SURVEY REPORT ON ZEOLITE ORE MINING NEAR BOWIE, ARIZONA

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Industrial Hygiene Section
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National Institute for Occupational Safety and Health
Cincinnati, Ohio

PURPOSE OF SURVEY: To measure the concentration and characterize the composition and morphology of airborne particulate material generated during mining of zeolite ore, and to determine the feasibility of including the miners in a study of possible health effects associated with exposure to airborne zeolites.

PERSONNEL CONTACTED:

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STANDARD INDUSTRIAL CLASSIFICATION OF PLANT: 1429

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ABSTRACT

Zeolite minerals are crystalline aluminosilicates which are capable of reversibile adsorption of molecules. The properties of ion exchange and dehydration have presented a wide variety of uses and potential uses for zeolites including application in pollution control, production of synthetic fuels, agriculture, etc. Reports of pleural mesotheliomas among residents of Turkish villages where certain types of zeolites naturally occur resulted in a NIOSH study of available information on natural and synthetic zeolites. As part of the study, a survey was performed during zeolite ore mining from formations near Bowie, Arizona. Results of this survey showed that miners were not exposed to fibrous zeolites, and that fibrous zeolite varieties were absent, or present in very small traces in the zeolite ore, clay, and overburden at the mining site.

CONTENTS

INTRODUCTION

Zeolites are crystalline hydrated aluminosilicates of alkali and alkaline earth elements, specifically sodium, potassium, magnesium, calcium, strontium, and barium. The existence of zeolites has been recognized since the 1750's, and they have been found in rocks which are diverse in age, lithology, and geologic setting.[1] For approximately 200 years, most of the interest in zeolites was confined to igneous rock occurrences which yielded crystals of interest to mineralogists and collectors. Research into the chemical characteristics of zeolite minerals revealed that dehydrated zeolite crystals would adsorb small organic molecules but not large ones, a phenomenon described as molecular sieving.[2] During the 1930's and 1940's research continued into the dehydration, adsorption, and ion-exchange properties of the zeolite minerals. As a wide variety of potential commercial applications became apparent, development of synthetic crystalline zeolites and the exploration of reported non-igneous zeolite occurrences proceeded. By the late 1950's, a synthetic zeolite known as Linde Type A was under development by Union Carbide Corporation. Exploration during the 1950's revealed that very finely crystalline zeolites occurred widely and abundantly in sedimentary formations.

About half of the approximately 40 naturally occuring zeolite minerals, occur in sedimentary deposits. Eight zeolites make up the major portion of the zeolites found in sedimentary rock; these are analcime, chabazite, clinoptilolite-heulandite, erionite, ferrierite, laumontite, mordenite, and phillipsite. Of these, analcime and clinoptilolite are by far the most abundant.[1] Zeolite minerals are found in abundance throughout the western United States, especially in California, Nevada, Arizona, Colorado, Wyoming, and Oregon. Research has disclosed a wide variety of uses and potential uses for zeolites, including applications in pollution control, production of synthetic fuels, petroleum production, agriculture, mining, metallurgy, and other miscellaneous applications.[2]

BACKGROUND

Reported Health Effects

In 1975 Y.I. Baris, M.D., Chairman, Department of Chest Diseases, Hacettepe School of Medicine, Ankara, Turkey and co-workers reported an extremely high incidence of pleural disease among the inhabitants of Karain, a village in central Turkey.[3] A retrospective study of residents who had died since 1970 and a study of the occupational and environmental exposures to the village residents led the investigators to conclude that the reported pleural disease among residents of Karain was mesothelioma, which was prevalent at a rate of at least 1.3%. The investigators further concluded that the cause of this disease was the location of the village and the villagers' inhalation of large amounts of dust during the cultivation of scallions and potatoes. In 1978 Baris suggested that the diseases may have been caused by small amounts of asbestos in the drinking water of Karain.[4] It was reported that asbestiform fibers had been found in the pleura of two persons who died of mesothelioma.

In 1977 Baris reported his findings to the International Union Against Cancer (IUAC), and in October 1977 researchers from the IUAC and the Imperial College, London, visited Karain and other villages in the Cappadocia region of Turkey, collecting samples of road dust, building blocks, and other materials, and examining residents of the area. Their findings confirmed the diagnosis of mesothelioma, and examination of the rock and soil samples by electron microscopy revealed needle-shaped particles of the zeolite mineral erionite less than 0.25 micrometers (μm) in diameter and up to 5 μm in length.[5] On the basis of these findings, and the fact that asbestos was not found in Karain, Baris concluded that the respiratory diseases were related to exposures to materials other than asbestos.[4] Preliminary results of the studies were presented in December 1977 and July 1978 by researchers from Llandough Hospital, Cardiff, Wales. These results suggested that exposures to erionite, a zeolite mineral, may be the cause of the mesotheliomas observed by Baris.[5]

NIOSH Study of Zeolites

In August 1978 NIOSH selected zeolite as a subject for study. Under a contract, SRI International performed a review of available information on zeolites and reported their findings to NIOSH in October 1978.[6] NIOSH contacted a number of industrial producers and users of natural and synthetic zeolites to obtain samples of as many zeolites as possible for microscopic analysis, and to assess the extent of the production and use of zeolites. These inquiries indicated that the most active commercial mining site in the United States was operated under contract by the Union Carbide Corporation. The site is located near Bowie, Arizona in formations containing chabazite and erionite.[7] The zeolite mined from the Bowie area is primarily used in the production of acid-resistant molecular sieves for use in drying and purifying chemical process streams. According to representatives of the Linde Division, Union Carbide Corporation, chabazite is the zeolite mineral which provides the characteristics desired for the acid resistant molecular sieves. A visit to the mining site was arranged with Union Carbide Corporation and performed by a NIOSH survey team in May 1979. This report describes the survey performed at the zeolite mining site near Bowie, Arizona.

DESCRIPTION OF ZEOLITE ORE MINING

The mining of zeolite from the Bowie deposits can be divided into two major tasks: the location and preparation of suitable mining sites (known as pits), and the actual removal of zeolite ore from the pits. At the time of this survey, all sites which were to be mined in 1979 had been located and prepared for ore removal, consequently, those activities were not included in the study.

Site Location and Preparation

The first step in mining is the identification of suitable deposits of zeolite ore. Test cores are drilled to locate zeolite beds which contain material of the desired purity and quantity. When a suitable deposit is found, overburden is removed with scrapers and graders until the top of the ore bed is exposed. The top of the bed is then swept with a road broom, any remaining overburden is removed with picks and shovels, and the top of the bed is blown clean with compressed air. The ore beds are typically about 200 feet by 100 feet in plan, and 20 to 50 feet below the surrounding terrain.

Mining

The zeolite ore is removed by work crews of 6 to 9 men. These workers are employed by a labor contractor who also provides laborers for agricultural work. Work in the zeolite pit typically begins at about 7 a.m. Mining begins at the edges of the ore bed and proceeds toward the center of the pit. The contractor operates a tractor equipped with a front-end loader and a backhoe. Using the backhoe, the contractor positions the leading edge of the bucket beneath the zeolite layer and lifts the bucket upward, causing sections of the zeolite ore to break free. The sections of ore range widely in size; generally, pieces larger that approximately 4 feet square are broken into smaller pieces with the backhoe and by workers with sledge hammers. The contractor moves around the perimeter of the ore bed on the tractor, breaking pieces of zeolite free from the clay beneath it. The other 5 to 7 workers are stationed around the edge of the bed and as pieces of ore are broken loose, the workers pick them up and remove the thin layer of clay which adheres to the bottom of the ore using hand tools. As each piece of ore is cleaned, it is dropped into a plastic bucket which is emptied onto a large ore pile in the center of the pit. Larger pieces of ore are carried individually after cleaning and thrown onto the ore pile. On the day of the survey, work proceeded in this fashion from about 7 a.m. to 2:30 p.m., with a 30-minute break for lunch. Near the end of the workday, the contractor loaded a large dump truck with ore from the pile in the center of the pit. The workers and the truckload of ore left the pit at approximately 3 p.m. The ore was dumped near a railroad siding in Bowie, where it is shipped by rail to Union Carbide crushing and processing facilities as needed.

Historical Information

The presence of chabazite in the sedimentary rock near Bowie, Arizona was first reported by Lowe in 1876.[2] The NIOSH review of information on zeolites found that claims in the Bowie, Arizona area are owned by WR Grace and Company, Norton Company, and Union Carbide Corporation.[6] The first commercial mining of natural zeolite in this country is thought to have been performed in the early 1960's when

Union Carbide Corporation began mining near Bowie, Arizona for production of Type AW-500 molecular sieve.(6) Mumpton reported that between 1970 and 1972, approximately 265,000 pounds of chabazite/erionite were mined by Union Carbide from the Bowie deposits.(7) The mining contractor indicated that the extent of the mining activity in 1979 (6 to 9 men working from 4 to 6 months per year) was typical of that performed over the past several years. Mining was conducted in about 7 pits between November 1978 and May 1979.

DESCRIPTION OF WORK FORCE

Union Carbide's present contractor for mining has had the contract for 2 years. The contractor employs about 8 temporary stoop laborers to mine the zeolite ore. The men do agricultural labor the rest of the year, e.g., cotton and pecan farming. They come from the San Carlos Indian reservation and from Northern Arizona to live in Bowie for the length of the time they work at the mine.

In 1979, about 8-14 men (Indians and Mexicans) worked at the mine. The total number of laborers was about the same in 1978. There is no real continuity of employment, probably due to the intermittent nature of the work; however, the contractor stated that a few of the men liked the work and had come back from last year. Four of the workers were asked if they had ever worked as zeolite miners before; all four stated that they had not.

The contractor has kept records of all the men who have ever worked for him, however, these records consist of only the social security application forms and contain no job histories.

DESCRIPTION OF SURVEY METHODS

Survey Limitations and Procedures

The sampling results represent an evaluation of conditions during zeolite ore mining on May 8, 1979. The mining operations performed were described as typical of the work performed in removing zeolite from the pit, however, operations such as removing overburden and sweeping the top of the zeolite ore bed were finished for the year and were not observed. On May 8, 1979, a strong west to northwest wind was blowing continuously at velocities of approximately 15-25 miles per hour in the early morning, and up to 30-40 miles per hour later in the day. This wind was reported by the contractor to be unusually strong; typically, the wind at that time of year is light and variable in direction.

Air samples were collected for total and respirable particulate material, free silica, and for characterization of particle composition and morphology. Upwind and downwind area samples were collected; area samples were also collected on the tractor which moved around the pit. Personal samples were collected on 6 workers as they worked on the ore bed. A diagram of the work area showing air sample locations is contained in Appendix A. Bulk samples of the zeolite ore from Pit 185, the overburden which had previously been excavated from the pit, and the clay removed from the zeolite ore were also collected.

Sampling and Analytical Methods

Total and Respirable Particulate Material

Samples for determination of total airborne particulate material were collected by passing air at a rate of 2.0 liters per minute (lpm) through Millipore matched-weight 0.8 μm pore size mixed cellulose ester (MCE) filters and pre-weighed MSA Model FWSB polyvinyl chloride (PVC) 5.0 μm pore size filters. Samples for determination of respirable particulate material were collected at a flow rate of 1.7 lpm, using pre-weighed MSA PVC filters preceded by a 10-mm nylon MSA cyclone.

Samples collected on the matched-weight MCE filters were suitable for determination of total airborne particulate material and microscopic examination and characterization of the collected particles. Samples collected on the PVC filters were suitable for determination of total and respirable particulate material, and measurement of the free silica content of the particulate collected.

Microscopic Examination

Samples collected on the MCE filters were examined by phase-contrast optical microscopy at 400X magnification. The samples were prepared and analyzed in the manner prescribed by NIOSH Method P&CAM 239 for Asbestos Fibers in Air.[8] Analysis of samples by transmission electron microscopy (TEM) was performed at 17,000X magnification, utilizing selected area electron diffraction (SAED) and energy dispersive X-ray analysis (EDXRA) to identify the shape and elemental composition of the particles.[9]

Free Silica

The samples collected on the PVC filters were analyzed for total and respirable quartz and cristobalite using an X-ray diffraction method based upon NIOSH P&CAM Method No. 109.[8]

Evaluation Criteria

Airborne Particulate Material

The Occupational Safety and Health Administration (OSHA)[10] and Mine Safety and Health Administration (MSHA)[11] standard for inert or nuisance dust is 15 mg/m^3 (total dust), and 5 mg/m^3 (respirable dust). Respirable dust is defined as the fraction of the total airborne particulate which will be collected on a PVC filter preceded by a 10-mm cyclone operated at a flow rate of 1.7 lpm.(12) This nuisance dust standard is applicable to particulates containing less than 1% quartz in the dust, as was the case for the samples collected at the zeolite mining site.

The American Conference of Governmental Industrial Hygienists (ACGIH) has established a Threshold Limit Value (TLV) of 10 mg/m^3 for total nuisance particulate and 5 mg/m^3 for respirable nuisance particulate. In its documentation of the TLV, the ACGIH states that the term "inert" is an inappropriate descriptor for nuisance dust, since "... there is no particulate material which does not evoke some cellular response in the lung when inhaled in sufficient amounts."(13) The TLV for nuisance particulates recognizes that inhalation of some materials does not cause changes in the architecture of the air spaces in the lung or cause collagen (scar tissue) to form, and that the tissue reaction is potentially reversible.

There is very little toxicological information on natural zeolites. A study performed by Timar, et.al. in 1966 indicated that intratracheal injection of clinoptilolite in rats caused a typical foreign-body reaction with granuloma formation within 10 days of injection.(14) No other changes were observed over the 1-year period of the study. In March 1980, a study by Suzuki, et.al. reported that peritoneal mesotheliomas had been observed in 2 of 11 mice sacrificed or found dead within a year after intraperitoneal injection of 10 mg of erionite particles 0.5-30 μm in length (1 μm average) and 0.05-0.2 μm in width (0.1 μm average).(15) No mesotheliomas were observed in 12 mice similarly treated with mordenite and in 7 untreated controls, however, extensive peritoneal fibrosis was observed in rats treated with both erionite and mordenite. A later report by Suzuki contains preliminary observations on an expansion of the study.(16) Thirty-one mice were added to the study, of which 10 were injected intraperitoneally with mordenite (5 mice at 10 mg, 5 mice at 30 mg), 10 were injected with erionite (5 at 10 mg, 5 at 30 mg), 5 were injected with 10 mg of chrysotile asbestos, and 6 mice were untreated controls. No animals were sacrificed, and by 11 months after injection, 16 mice had been found dead, including all 5 treated with 30 mg erionite, 3 treated with 10 mg erionite, 3 treated with 30 mg mordenite, 1 treated with 10 mg mordenite, and 4 treated with 10 mg chrysotile asbestos. Of the mice treated with erionite, 5 of 8 found dead had developed malignant peritoneal tumors, and 3 of these were mesotheliomas. Both erionite and mordenite were found to induce fibrosis in the peritoneum of the mouse, with erionite being more productive than mordenite. One of the mice treated with chrysotile asbestos was found with a malignant peritoneal mesothelioma. The study is continuing at this time.

Studies of the effects of exposure to zeolite particles among human subjects are extremely limited. Some early reports by Baris were described in the introduction to this report. Mumpton has studied the Turkish villages where mesotheliomas were found and several other villages in the region and concluded that the data are "equivocal" concerning positive correlation between the presence of zeolites (including erionite) and the incidence of pleural mesothelioma.[5] The most recent publication by Artvinll and Baris[17] describes the expansion of their studies in the village of Tuzkoy, where Mumpton identified erionite, chabazite, and possibly mordenite.[5] The village of Kizilkoy (approximately 6 kilometers south of Tuzkoy) was used as a control. There have been no cases of mesothelioma discovered among residents of Kizilkoy, and samples of bedrock, building blocks, and quarry stone from Kizilkoy showed only a possible trace of chabazite.[5] Artvinll and Baris found two cases of pleural mesothelioma among 312 persons studied in Tuzkoy (with a third case possible), with no cases found in Kizilkoy among 95 persons studied. The authors concluded that the zeolites probably caused the mesotheliomas found in Tuzkoy.[17]

RESULTS AND DISCUSSION

Total and Respirable Particulate Material

Personal and area samples were collected from approximately 8 a.m. until 2:30 p.m. during zeolite mining on May 8, 1979. Temperatures ranged from 68 to 90°F during the sampling period. Sample volumes were corrected for temperature and the altitude (3600 feet) at which the samples were collected. Total particulate concentrations observed in personal samples from workers mining zeolite ore are reported in Table 1. The locations of sampling points are shown in Appendix A.

Area samples were collected in the vicinity of the mining activities in Pit 185. Because the workers were performing heavy physical activity (lifting and carrying pieces of ore, swinging sledge hammers, etc), it was not practical to collect personal respirable dust samples using 10-mm cyclones. Area samples were collected with total and respirable particulate samplers side-by-side in order to determine the approximate percentage of the particulate material which is considered respirable. Results of area samples are presented in Table 2.

Free Silica

All samples analyzed for total and respirable quartz and cristobalite were found to be below the analytical limit of detection (0.03 mg).

Microscopic Examination

Airborne Particulate Material

Thirteen personal and area samples collected on Millipore MCE filters and a field blank were examined by phase-contrast optical microscopy at 400X magnification. Five of the thirteen samples showed very small numbers of fibers, defined as particles with a physical dimension longer than 5 µm and a length to diameter ratio of 3 to 1 or greater. Four of these samples were personal samples collected on laborers working on the downwind side of the pit, and the fifth sample on which fibers were observed was a downwind area sample. The results of optical microscopy are presented in Table 3.

Three of the samples were selected for examination by TEM. Samples 004M, 009M, and 010M were chosen because they represented examples of light and heavy particle loadings, and one sample (004M) showed a small number of fibers under optical microscopy. The three samples were examined by TEM at 17,000X magnification. Examination of sample 004M showed large numbers of particles of various sizes which were composed of aluminum (Al), silicon (Si), potassium (K), calcium (Ca), and iron (Fe) by EDXRA. In scanning 10 fields (sample 004M) one fiber of 0.06 µm diameter and 1.76 µm length was observed. This fiber contained only sulfur when analyzed by EDXRA and did not yield a clear diffraction pattern by SAED. Large numbers of particles of various sizes containing Al, Si, K, Ca, and Fe were also observed in sample 009M, while eight fibers ranging from 0.18-0.6 µm in diameter and 1.8 µm to more than 6 µm in length were found in the examination of 10 fields. These fibers showed only sulfur by EDXRA and ambiguous diffraction patterns by SAED. Similar results were obtained for sample 010M, with a variety of particles containing Al, Si, K, Ca, and Fe observed in 10 fields, and 4 fibers containing sulfur found with diameters of 0.06 µm and lengths ranging from 2.2 µm to more than 6 µm. Photographs of the particles and EDXRA and SAED patterns are included as Appendix B. The presence of the sulfur-containing fibers was not confirmed when samples 004M, 009M, and 010M were re-mounted and examined by TEM. It is suspected that these fibers were contaminants introduced during the first sample mounting procedure.

Bulk Samples

Samples of zeolite ore from Pit 185, overburden which had been removed from the pit, and clay from beneath the zeolite bed were examined by TEM. Samples were prepared by dispersing a portion of the bulk material in alcohol using an ultrasonic probe agitator and depositing a portion of the dispersion on a carbon-coated TEM grid. Photographs of the particles and EDXRA and SAED patterns are included as Appendix C. The zeolite ore from Pit 185 was found to contain small platy Ca-Fe rich aluminum silicates with some minute traces of Mg, K, and Na. The sample was fairly uniform in composition and size range (1-10 µm diameter particles). One fiber was observed while scanning 75 fields. The fiber was 0.5 µm in diameter and 3.5 µm in length, and was composed of Al, Si, Fe, Ca, and K. Photographs of particles and EDXRA patterns for reference samples of erionite and chabazite are included as Appendix D.

The overburden from Pit 185 contained a wide variety of particles with one fiber observed while scanning 60 fields. The fiber was 0.6 µm in diameter and 6.7 µm in length and contained Si, Mg, Ca, and Fe. Examination of clay from Pit 185 showed four fibers in 40 fields scanned;

two of these fibers were identified as chrysotile asbestos. Since no asbestos minerals were found in any other samples, these two observed chrysotile fibers may have been a contaminant introduced during the microscopic examination. The other two fibers were 0.2 µm by 2.0 µm and 0.1 µm by 1.8 µm in diameter and length respectively, and contained Si, Al, and traces of Ca, Fe, and Na.

SUMMARY AND CONCLUSIONS

Workers mining zeolite ore on May 8, 1979, were not exposed to total or respirable particulate material in excess of legal or recommended exposure limits. Area samples for measurement of total and respirable particulate material collected side-by-side indicated that respirable particulate material comprised 0.4 to 33 percent of the total airborne particulate collected. Sampling was performed on closed-face matched-weight MCE filters with open-face cassettes so the filters would be suitable for microscopic examination. Comparison of side by side samples collected with open-face cassettes containing matched-weight 0.8 µm MCE filters and closed-face cassettes containing 5.0 µm PVC filters indicated that the mass of particulate material collected on open-face MCE filters exceeded that collected on PVC filters by factors of 1.25 to 5 (Table 2). Consequently, the personal samples collected on matched-weight MCE filters for particle analysis and total particulate material probably overestimate worker exposures to total particulate material.

Microscopic examination of airborne particulate material and bulk samples collected at the mining site indicated that the air samples generally contained irregularly-shaped particles, with a very small number of fibers in 5 of 13 samples. Examination by TEM with EDXRA and SAED revealed that the irregularly-shaped particles were composed of Al, Si, K, Ca, and Fe, while the fibrous varieties showed only a peak for sulfur by EDXRA. Re-examination of these samples did not confirm the presence of these fibers. The bulk samples of ore, overburden, and clay contained very small number of fibers, with one fiber containing Al, Si, Fe, Ca, and K observed in a preparation of the ore; one fiber containing Si, Mg, Ca, and Fe in the overburden; and four fibers in the overburden, of which two were chrysotile asbestos (a possible laboratory contaminant) and the other two containing Si, Al, and traces of Ca, Fe, and Na. Microscopic examination of air and bulk samples indicated that workers mining zeolite ore from Pit 185 on the day of the survey were not exposed to fibrous zeolite, and such fibrous zeolites varieties were absent or present in very small traces in the ore, clay, and overburden.

It is not feasible to conduct a retrospective mortality study on the miners, due to the small number of workers involved in mining, the insufficient latency period, and the lack of exposure to fibrous zeolite.

TABLE 1

Laborer's Personal Exposures To Total Particulate Material

Sample Number	Sample Period (min)	Concentration (mg/m^3)	Remarks
002M	335	2.23	Working Upwind
003M	135	5.76	Working Downwind
005M	237	1.35	Working Downwind
008M	336	0.43	Working Upwind
009M	337	1.90	Working Downwind
012M	271	2.46	Working Downwind
013M	205	2.16	Working Downwind
014M	103	1.39	Working Downwind

All samples collected on Millipore matched-weight 0.8 m MCE filters, with open-face cassettes.

TABLE 2

Concentrations of Total and Respirable Particulate in Mining Area - Pit 185

Sample Number	Sample Period (min)	Concentration (mg/m^3)	Remarks
004M[a]	172	13.69	Open-face MCE filter, total, downwind
2348[a]	138	2.60	Closed-face PVC filter, total, downwind
2332[a]	130	0.59	Cyclone, PVC filter, respirable, downwind
006M	324	0.55	Open-face MCE filter, total, upwind
010M[b]	292	0.03	Open-faced MCE filter, total, upwind
2339[b]	302	0.01	Closed-face PVC filter, total, upwind
011M[c]	155	4.77	Open-face MCE filter, total, downwind
2353[c]	272	0.41	Cyclone, PVC filter, respirable, downwind
001M[d]	394	1.26	Open-face MCE filter, total, tractor
2319[d]	394	1.01	Closed-face PVC filter, total, tractor
2336[d]	394	0.17	Cyclone, PVC filter, respirable, tractor
2342	138	1.36	Cyclone, PVC filter, respirable, downwind
2311	118	0.71	Closed-face PVC filter, total, downwind
2322	132	0.01	Cyclone, PVC filter, respirable, upwind

a, b, c, and d designate sets of samples collected side-by-side for comparison of total and respirable particulate.

TABLE 3

Summary of Optical Microscopy - Air Samples from Pit 185

Sample Number	Microscopist's Description
001M	Heavy particulate, no fibers
002M	Medium - heavy particulate, no fibers
003M	Heavy particulate, small number of fibers
004M	Heavy particulate, no fibers
005M	Moderate particulate, no fibers
006M	Moderate particulate, no fibers
008M	Moderate particulate, no fibers
009M	Heavy particulate, small number of fibers
010M	Light particulate, no fibers
011M	Heavy particulate, small number of fibers
012M	Medium - heavy particulate, small number of fibers
013M	Heavy particulate, small number of fibers
014M	Moderate particulate, no fibers
Blank	No particles observed

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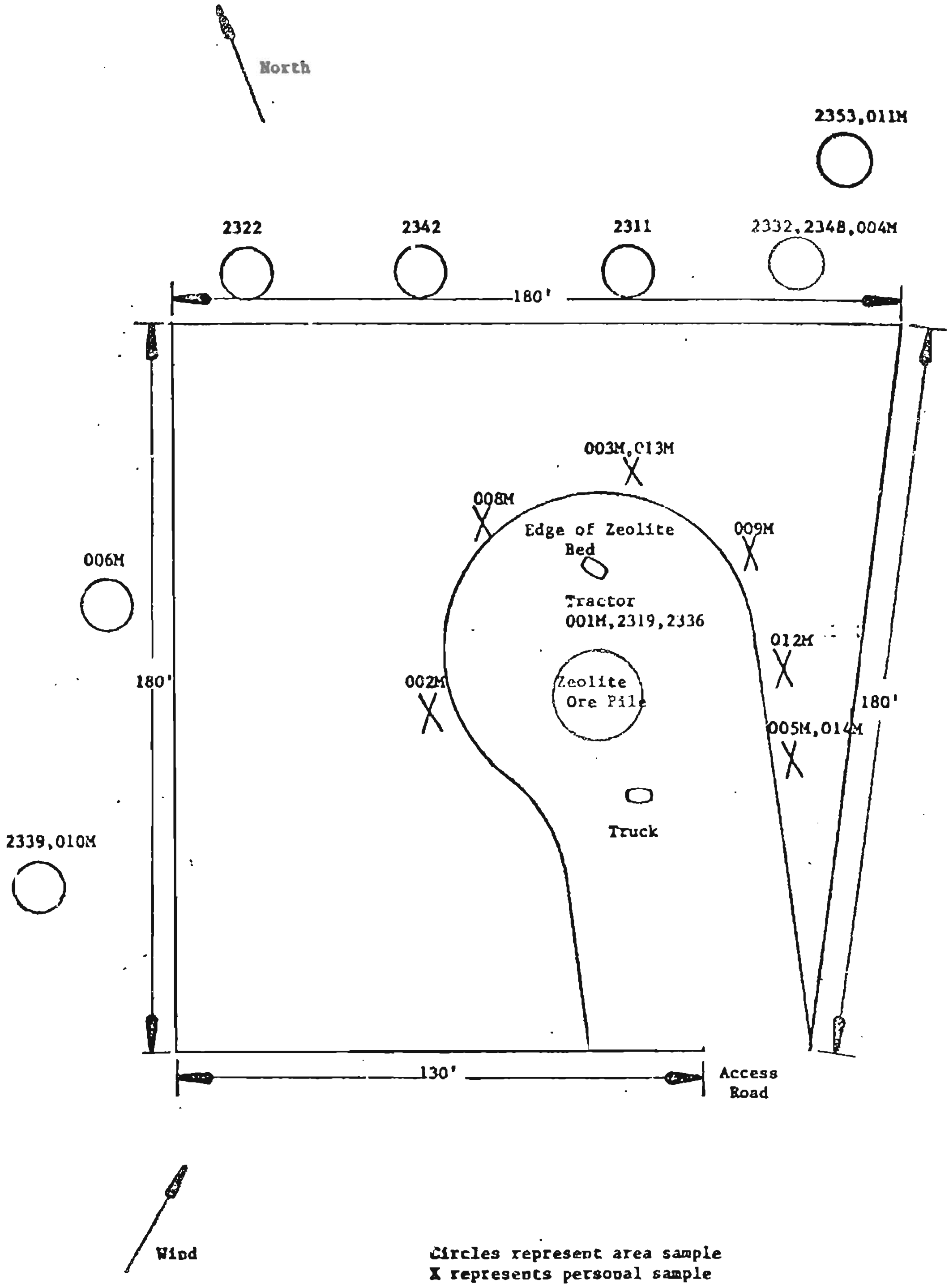
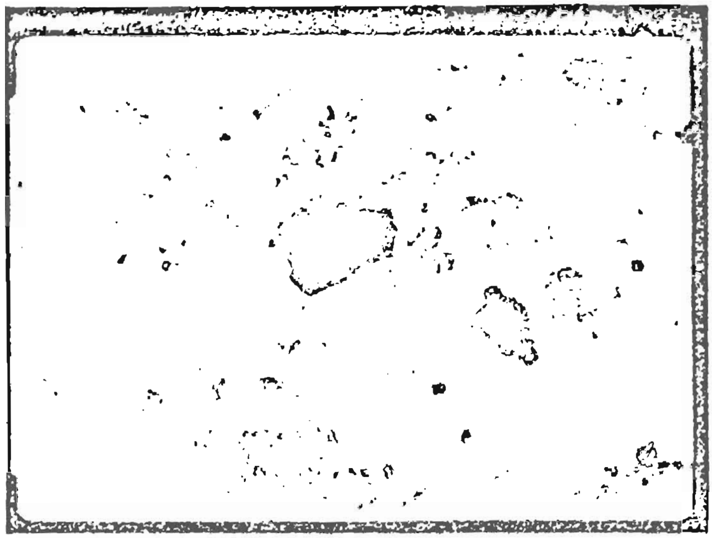
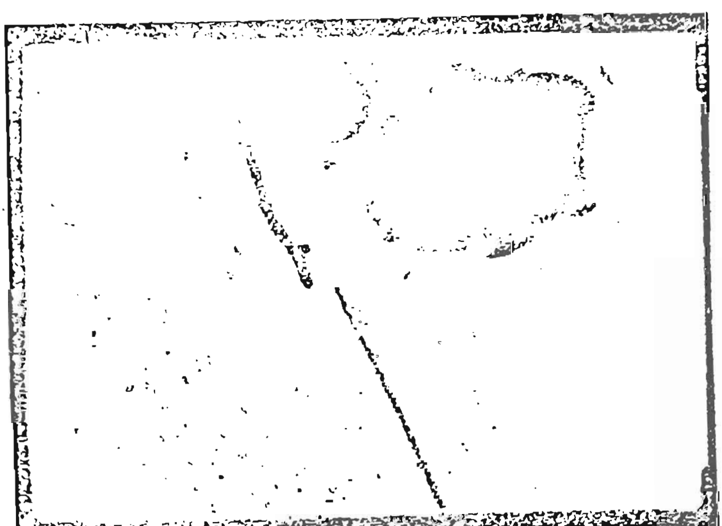
APPENDIX A



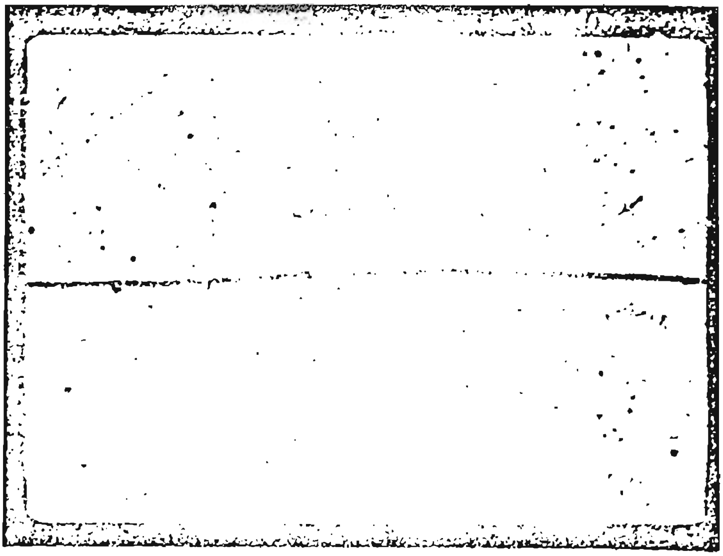
SAMPLING LOCATIONS - PIT NO. 185

APPENDIX B

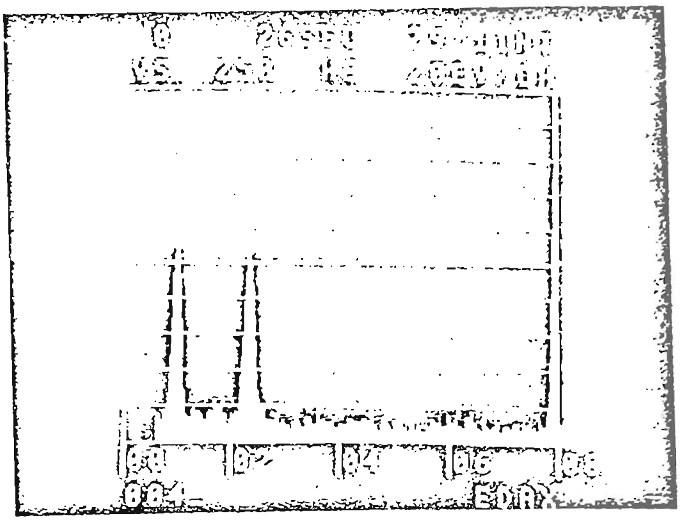




Fibrous and Non-Fibrous Particulate Material
From Air Samples 004m and 010M. Magnification = 17,000X



Fibrous Particle Observed in Air Sample 004M.
Magnification = 17,000X



EDXA Spectrum of Fibrous Particle Shown Above.
Elemental Analysis Shows Secondary Copper Peak From
The Grid and Peak Corresponding To Sulfur.

APPENDIX C

Photo 714 - Pit 185 clay - possible Zeolite fiber 0.1 x 1.8 μm - composition is a Ca, Fe aluminum silicate. (mag. = 10,000X).

Photo 710 - Pit 185 Clay: Typical field showing particulate size distribution and two possible Zeolite fibers (lower center). Magnification = 1700X

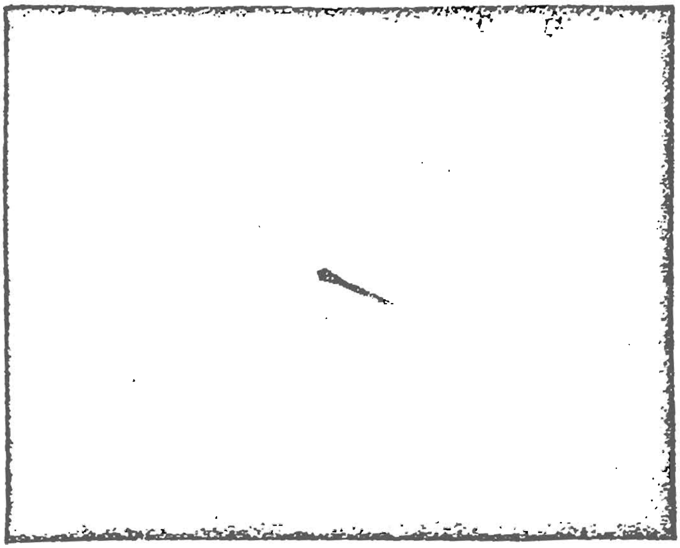
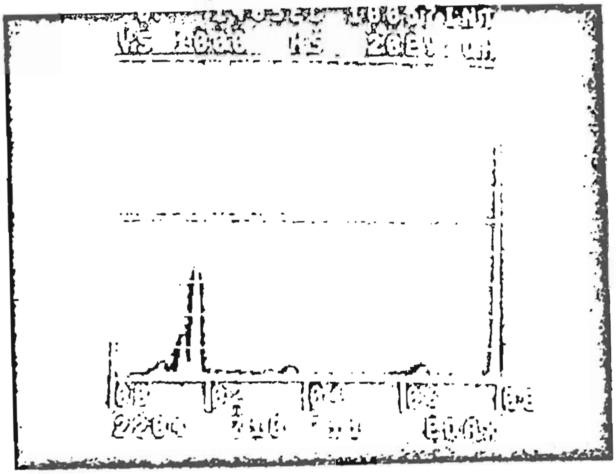
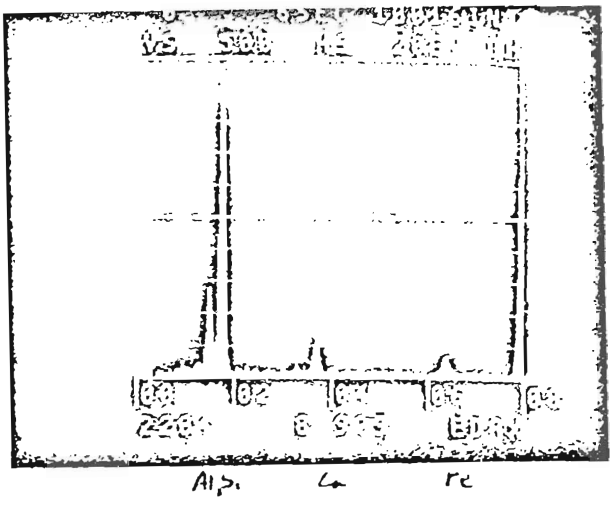


Photo 711 - Selected Area Electron Diffraction pattern of a possible Zeolite fiber in Pit 185 clay sample.



EDAX spectrum of possible Zeolite fiber in photos 710 and 711



EDAX spectrum of non-fibrous Zeolite ore particle

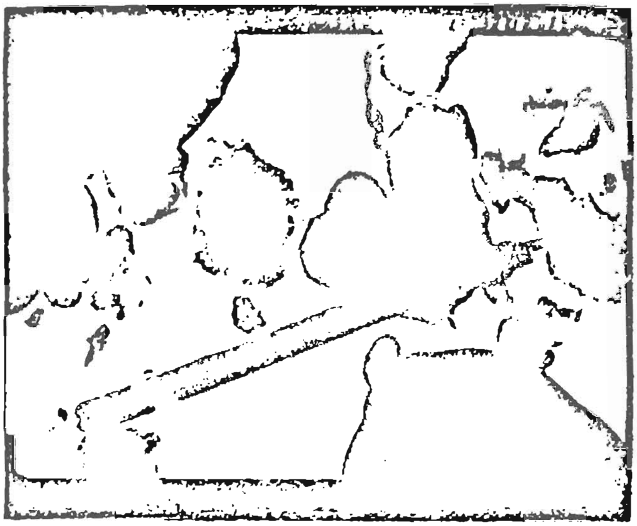
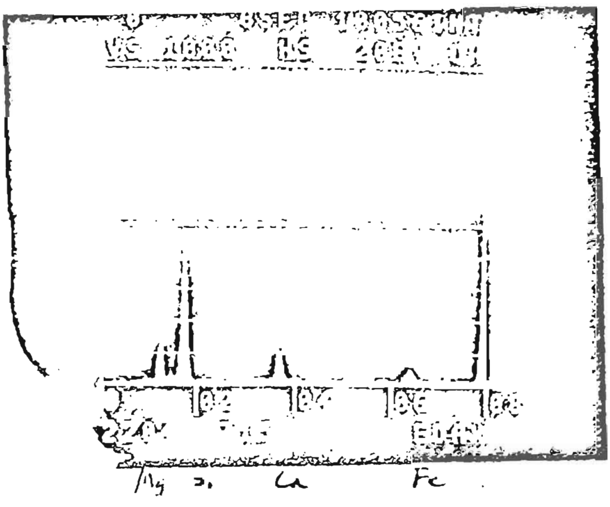


Photo 715 - Pit 185 overburden - photo of large fiber on grid (0.6 x 6.7 μm)
mag = 10,000X



EDAX spectrum of fiber pictured above.

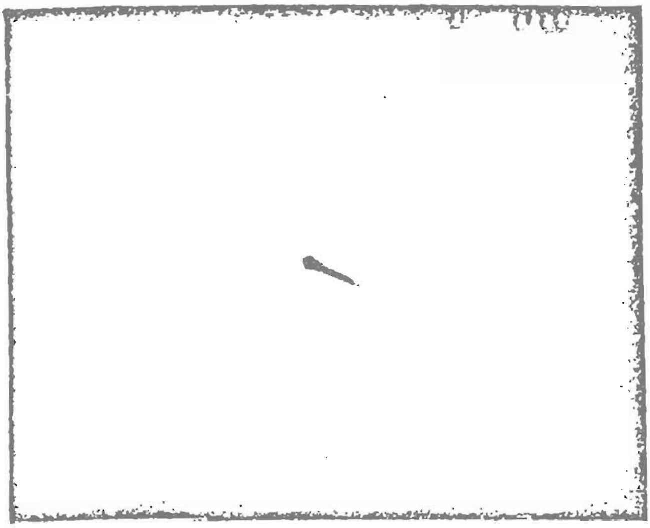
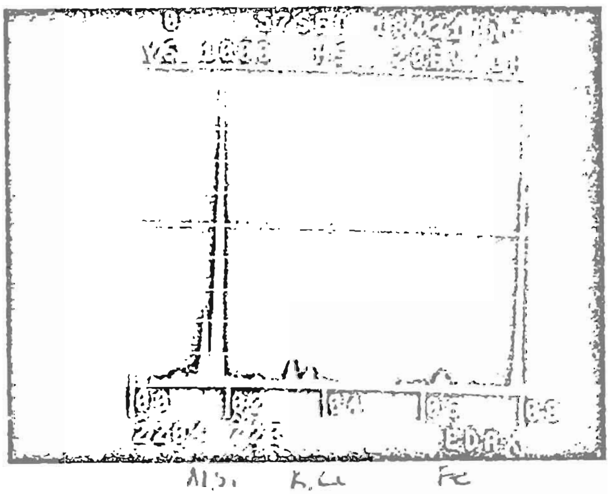


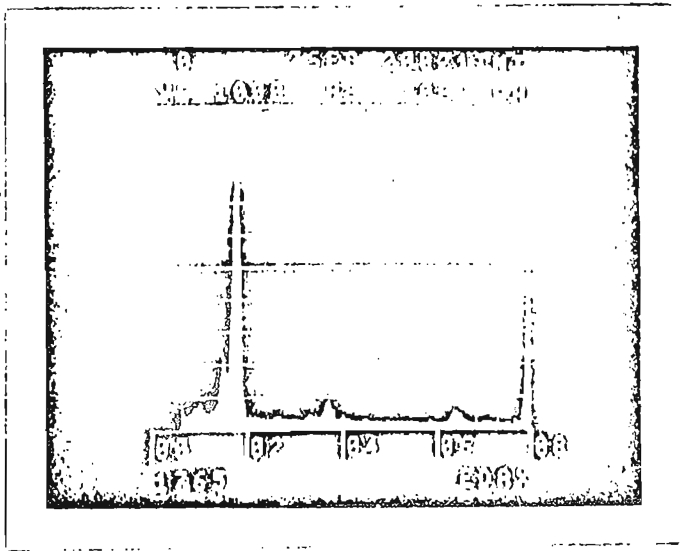
Photo 723 - Diffraction pattern of possible Zeolite fiber 0.5 x 3.5 µm - Zeolite ore sample



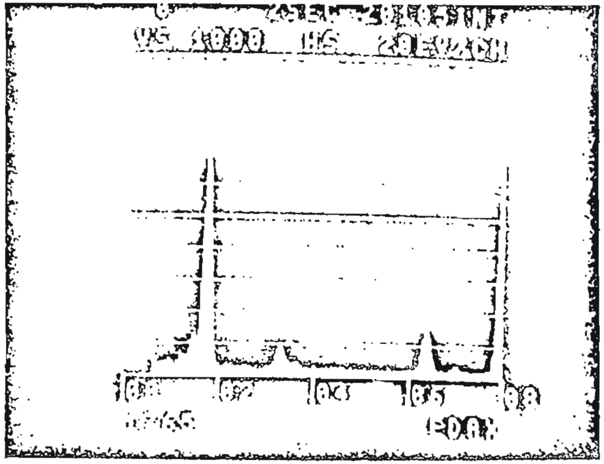
EDAX spectrum of above fiber in the Zeolite ore.

APPENDIX D

REFERENCE MATERIALS:
Erionite and Chabazite



Chabazite: Particle composition Si with Al and traces of Ca, Fe



Erionite: Blade shaped fiber composition Si with small amounts of Al, K, and Fe

Erionite: Blade and platy shaped particles: Mag: 13,000 X