chabazite, erionite and phillipsite and the only high-grade deposits of ferrierite has been reported in central Nevada.(5) There are an estimated 10^7 tons of erionite and 5×10^6 tons each of phillipsite and mordenite, located in near-surface deposits in the Basin and Range province of the western United States.(9)

Gude and Sheppard (12) reported the occurrence of a woolly erionite in Nevada identical in appearance to the type locality near Durkee, Oregon. The report investigated the occurrence, the geological setting, and the physical and chemical properties of the woolly erionite. The investigators concluded that neither chemical nor physical properties distinguish woolly erionite from other erionites and the question was raised as to why the woolly erionite formed in Nevada and Oregon rather than the common, prismatic acicular variety of erionite.

Mumpton (13) described the occurrence of six zeolites: clinoptilolite, erionite, chabazite, phillipsite, analcime, and mordenite. Mumpton illustrated their morphology with scanning electron micrographs. Over 100 rock specimens were examined by the SEM (scanning electron microscope). The sedimentary erionites examined were reported not to occur as fibers but as clusters of acicular needles. The acicular needles from a deposit near Eastgate, Nevada were 10-20 mm (micrometer) in length and 1-3 mm thick. Erionite from Hector, California and Bowie, Arizona occurred in a similar habit. Bean-shaped bundles of needles were reported to be the common habit of erionite in these two deposits. Each bundle was reported to be 20 mm in length and 10 mm thick and to consist of hundreds of individual needles. The individual needles were reported to be slightly less than 1 mm thick. Mordenite was examined as a constituent of clinoptilolite specimens and from monomineralic deposits in California and Nevada. The mordenite occurred as thin, curved fibers a few tenths of a micrometer in diameter in the clinoptilolite specimens and had length to width ratios of 100 or more. Interlaced mordenite fibers or "rats nest's" of fibers were common in the mordenite-rich monomineralic samples from Nevada and California.

CLASSIFICATION

Based upon their mode of occurrence, mineral composition, and geologic origin, Mumpton (10) grouped zeolite deposits in sedimentary rocks into six major types. The grouping is to clarify what zeolites occur in which deposits, the geologic environment of the deposit, how they were formed, and which ones are or may be of commercial importance. The grouping is not all inclusive or rigid.

Type I - Formed from volcanic material in 'closed' systems of ancient and present-day saline lakes. These deposits are abundant in western U. S. and may contain chabazite, erionite, phillipsite and clinoptilolite.

Type II - Formed from volcanic material in 'open' systems of freshwater lakes or groundwater systems. Characterized by the presence of clinoptilolite and/or mordenite and absence of erionite and chabazite.

Type III - Formed from volcanic material in near-shore or deep-sea marine environments. These deposits are abundant in Japan and relatively rare in the U. S. (a South Dakota deposit may fit this type). The deposits are massive and homogenous and grade into vertical zones of analcime/heulandite and laumontite.

Type IV - Formed by low-grade burial metamorphosis of volcanic and other material in thick sedimentary sequences. Analcime and heulandite/clinoptilolite are common. Deposits are impure.

Type V - Formed by hydrothermal or hot-springs activity. Impure deposits that have a trend downwards of mordenite, analcime, heulandite, laumontite, and wairakite.

Type VI - Formed in lacustrine or marine environments without direct evidence of volcanic precursor material. Analcime and clinoptilolite zones in sedimentary rocks of New Jersey and western U. S. are an example of this type.

Type I zeolites are abundant in many ancient and present-day saline lakes of the western United States. The deposits are flat-lying, a few centimenters to a few meters thick, and are interbedded with siltstones and bentonites. Large-pore zeolites such as erionite are generally restricted to Type I deposits. Erionite has not been found in any great quantity in other types of deposits. Type I deposits can be found in the Green River formation of Wyoming, Utah and Colorado.(10)

ZEOLITE OCCURRENCES

Erionite is a common authigenic zeolite in the altered silicic tuffs of lacustrine deposits in north-central Nevada and has been recognized in silicic bedded tuffs from many western states. Extensive pure beds of erionite occur in southeastern Oregon, southeastern California, and north-central Nevada.(14)

Mumpton (10) reported that six mineable deposits of erionite are known. Two of these have been mined. Small amounts of ore were produced from a 400-acre area in Pine Valley, Eureka County, Nevada by Union Carbide in the 1960's. Union Carbide claimed a 500-acre area in Jersey Valley, Pershing County, Nevada. Mumpton reported that this property has been mined by both underground and open-pit methods for internal use.

Small amounts of mordenite have been mined from two localities near Union Pass, Mohave County, Arizona and Rome, Malheur County, Oregon, by Union Carbide and Norton, respectively.

The Rome, Oregon material occurs in a 5-10 meter thick bed in a lacustrine formation and is associated with beds of erionite, phillipsite and clinoptilolite. The presence of about 5-10% fluorite in the mordenite ore has reportedly attracted the interest of several mining companies.(8)

The erionite deposits near Rome, Oregon, were quarried in the past by the Anaconda Company, Norton Company, and Occidental Mining Corporation. A dozen 50 year old buildings (early ranch houses) in nearby Jordan Valley are constructed from zeolite found in this area.(5) Dimension stones of zeolite are reportedly also used in Jersey Valley, Nevada.(10)

Table 1 lists the location of identified erionite, mordenite, chabazite, and phillipsite occurrences. Appendix 1 is a list of the metal/nonmetal mines located in counties that have identified erionite occurrences. Information contained in Appendix 1 was taken from MSHA's (Mine Safety and Health Administration) Health and Safety Analysis Center directory of March, 1981. These mines are examples of operations where zeolites <u>may</u> occur as contaminants. The appendix is intended only to list the mines existing in counties where deposits of zeolites have been reported to occur.

The available results of samples analyzed during an MSHA fiber survey did not find any zeolites present in any mines sampled. Three out of five samples taken from two mills in San Bernardino County, California, did have fibrous minerals present. One sample contained 7.1% talc mineral fibers and 7.1% asbestos (tremolite), another contained 9.1% asbestos (anthophylite), and the third contained 21.4% talc mineral fibers (talc in an asbestiform habit). No other mines were sampled in counties where there has been an identified erionite deposit. The results of MSHA personal samples for asbestos taken from January 1974 to July 1980 were also reviewed. No samples were taken in any mines in any of the counties with a reported erionite deposit.

TABLE 1

CHABAZITE, ERIONITE, MORDENITE AND PHILLIPSITE OCCURRENCES IN SEDIMENTARY ROCKS[1/]

LOCALITY #	LOCALITY	ZEOLITES
1	Near Bearbones Mountain, Lane County, OR	Mordenite
2	Vicinity of Stein's Pillar, Crook County, OR	Mordenite
3	Near Durkee, Baker County, OR	Erionite
4	Near Rome, Malheur County, OR	Erionite, mordenite phillipsite
5	West face of Hart Mountain, Lake County, OR	Mordenite, phillipsite
6	Near Harney Lake, Harney County, OR	Mordenite, phillipsite
7	Beaver Rim, Fremont County, WY	Chabazite, erionite, phillipsite
8	Near Split Rock, Natrona County, WY	Phillipsite
9	Near Green River, Sweetwater County, WY	Mordenite
10	Near Mud Buttes, Butte County, SD	Phillipsite
11	Sheep Mountain Table, Shannon County, SD	Erionite
12	Near Creede, Mineral County, CO	Mordenite
13	Pine Valley, Eureka County, NV	Erionite, phillipsite
14	West flank of the Shoshone Range, Lander County, NV	Erionite
15	Reese River, Lander County, NV	Erionite
16	Jersey Valley, Pershing County, NV	Erionite, phillipsite
17	Near Lovelock, Pershing County, NV	Mordenite
18	Near Copper Valley, Churchill County, NV	Mordenite
19	Near Eastgate, Churchill County, NV	Erionite

TABLE 1 (Continued)

CHABAZITE, ERIONITE, MORDENITE AND PHILLIPSITE OCCURRENCES IN SEDIMENTARY ROCKS[1/]

LOCALITY #	LOCALITY	ZEOLITES
20	Teels Marsh, Mineral County, NV	Phillipsite
21	Near Silver Peak, Esemeralda County, NV	Mordenite, phillipsite
22	Nevada Test Site, Nye County, NV	Chabazite, mordenite
23	Owens Lake, Inyo County, CA	Erionite, phillipsite
24	Lake Tecopa, Inyo County, CA	Chabazite, erionite, phillipsite
25	Searles Lake, San Bernardino County, CA	Phillipsite
26	Mojave Desert, eastern Kern County and San Bernardino County, CA	Chabazite, erionite mordenite, phillip-site
27	Near Lipomo, San Luis Obispo County, CA	Mordenite
28	Union Pass, Mohave County, AZ	Mordenite
29	Near Wikieup, Mohave County, AZ	Chabazite, erionite, phillipsite
30	Near Horseshoe Reservoir, Maricopa County, AZ	Erionite, phillipsite
31	Near Morenci, Greenlee County, AZ	Mordenite
32	Near Bear Springs, Graham County, AZ	Chabazite, erionite, phillipsite
33	Along San Simon Creek, Cochise and Graham Counties, AZ	Chabazite, erionite

1/ From Olson.(3)

U. S. DEPOSITS AND PRODUCTION RATES

More than 300 individual occurrences of 6 different zeolite varieties are known in 25 states. Only about a dozen of these have produced more than experimental quantities of ore. Table 2 lists the various locations of zeolite deposits that are or have been mined. These deposits are regarded as capable of producing many thousands of tons of zeolites.

Zeolite mining operations operate intermittently. The intermittent nature of zeolite mining in the U. S. is partly due to the time required for applied research and development into the commercial application of the zeolite ore material. For example, few uses were apparently found for a mineable erionite deposit in Pine Valley, Eureka County, Nevada, while a similar mineable erionite deposit in Jersey Valley, Pushing County, Nevada, was used by Mobil Oil for internal use.(10) To date, zeolite ore has primarily been mined for a few months, the ore stockpiled, and no further mining performed until more experimental quantities are required. There has never been a question that with time, applied research, and market development, natural zeolites would be used for many diverse commercial applications.

The United States is expected to remain self-sufficient once new markets and uses develop and to become a major exporter due to the large potential of zeolite resources. Sheppard (8) estimated that the total identified, hypothetical, and speculative zeolite resources in the U. S. is 10 trillion tons.

Production figures for natural zeolites in the United States have not been published because they have never been mined on a large commercial scale. Natural zeolite production in the United States in 1977, 1978, and 1979 has been estimated at 5,000 tons per year.(15)

TABLE 2

MINING LOCATIONS[1/]

LOCATION	ZEOLITE SPECIES
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, Colorado	clinoptilolite
Castle Creek, Idaho	clinoptilolite
Fish Creek Mountains, Nevada	clinoptilolite
Buckhorn, New Mexico	clinoptilolite
Mixed:	
Bowie, Arizona	chabazite, erionite
Wickieup, Arizona	analcime, chabazite, clinoptilolite, erionite, phillipsite
Lake Tecopa, California	analcime, chabazite, clinoptilolite, erionite, phillipsite
Lovelock, Nevada	mordenite, clinoptilolite
East Gate, Nevada	erionite, clinoptilolite
Pine Valley, Nevada	erionite, phillipsite

1/ Information from SRI International report prepared for NIOSH. (5)

MINING AND PROCESSING

Most zeolite mining operations are open-pit surface mines which aim to extract a very pure ore. The overburden is first removed and stored or disposed. High grade ore is then removed in the ore stripping operation. This is followed by breaking the ore into pieces in an attempt to separate and clean the mineral. The extracted mineral is then stockpiled in ground piles, silos, bins or sheds. Stockpiles may sometimes be held for a year or more. Little processing is performed at the mining site.(6)

Other processing operations may include crushing, pulverizing, grinding, and screening in order to segregate particle sizes. The natural zeolite may then be mixed with a binder (such as clay or lignin), calcined, or extracted. No information was available as to what, if any, processing is performed beyond this point.(5)

COMMERCIAL UTILIZTION

All commercial applications of natural zeolites make use of one or more of their physical or chemical properties which include ion exchange, adsorption and related molecular sieve phenomena; dehydration and rehydration; and siliceous composition. Several of the most important uses include their use as a raw material in the production of pozzolanic cements and concretes; as inexpensive dimension stone; as lightweight aggregate; as filler in paper (possible replacement for kaolinite as a filler and bulking agent); in ion-exchange processes; in air separation processes; as dietary supplements for swine and poultry; in agricultural fertilizers to control the release of cations; and for drying and purifying acidic gases.(10) Two recent commercial applications have been: the use of zeolites in solar powered refrigerators and in solar collectors that heat in the winter and cool in the summer (16); and four 300 liter columns packed with zeolites are being used at the Three Mile Island nuclear power plant to remove the bulk of the principal radioactive isotopes from contaminated water.(17) Table 3 lists the principal suppliers and users of natural zeolites.

Natural zeolites do not offer the same attributes--purity, predictable performance, etc.--that a large volume application demands and which synthetic zeolites do offer. Except for their use in laundry detergents, synthetic zeolites have been a specialty business with low volumes and high prices; however, synthetic zeolites for use as detergent builders have recently gained an estimated market of 300 million pounds per year. The demand in the detergents industry has caused the development of low cost synthetic zeolites. The development of new applications by zeolite producers is anticipated to expand the zeolite specialties market.(18)

TABLE 3

SUPPLIERS AND USERS OF NATURAL ZEOLITES[1/]

SUPPLIERS	USERS
1. W. R. Grace & Co. Davison Chemical Division Baltimore, Maryland	1. Mobil Oil Corp. New York, New York
2. Norton Company Chemical Process Products Div. Akron, Ohio	2. Shell Oil Company Shell Chemical Houston, Texas
3. Union Carbide Corp. Linde Division Tarrytown, New York	3. Union Carbide Corp. Tarrytown, New York
4. N. L. Industries Tallmade, Ohio	4. Exxon Chemical Co., USA Houston, Texas
5. Anaconda Company Denver, Colorado	5. Reserve Synthetic Fuel, Inc. Signal Hill, California
	6. Rosemount Plant of Minn.
	7. Tahoe-Trucker Sanitation District Plant of CA
	8. Occoquan Sewage Authority of Fairfax County, VA

1/ Information from SRI International Report prepared for NIOSH.(5)

ANIMAL TOXICITY

There is very little information in the literature concerning the toxic effects of natural zeolites to either humans or experimental animals. In a 1966 study, Timar et al.(19) found that intratracheal injections of clinoptilolite (a nonfibrous variety) in rats caused a typical foreign body reaction with granuloma formation within 10 days of injection. No other changes were observed during the one-year study period.

Suzuki, et al.(20) reported that peritoneal mesotheliomas were observed in 2 of 11 mice sacrificed or found dead within a year after intraperitoneal injection of 10 mg (milligrams) of erionite (fibrous variety) particles (1 mm average length and 0.1 mm average width). No mesotheliomas were observed in 12 mice similarly treated with mordenite (nonfibrous variety) and 7 untreated controls. Extensive peritoneal fibrosis was observed in the mice treated with both erionite and mordenite.

Suzuki(21) later expanded this study. Forty-five Swiss albino male mice were injected intraperitoneally with a single administration of 10 or 30 mg of zeolite (erionite or mordenite). Thirteen untreated mice and five mice treated with 10 mg of chrysotile were used as controls. The method for determining the size distribution of the injected materials was not reported. The source of the zeolites (i.e. the location of the deposit from which the material was collected) was not reported. Chemical analyses (selected area electron diffraction and energy dispersive x-ray spectra) were performed by high resolution analytical electron microscopy. The peritoneum and abdominal organs were examined by means of gross anatomical observation, light microscopy, histochemistry, and electron microscopy. Ninety percent of the chrystotile (Calidra) was shorter than 1 mm with widths less than 1000 angstroms. Ninety-five percent of the erionite fibers were shorter than 8 mm in length and 94.4% were less than 1 mm in width. A mixture of fibrous and granular types of mordenite was used. Definitions of the terms fibrous and granular were not given. Ninety-eight and six tenths percent of the granular mordenite was shorter than 5 mm in the long axis and 83.6% was less than 1 mm in the short axis. Ninety-eight and two tenths percent of the fibrous mordenite was shorter than 5 mm in length and 96.4% was shorter than 0.5 mm in width.

The study found that the erionite had carcinogenic and fibrogenic effects. The effects were found to be similar to those of asbestos. The effects included malignant mesothelioma and fibrosis in the mouse peritoneum, frequent appearance of bloody ascites, association of hyaline degeneration of fibrotic lesions, and dissemination of neoplastic tissue along the surface of the mouse peritoneum. Suzuki noted one difference between the cell type of the neoplastic cells in asbestos-induced human malignant mesothelioma and erionite-induced mouse malignant mesothelioma. The fibrous form is not as frequently seen in human mesothelioma.

Peritoneal tumor was not seen in the mordenite animals. Schaumann body-like structures and coated zeolite fibers were occasionally observed in the fibrotic lesions induced by either erionite or mordenite. Suzuki concluded that information currently available is insufficient to fully evaluate the pathobiological potential of zeolites and whether zeolites other than fibrous erionite are carcinogenic or fibrogenic in the human.

Moatmed, et al. (22) reported that fibrous erionite may produce inflammation and ferruginous bodies when injected into male mice. The erionite used during this study was from a deposit near Eastgate, Nevada. A significant portion of the fibers were long and thin (2 mm diameter and 10 mm lenth).

During a visit to NIOSH (Morgantown) in June, 1981, Dr. J.C. Wagner reported that erionite from a Rome, Oregon deposit was one of the most productive minerals with respect to producing tumors in laboratory animals. This finding has not been published but corroborates the study by Suzuki.(20-21)

HUMAN HEALTH EFFECTS

An extremely high incidence of pleural mesothelioma (22 cases/10,000 people) in a village (Karain) in central Turkey (Cappadocia) was reported by Baris, et al. in 1975.(1) Several other respiratory disorders were also detected.

In October 1977, researchers from the IUAC (International Union Against Cancer) and the Imperial College, London, visited the village and other villages in the region to collect samples of road dust, building blocks, and other natural products used by the inhabitants, and to examine residents of the area. The mesothelioma diagnoses of Baris were confirmed histologically by the IUAC. Examination of rock and soil samples by EM (electron microscopy) revealed needle-shaped particles of erionite less than 0.25 mm in diameter and up to 5 m in length. Further results of the 1977 study were presented in December, 1977 and July, 1978 by researchers from Llandough Hospital, Cardiff, Wales.(4)

Artvinll and Baris (2) described the expansion of this study to a second village (Tuzkoy) where Mumpton (4) identified erionite, chabazite, and possibly mordenite. A village (Kizilkoy) six kilometers south of this second village where there have been no cases of mesothelioma, was used as a control. Samples of bedrock, building blocks, and quarry stone from the control village showed only a possible trace of chabazite. Artvinll and Baris found two cases of pleural mesothelioma among the 312 villagers studied in the second village with no cases found in the control village. The study concluded that zeolites probably caused the mesotheliomas.

Sebastien, et al.(23) assessed mineral fibers in lung samples from two cases of pleural mesothelioma in Tuzkoy using the light microscope and the analytical transmission electron microscope. Zeolite (erionite) fibers and ferruginous bodies, formed around zeolite fibers, were frequently encountered in the samples. Under the light microscope zeolite bodies were morphologically identical to typical asbestos bodies. The investigators concluded that it is still an open question whether exposure to mineral fibers (zeolite) is different in mesothelioma villages than in neighboring control villages.

Casey, et al.(24) suggested that a patient's pleural and parenchymal fibrosis may have been related to exposure to fibrous zeolites. History-taking by several clinicians did not find a significant asbestos exposure for the 52 year old male Elko, Nevada resident. The patient had been employed as a long distance truck driver and heavy equipment operator in the Nevada desert. Zeolites have been reported to occur in the lake beds of the Basin and Range province, including the region surrounding Elko. Road dust taken near irrigated farms in the Reese River Valley of Nevada reportedly contain erionite.

Rom, et al.(25) found no unusual occurrence of pleural chest disease in a hospital based survey but suggested that ranches and communities near fibrous erionite deposits with a greater potential for exposure should be studied with epidemiologic techniques. It was also suggested that the once proposed location for the MX missiles in the desert valleys of Utah and Nevada could expose workers to fibrous erionite.

Volume 30 of the Evaluation of the Carcinogenic Risk of Chemicals to Humans by the World Health Organization's International Agency for Research on Cancer is a critical review of data on carcinogenicity of mineral fibers, including zeolites.(26) In that review Wagner (27) reports that: the vast majority of erionite fibers have diameters that are well above the size of creating a potential problem; only the deposits near the two villages in Turkey have been shown to have produced mesotheliomas; and only two other deposits - one in Oregon, and one in New Zealand - have been shown to contain fibers with diameters in a suspected danger range. The suspected danger range is diameters less than 5 mm and a length of 5 to 30 mm for the development of mesotheliomas, and diameters of 2 mm or less and a length of 10 to 50 mm for pulmonary fibrosis.

Yazicioglu (28) reported that pleural calcifications amongst inhabitants of villages and towns in southeast Turkey were caused by the inhalation of chrysotile asbestos. A raw material for painting the walls and floors of the houses in the study area was identified by the State Mining Investigation Institute in Ankara, Turkey as chrysotile asbestos in fiber form and included some talc.

Spurny, et al. (29) reported preliminary examinations of soil samples from the Cappadocia area of Turkey and tumor tissues of autopsied mesothelioma patients from the area. A main objective of the study was the preparation of a well defined fribrous mineral sample from Cappadocia and erionite sample from the state of Nevada. In vivo experiments were then performed with the two well defined samples-the fibrous mineral sample form Cappadocia and the erionite sample from Nevada. SEM, EDXA (energy dispersive x-ray analysis), TEM (transmission electron microscopy), SAED (selected area electron diffraction analysis), XRD (x-ray diffraction analysis), XRF (x-ray fluorescence spectroscopy), and LAMMA (mass spectroscopy) were the analytical methods used.

EDXA revealed similar chemical compositions for single fibers found in a fibrous mineral sample from Cappadocia and in ashed pleural tissue of mesothelioma cases from the Cappadocia area. The investigators concluded that the fiber type found in the pleural tissue was very similar to the fiber types identified in the soil samples from Cappadocia.

The investigators concluded that the "majority of the mesotheliomas and other diseases found" could be explained by environmental exposure to asbestos fibers and for areas without asbestos the explanation "is supposed to be" the exposure to environmental fibrous zeolites.

Rohl et al. (30) performed mineralogical characterizations of dust samples from Cappadocian villages where mesothelioma was known to occur and from villages where mesothelioma was not known to occur. Dust samples included settled house dust, whitewashes, soil, tuff outcroppings, and building stone. Lung tissue specimens of patients with mesothelioma who lived in the villages of Karain, Tuzkoy, and Sarihidir were obtained for analysis also. Analytical techniques employed included PLM, XRD, and TEM (equipped with EDXA). The study reported that the dust and lung samples contained several different kinds of fibrous minerals, including asbestos and fibrous erionite.

ENVIRONMENTAL DATA

Mumpton has studied the region in Turkey and concluded that the data are "equivocal" with regards to a positive correlation between the presence of erionite and the incidence of malignant pleural mesothelioma.(4) The study was conducted to determine the zeolite content of bedrock, building blocks, road dusts, soils, etc. from both mesothelioma (Karain and Tuzkoy) and non-mesothelioma villages in the Cappadocia region . Eighty-one samples of bedrock, quarry products, and local building blocks were collected from 15 towns and villages and 5 field locations within a 25 kilometer radius of Nevsehir, a town located between Karain and Tuzkoy. Thirteen wells and water sources in various villages were also sampled. Samples were examined by XRD techniques. SEM micrographs were also obtained. Erionite was found to be present in samples from only one of the two mesothelioma villages and in samples from a non-mesothelioma village. Other species of zeolites were found to be rare in the other mesothelioma village and in three non-mesothelioma villages. Mumpton concluded that the data suggested that no correlation existed. The only ubiquituous mineralogical parameter found by Mumpton was an abundance of fresh volcanic glass and cristobalite.

In a May, 1979 NIOSH survey of an Arizona zeolite (chabazite) mine, it was found that miners were not exposed to fibrous zeolite or to total or respirable particulate material in excess of existing or recommended exposure limits.(6) The air samples collected were examined by phase contrast optical microscopy at 400x magnification. The samples were prepared and analyzed in the manner prescribed by NIOSH Method 239 for asbestos fibers in air.(31) Air samples were also analyzed by TEM at 17000x magnification, utilizing SAED and EDXA to identify the shape and elemental composition of the particles. Five of thirteen air samples examined by phase contrast microscopy had a "very small number of fibers" present. A fiber was defined as a particle with a physical dimension longer than 5 mm and a length to diameter ratio of 3 to 1 or greater. No estimate was given on the number of fibers present. Four of the five samples with fibers present were personal samples.

Three samples were examined by TEM. One sample was chosen because it represented a light particle loading, one represented a heavy particle loading, and the third had shown a small number of fibers under optical microscopy. Ten fields were examined for each sample. Fibers were found in only trace amounts in the ore, clay, and overburden. Based upon the above findings, the small number of miners involved, and the insufficient latency period, it was determined that a retrospective mortality study was not feasible.

As part of the surveillance program's investigation into natural zeolites three site visits were made by a NIOSH field industrial hygienist. The three sites visited were all located in Oregon and included a nonmetal mine located near a reported occurrence of erionite, a small plant which occasionally mines and mills clinoptilolite (a nonfibrous variety of zeolite), and a large zeolite deposit (erionite, phillipsite, and mordenite) not currently being mined.

Bulk and filter samples from the nonmetal mine were analyzed by PLM, EM (SEM and TEM), and XRD for the presence of zeolites. The NIOSH laboratory in Cincinnati, Ohio and the Illinois Institute of Technology Research Institute (IITRI), a NIOSH contract laboratory, performed the analyses.

The NIOSH laboratory analyzed six bulk and nineteen filter samples from the nonmetal mine by TEM. The analysis was restricted to determining whether there was any contamination of the ore from a nearby zeolite deposit. The bulk samples were prepared by ultrasonically suspending a portion of the sample in ethanol and placing an aliquot of the suspension on a 200 mesh carbon coated TEM grid. The filter samples were prepared for TEM analysis by using the NIOSH standard procedure outlined in NIOSH publication 77-204.(32) Both the bulk and filter samples were examined by TEM and analyzed for elements by EDXA. For each sample 50 particles were analyzed by EDXA. There were no fibrous (aspect ratio of 3 to 1 or greater) aluminum silicates or fibrous particles observed on any of the sample preparations. All of the samples contained aluminum and calcium silicates. It is possible that some of the silicates might have been zeolites; however, none of them occurred as fibers.

IITRI analyzed three bulk samples from the nonmetal mine to determine whether the samples contained zeolites, and specifically erionite, at concentrations of 5% by weight or greater.(Appendix 2) XRD, PLM, and SEM techniques were employed. XRD was used to check for the possible presence of any zeolites. PLM and SEM were used to survey the samples for the presence of fibrous minerals. A density separation was also used to determine the mass percentage of the respirable portion of the sample in the density range less than or equal to 2.50 grams per cubic centimeter. Zeolites have densities which are less than or equal to 2.50 grams per cubic centimeter. The XRD patterns did not show any indication of the presence of erionite or any detectable quantities of zeolites. Each sample was mounted in 1.515n refractive index fluid and examined by PLM. No mineral fibers or zeolites were detected in any of the samples. Each sample was next subjected to ultrasonics, filtered, coated with carbon in a vacuum evaporator, and examined at 1000x,3000x, and 5000x by SEM. Scanning was performed at zero degrees tilt. When a particle appeared to be a fiber (aspect ratio of 3 to 1 or greater), it was centered and examined at higher magnification. The particle was slowly tilted to forty degrees while being examined to determine if the fiber morphology persisted. No mineral fibers were found in any of the samples. Mineral fragments with length to diameter ratios greater than 3 to 1 were present in the samples.

Bulk and settled dust samples from the clinoptilolite mine/mill were analyzed by PLM and TEM techniques for the presence of mineral fibers. The NIOSH laboratory in Cincinnati, Ohio performed the analyses. The samples were ground using a mortar and pestal when necessary. A portion of the rock dust was suspended in alcohol by ultrasonic agitation. An aliquot of the suspension was deposited on a 200 mesh copper grid and glass slide for PLM and TEM analysis. TEM analysis revealed that there were no fibrous minerals present in any of the sample preparations. Elemental composition from EDXA and PLM observations indicated that all seven samples were very similar in composition. A more extensive mineral characterization (utilizing XRD, etc.) was not undertaken because there were no mineral fibers present in any of the sample preparations.

Seven bulk rock samples from a zeolite deposit near Rome,Oregon were collected by NIOSH. Two separate areas of the deposit were sampled, an area south of Rome and an area north of Rome. The samples were collected from various strata at each area. The samples were identified macroscopically at the sites by geologists as to their primary zeolitic phase: phillipsite, erionite, or mordenite. NIOSH examined the samples by TEM, SAED, and EDXA. Portions of five of the samples (A-1, A-2, A-3, A-5, and A-7) were subsequently sent to IITRI for a mineralogical and morphological characterization of the zeolite phases.(Table 4) PLM, x-ray fluorescence(XRF), XRD, and electron microscopy techniques were used for the characterizaton.(Appendix 3)

TABLE 4 SAMPLE DESCRIPTIONS

Sample No.	Primary Zeolite Phase Identified Macroscopically	Area of Deposit	IITRI Analysis
A-1	Phillipsite	North	Yes
A-2	Mordenite	North	Yes
A-3	Erionite	North	Yes
A-4	Erionite	North	No
A-5	Erionite	South	Yes
A-6	Phillipsite	South	No
A-7	Mordenite	South	Yes

PLM was used by IITRI to determine particle morphology for the zeolite minerals and to identify nonzeolite minerals. Sections from each sample were selected to be representative of the visual appearance of most of the sample. The selected sections were vacuum impregnated with mounting resin to support the samples which were friable and porous. Two perpendicular thin slices were prepared from the same section of each sample. The first section was selected to be parallel to the longest chord through each specimen. The second section was cut normal to the first section. This was an attempt to exaggerate any preferred orientation of the crystals in the rock and to provide an easier recognition of fibrous shapes. The PLM analysis by IITRI did not find any of the five samples to be fibrous.

IITRI took selected rock fragments and powder from each of the five samples to obtain a representative sample for XRD analysis. Two sets from each sample were analyzed by XRD to verify peak postion and intensity. A third powder pattern was also prepared using thick, packed powders because of poor agreement between the designated zeolites in the samples and standard zeolite XRD patterns from the JCPDS (Joint Committee on Powder Diffraction Standards). The two mordenite samples, A-2 and A-7, were the only samples which approximately matched their JCPDS reference patterns. The other three samples, samples A-1, A-2, and A-5, did not match the JCPDS patterns for phillipsite or erionite. These three did contain a number of x-ray lines characteristic of the zeolites. The samples did not match any other zeolites or minerals.

A 10 mg portion of the samples prepared for XRD was used for XRF analysis. The elemental compositions obtained agreed reasonably well with published data.

All five samples submitted to IITRI were initially analyzed by NIOSH using TEM for SAED and EDXA microanalysis, as well as for particle morphology. The NIOSH analysis had shown the presence of mineral fibers in scrapings from each sample. The definition for mineral fibers was a length to diameter ratio of 3 to 1 or greater and an elemental composition typical of minerals (i.e., containing silica, aluminum, and various alkali, or alkaline earth elements). The initial NIOSH TEM analysis of the samples entailed scraping powder from each rock sample. IITRI initially prepared the samples for EM analysis by hand grinding a mixture of a few rock fragments and an estimated proportion of the loose powder in each sample container. A millite mortar and pestle were used to hand grind the samples. The grinding was considered complete when the powder appearred to be finely divided, uniform in size and free flowing. The samples were not sieved or sized microscopically. A small quantity of the hand ground powder was placed in a beaker containing isopropanol, dispersed ultrasonically for approximately 15 minutes, and vacuum filtered through a 0.1 mm pore polycarbonate filter. The vacuum pump was operated until the filter appeared dry. A segment of each filter was carbon coated for SEI examination.

SEI was used by IITRI because the initial NIOSH analysis had employed TEM. The particle morphology observed differed substantially with the fibrous morphology described by the initial NIOSH analysis. The differences between the results obtained by NIOSH and those by IITRI were attributed to: sample inhomogeneity, sample preparation, or method of analysis (TEM versus SEI). The primary difference in technique, excluding sample inhomogeneity, was found to be the method of analysis (TEM versus SEI).

IITRI next suspended the ground material in 95% ethanol, ultrasonicated, and placed a drop of the ethanol suspension directly on a 200 mesh carbon coated copper grid and dried the grid in place for examination by TEM/STEM/SEI. The samples were examined in the TEM mode before carbon coating and examined in all three modes, TEM/STEM/SEI, after carbon coating. The same sample preparation (suspension, ultrasonication, etc.) was used to mount powdered scalpel scrapings from the samples onto electron microscope grids. SEI/STEM image combinations were taken of the same subject area to illustrate viewing differences and to explore whether the differences contributed to the appparent morphology differences observed by NIOSH and IITRI.

IITRI found samples A-2 (mordenite) and A-7 (mordenite) to appear fibrous by TEM. These two samples were reported to appear prismatic by SEI. An edge transparency of the individual, elongated crystals was given as an indication that the particles were rounded. IITRI proposed this as a practical method for distinguishing mineral fibers (round) from elongated cleavage fragments (flat) of prismatic crystals.

Sample A-1 (phillipsite), A-3 (erionite), and A-5 (erionite) were found by IITRI to have a fiber content estimated at less than 1%. These IITRI estimates only agreed with a NIOSH estimate of less than 1% fiber content for sample A-5. The differences in fiber content estimates was attributed to the method of sample preparation - grinding by IITRI versus scraping by NIOSH.

Figures 1-15 are NIOSH photographs of the TEM, EDXA, and SAED results.

Sample A-1 (Figures 1 and 2) was taken from the phillipsite zone of the deposit. NIOSH TEM analysis showed that approximately 2 to 10% of the particles in sample A-1 were fibers (length to diameter ratio of 3 to 1 or greater).(Figure 1) The large fibers showed compositions such as that in Figure 2. The large fibers ranged in size from 4 mm to approximately 40 mm in length and did not commonly occur in loosely packed bundles or clusters. The small fibers were commonly less than 2 mm in length and less than 0.1 mm in diameter. XRD patterns for Sample A-1 did not match the JCPDS phillipsite patterns or any zeolite patterns. The pattern did not match well with any standard mineral pattern. The elemental composition for Sample A-1 obtained by XRF agreed with the composition for phillipsite taken from published data, except for a lower aluminum content.

EM analysis by IITRI concluded that sample A-1 had an estimated fiber content of less than 1%. PLM analysis for sample A-1 found one mineral phase, presumably a zeolite, to compromise an estimated 90% of the volume of the sample. Discrete prismatic crystals in the sample displayed a hexagonal shape and exhibited undulose extinction. Fibers were estimated to account for less than 2% of the sample based on PLM observations. The two thin sections prepared for PLM analysis displayed similar crystal morphologies, indicating a random orientation of the cyrstals; however, the surface of the prismatic crystals displayed very minute, parallel striations.

Sample A-2 (Figures 3, 4, and 5) was taken from the mordenite zone of the deposit located north of Rome. TEM analysis by NIOSH estimated that approximately 65 to 80% of the sample (Figures 3 and 4) was composed of very small individual fibers and fiber clusters. The individual fibers were generally 0.2 mm in diameter and ranged from 0.5 mm to 10 to 20 mm in length.

Sample A-7 was collected from a mordenite zone of the deposit located south of Rome. The NIOSH analysis concluded that the sample was nearly identical macroscopically to sample A-2. The majority of the fibers were small, 0.01 to 0.5 mm in diameter and up to 4 mm in length.(Figure 14) Some hexagonally shaped clay minerals with a high potassium content were also observed. The analyses performed by NIOSH revealed that sample A-7 was very similar in morphology and composition to sample A-2.(Figure 15)

The IITRI analysis also found samples A-2 and A-7 to be similar. The XRD patterns for the mordenite samples matched JCPDS reference patterns for mordenite. The elemental compositions for the two samples obtained by XRF were within reasonable limits of published data. The EM results indicated samples A-2 and A-7 to be predominantly fibrous. These two samples were the only ones to show distinct fibers by EM. Neither of the samples displayed fibers visually or by PLM. The two mordenite samples, each from a different location in the deposit, were quite similar when observed by PLM. Neither sample exhibited parallel bundles typical of fibrous mineral habits. In both samples quartz and calcite occurred as large inclusions in a very fine grained matrix which was presumed to be mordenite.

Samples A-3 and A-4 (Figures 6-11) were taken from the erionite zone of the deposit. The NIOSH analysis found that fibers constituted 10 to 30% of sample A-3 and occurred both singly and in bundles.(Figures 6 and 7) The fibers ranged in size from 0.02 to 0.5 mm in diameter and 0.5 to 60 mm in length.

Based on XRD data and the JCPDS reference for erionite IITRI concluded that the erionite content of sample A-3 was less than 10%, if any. IITRI did not analyze sample A-4 because samples A-3 and A-4 were taken from the same strata and location of the deposit in Oregon. The elemental composition for sample A-3 was found to be similar to the composition of erionite reported in published data. The EM analysis concluded that sample A-3 had a fiber content of less than one percent. Similar particle morphologies were observed regardless of the preparation method. PLM analysis found sample A-3 to morphologically resemble sample A-1 (phillipsite). Sample A-3 contained calcite coated with geothite. The zeolite phase in sample A-3 was uncoated. PLM observations found the sample to consist of randomly oriented, irregular crystals which tended towards stubby prisms.

The NIOSH analysis found sample A-4 to contain 8 to 20% fibrous material. (Figures 9-11) The fiber sizes ranged widely from 0.02 to 3.0 mm in diameter and from 0.5 to 60 mm in length. Some fibers exhibited acicular habit and showed evidence of right angle cleavage. The elemental composition varied in sample A-4 with the presence of greater amounts of calcium in some of the fibers.(Figure 11) Sample A-4 was not analyzed by IITRI.

Sample A-5 was collected from the erionite zone of the depost. The NIOSH analysis found that fibrous material made up less than 1% of the sample.(Figure 13)

Based on XRD data and the JCPDS reference for erionite IITRI concluded that sample A-5 could not be matched to erionite and more resembled sample A-1 (phillipsite). Sample A-5 was not identified by XRD even though it was composed of a primary phase that was probably a zeolite. The elemental composition of sample A-5 was found to be similar to the composition of erionite reported in published data. SEI examination found a great similarity between samples A-3 and A-5. Electron microscope analyses concluded that sample A-5 had a fiber content of less than 1%. This IITRI estimate was the only agreement with NIOSH findings on fiber content. PLM observations found sample A-5 to have a morphology similar to sample A-1 (phillipsite). This similarity in morphology suggested to IITRI that samples A-1 and A-5 were from the same geological stratum even though separated by several miles.

Sample A-6 was collected from the phillipsite zone of the deposit. The NIOSH analysis found the particles in this sample to be equant, non-descript grains ranging from 0.02 to 5.0 mm in diameter. No fibers were observed on two separate preparations of the sample. Sample A-6 was not analyzed by IITRI.

Sample A-7 was collected from the mordenite zone of the deposit. The NIOSH analysis concluded that the sample was nearly identical macroscopically to sample A-2. The majority of the fibers were small, 0.01 to 0.5 mm in diameter and up to 4 mm in length.(Figure 14) Some hexagonally shaped clay minerals with a high potassium content were also observed. The analyses peformed by NIOSH revealed that sample A-7 was very similar in morphology and composition to sample A-2.(Figure 15)

The Bureau of Mines (33) studied the size and shape characteristics and habits of six common sedimentary zeolites and one rare wooly erionite. The rare wooly erionite is known to occur in only two locations in the U.S. and was studied only because of its extremely fibrous nature. Twenty-two zeolite samples were examined. The six zeolite phases identified in the samples were erionite, chabazite, mordenite, elinoptilolite, analeime, and phillipsite. XRD was used to identify the phases present in each sample. SEM was used to observe the crystal habits. Several erionite and mordenite samples were selected for length and width measurement by TEM after SEM had determined an acicular to fibrous habit. The samples were prepared for TEM analysis by light grinding in a mortar and pestle which was followed by filtration and ultrasonication. The wooly erionite was not subjected to grinding. The dimensions of fibrous and acicular zeolite mineral particles were compared to those of asbestos fibers. Twelve of the 22 samples examined during the study contained trace amounts to 100% acicular or fibrous mordenite or erionite. The mordenite studied was found to be acicular with a "fibrosity index" similar to amphibole cleavage fragments. The "fibrosity index" is the slope of the regression line of $\log_{10}$ width versus $\log_{10}$ length. The shape characterization of mineral particle populations based on a regression analysis of $\log_{10}$ width dependency on $\log_{10}$ length has been proposed and shown to provide a quantitative basis for distinguishing asbestos from other mineral particles.(34-35) The erionite samples studied were found to run the entire spectrum from less elongated than the acicular mordenite studied to similar to those of asbestos for the rare wooly erionite. The study concluded that because mineral habit is a highly variable property zeolite samples need to be carefully characterized for dimensional characteristics on an individual basis.

NUMBER OF WORKERS POTENTIALLY EXPOSED

Zeolite mining in the U. S. has been speculative and intermittent with only limited amounts of ore removed and stockpiled from approximately a dozen locations.

Due to the intermittent mining and because many of the companies involved consider information on this industry to be proprietary, specific information regarding the number of operations and workers involved is not readily available.(5) Active mining operations in the past several years have been limited to the western states of Nevada, California, Colorado, Arizona, New Mexico and Idaho. Companies and organizations involved are given in Table 5.

The NIOSH survey of Union Carbide's Bowie, Arizona operation found that approximately 8 to 14 workers mine the zeolite ore.(6) The number of workers should not vary from site to site due to the limited extent of mining at this time. The NIOSH survey also found that there is no real continuity of employment due to the intermittent nature of the work. Four of the eight men working at the site during the NIOSH survey were found not to have worked previously as zeolite miners.(6)

An estimated 40 to 50 miners have worked at the dozen zeolite deposits that have been mined in the past 20 years. An estimated 20 exploration geologists/mineralogists have been occupationally exposed to natural zeolites (fibrous and non-fibrous) during exploration efforts of the past 20 to 30 years.

The populations living/working in zeolite block buildings in small communities in Oregon and Nevada and small communities near deposits in the west <u>may</u> also have exposure to fibrous and non-fibrous varieties of zeolites.

TABLE 5

Companies and organizations that are or have been engaged in mining or research related to natural zeolites.1/

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

1/ Information obtained from SRI International report prepared for NIOSH. (5)

CONCLUSIONS

A fibrous variety (erionite) of the mineral zeolite has been correlated with an extremely high incidence of pleural mesothelioma among the inhabitants of two villages in central Turkey. A reconnaissance geological survey of the area in Turkey reported a negative correlation. The results of several animal toxicity studies provide evidence that fibrous varieties of the mineral zeolite may produce biological effects very similar to those classically associated with asbestos. These epidemiological and animal toxicity studies contribute additional evidence to the theory that any mineral particle of certain physical parameters may cause a biological effect (i.e., the mineralogical distinction between asbestos and nonasbestos mineral particles in a certain size range is not medically significant). A NIOSH industrial hygiene survey of the most active commercial U.S. mine did not find miner exposure to airborne fibers of zeolites. Based on these findings, the small number of miners involved, and the insufficient latency period, it was determined that a retrospective mortality study was not feasible. Future mining and future uses of zeolites must be assessed from the viewpoint of the potential health risks zeolites may pose and the impact on the exposed populations. The assessment should begin now with inhalation toxicology studies.

RECOMMENDATIONS

The results of the limited toxicity and epidemiological studies conducted to date need to be expanded and corroborated. Ongoing research into commercial applications of natural zeolites is expected to significantly increase mine production in the future. Future mining and future uses of zeolites should be assessed from the viewpoint of the potential health risks zeolies may pose and the impact on the exposed populations.

The zeolites used in animal toxicity studies need to be fully characterized because the different zeolite species have different physical attributes but very similar chemical compositions. Extensive research is needed to determine the tissue modification of different mineral species having well characterized size and shape distributions. The mineral characterization should include the exhaustive analyses performed by IITRI for NIOSH (see Environmental Data Section and Appendices 2 and 3) and the size and shape characterizations proposed by Shedd et. al. (32), Siegrist and Wylie (33) and Wylie (34). Animal toxicity studies of zeolites could contribute additional evidence to the theory that any mineral particle of certain physical parameters may cause a biological effect.

Further industrial hygiene surveys are not warranted at this time. The Environmental Investigations Branch of the NIOSH Division of Respiratory Disease Studies (DRDS) should consider the re-evaluation of occupational exposure to airborne fibers during the mining/milling of natural zeolites should there be an increase in zeolite mining/milling in the future.

The Environmental Investigations Branch (Mining Surveillance Section) of the NIOSH Division of Respiratory Disease Studies should keep informed of any increase in U.S. zeolite mining production. The Target Mining Project of the Mining Surveillance Section should be amended so that periodic updates of subjects such as zeolite could be performed. An update of this report would involve contacting the Bureau of Mines mineral commodity specialist for zeolites to determine whether there had been an increase in the amount of zeolites mined and contacting the Mine Safety and Health Administration to determine which mines had been active.

The Laboratory Investigations Branch of the NIOSH Division of Respiratory Disease Studies should consider a study to corroborate the findings of Suzuki(19,20) and Moatmed, et al.(21) The study should be an inhalation toxicity study with rats. Past animal toxicity studies with zeolites have all injected the zeolite into the trachea or peritoneum of the rat. An inhalation toxicity study would provide more conclusive evidence that fibrous zeolites are a serious potential problem.

The literature reviewed for this report did not contain references from other countries where zeolites are currently mined (Japan, Hungary and Italy). Inquiries to the appropriate agencies in these countries should be made concerning occupational health research into zeolites that they may be conducting.

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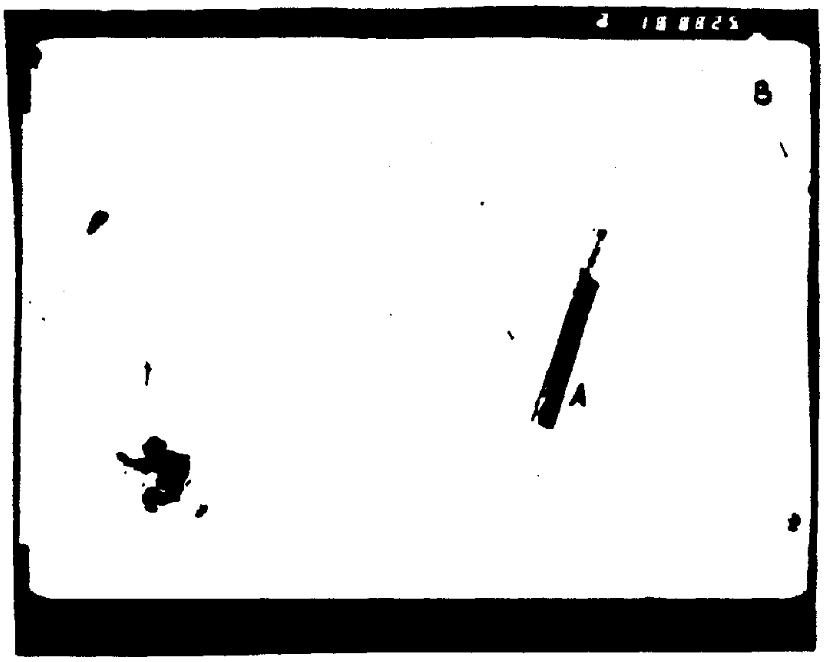


Figure #1 -- Photo 825, sample A-1 mag. = 10,000X
showing typical prismatic large fibers (A)
and small fibers (B) in sample.

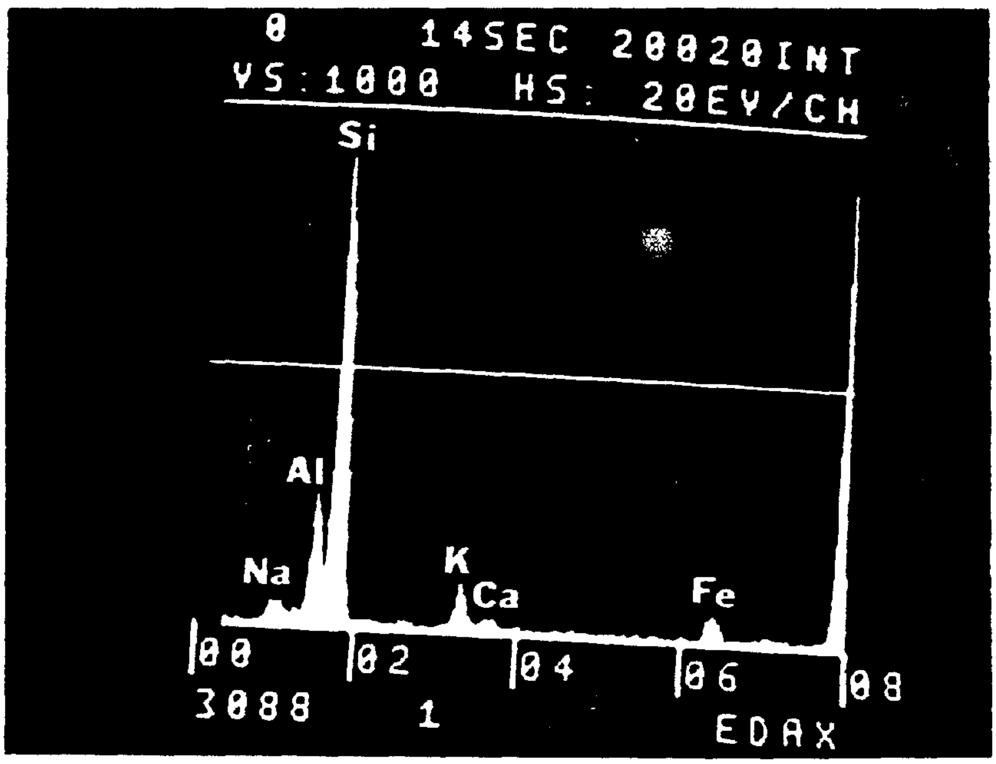


Figure #2 -- EDXA pattern of large fiber in sample A-1.

Figures 3 and 4 -- Sample A-2, photos 814 and 815 mag. = 10,000X. Photos show typical morphology of zeolite fibers and fiber clusters in sample A-2.

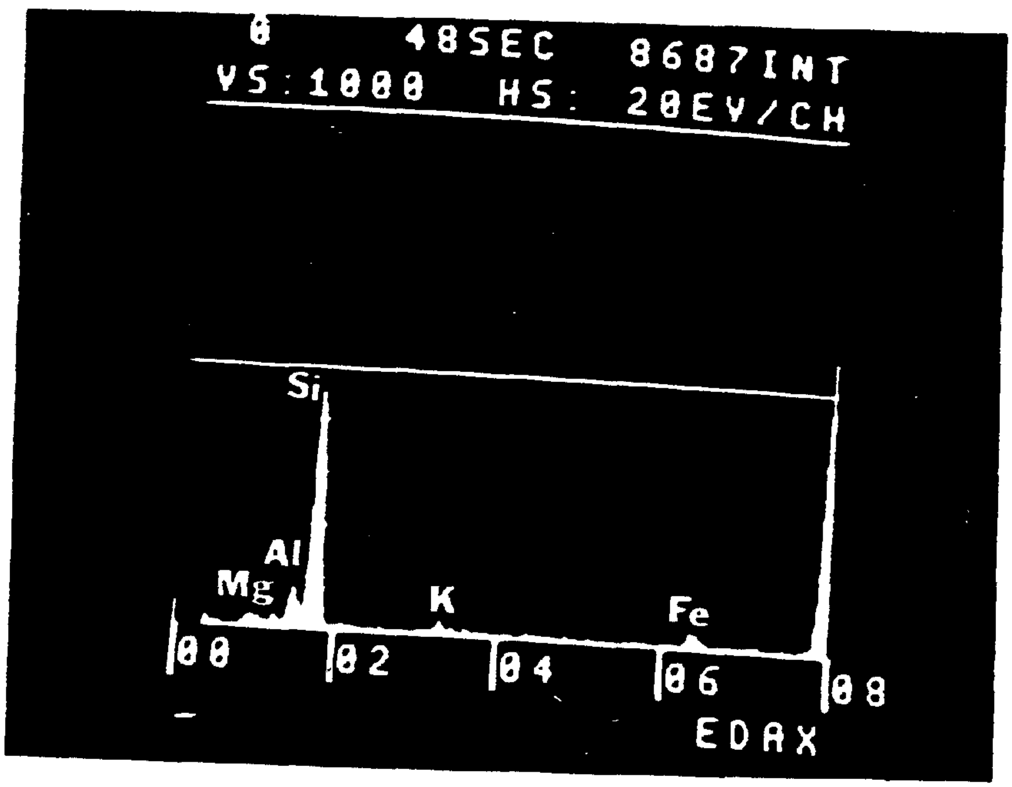


Figure #5 -- EDXA spectrum of fiber cluster in photo 815.

Figures 6 and 7 -- Sample A-3, photos 818 and 819 mag. = 3300X. Photos show wide range in sizes of fibers in the sample and the acicular or needle habit of some of the fibers.

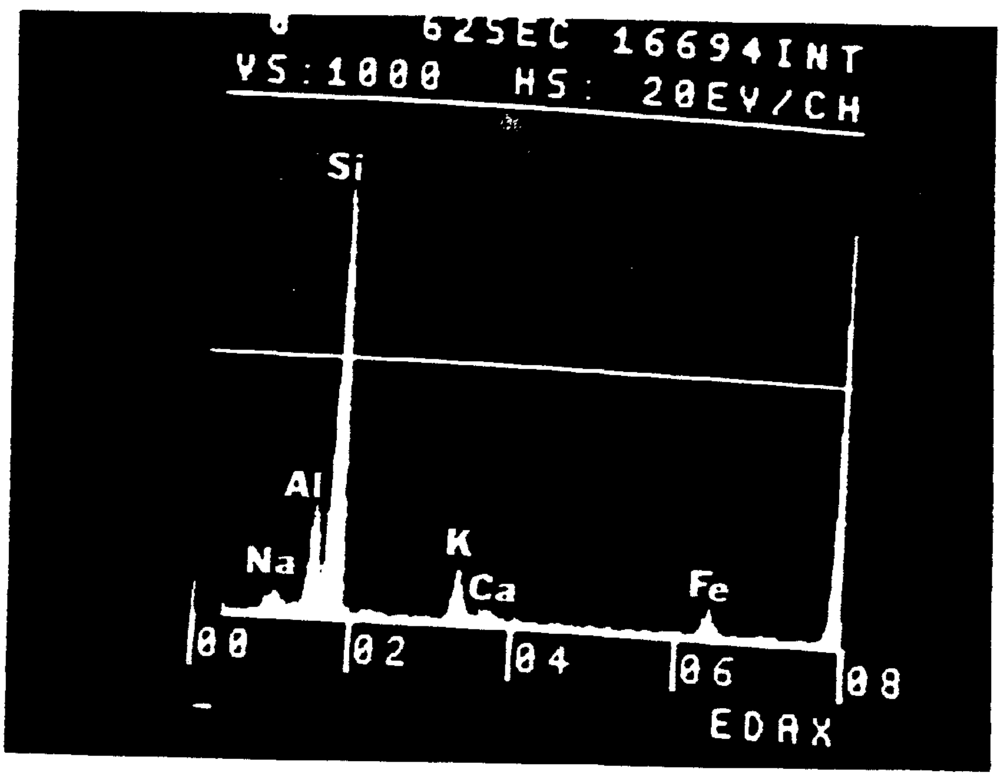
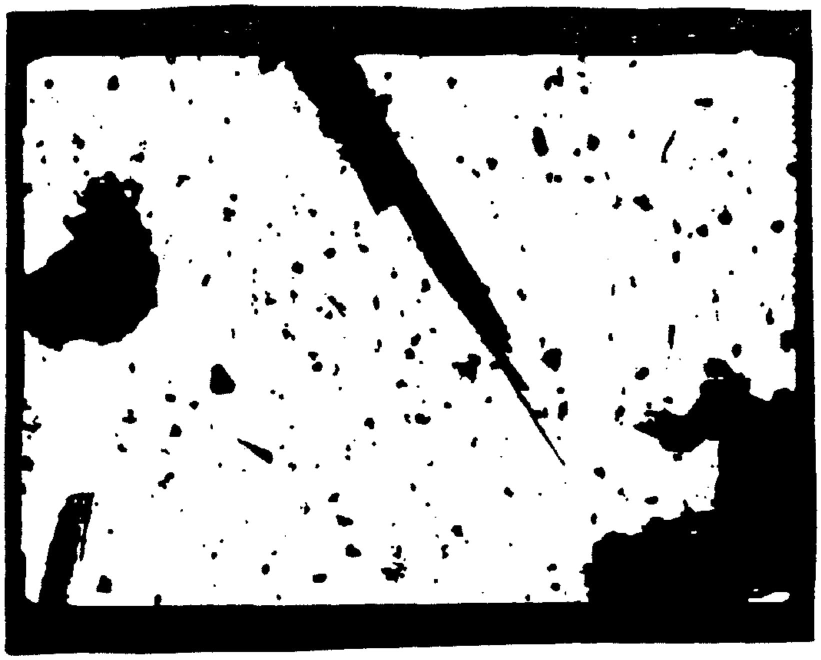


Figure #8 -- EDXA pattern of a large fiber in sample A-3, showing Na, Al, Si, K composition with traces of Ca and Fe.



Figures 9 and 10 -- Sample A-4, photos 821 and 822. Note fracture and cleavage habit of large fiber resulting in needle shape. Many of the fragmented pieces, although not fibrous, are prismatic in shape, such as particles A and B in Figure 12.

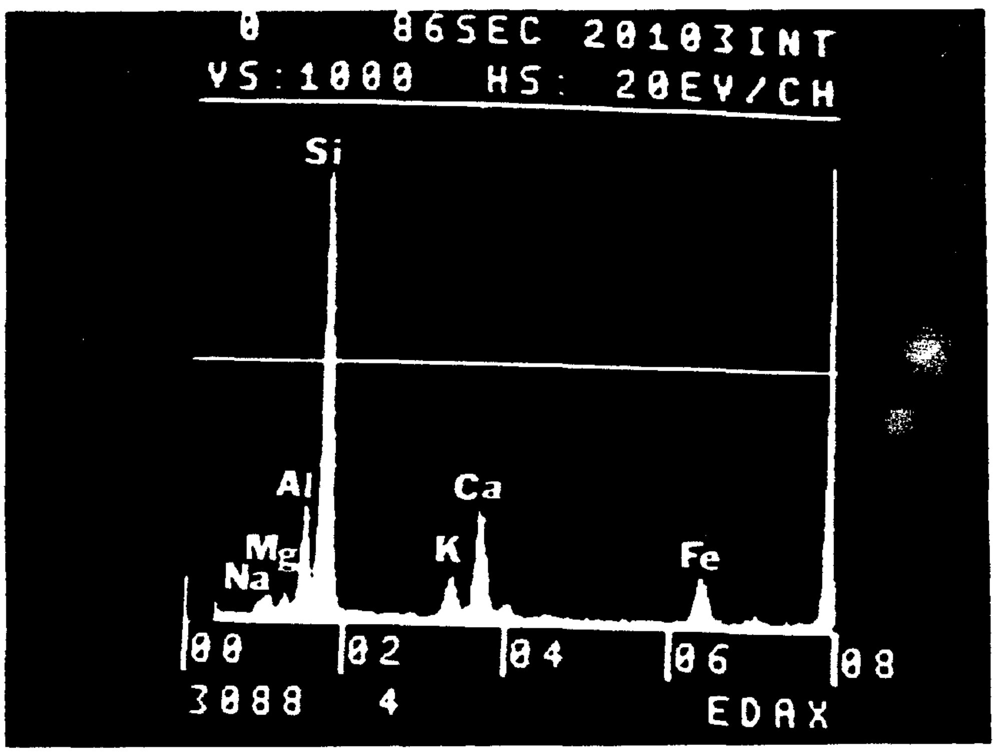


Figure #11 -- EDXA pattern of a large fiber in sample A-4.

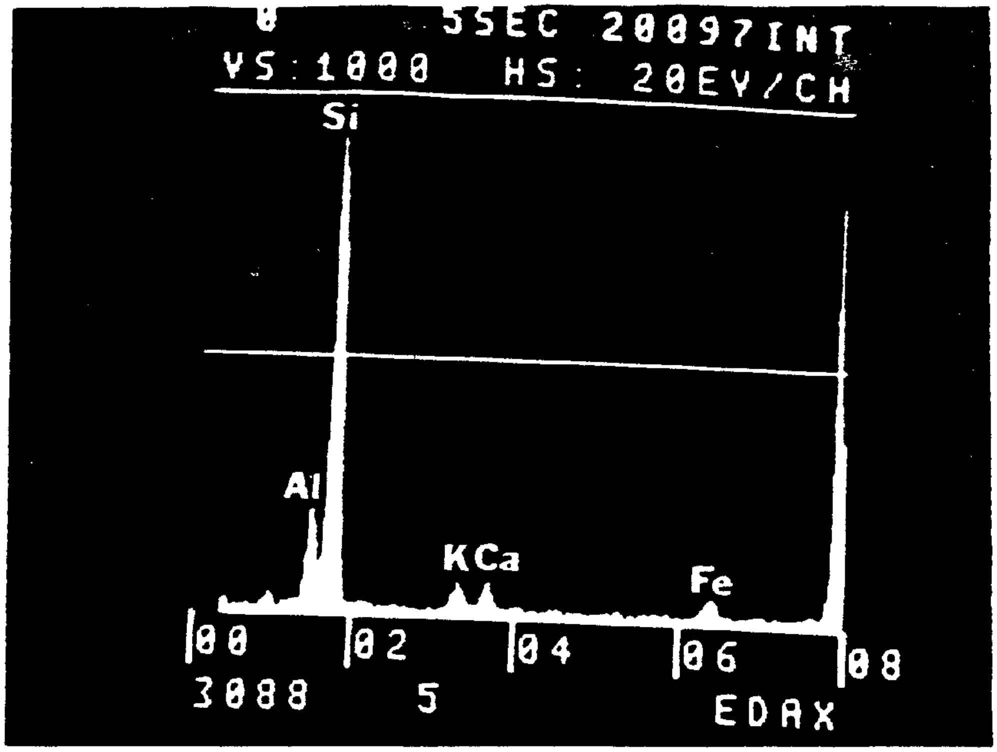


Figure #12 -- EDXA spectrum of the non-fibrous material in sample A-5.

Figure #13 -- Sample A-5, photo 824 mag. = 2000X
Typical particle morphology showing

Figure #14 -- Sample A-7, photo 820 mag. = 10,000X
Typical fiber morphology observed in sample A-7. Note similarity to sample A-2. (Figures 3 & 4)

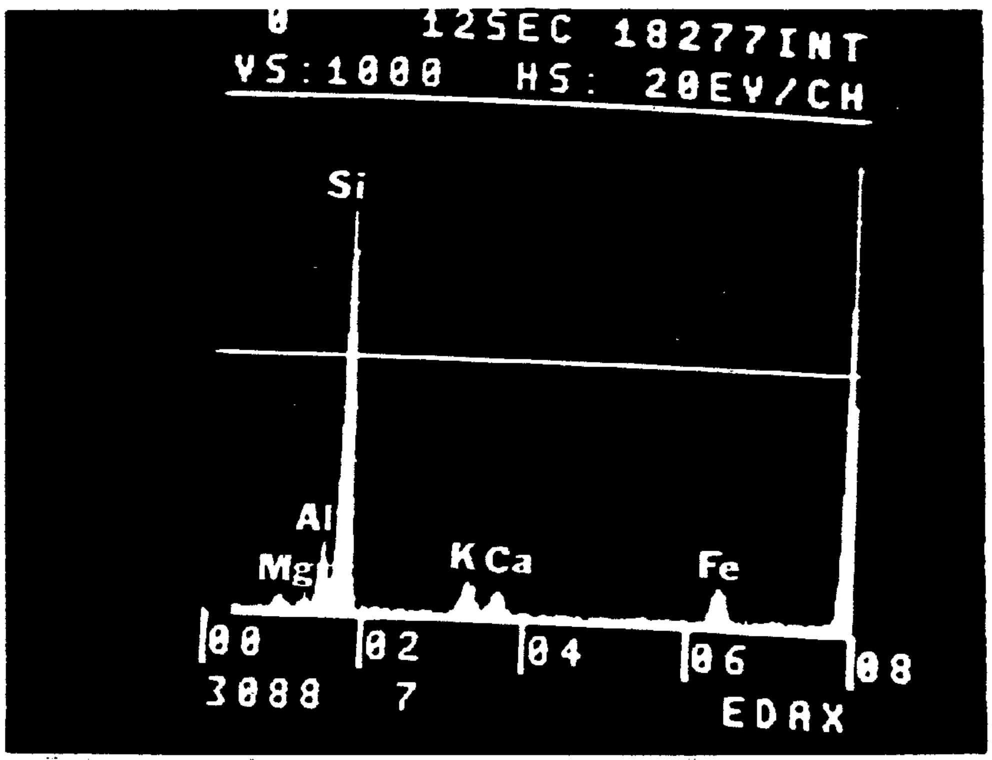


Figure #15 -- Sample A-7, EDXA spectrum of fibrous material in Figure 14.