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The Use of Natural Zeolites in Reducing
Heavy-Metal Concentrations at Mining Operations
and Impacted Lands

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ABSTRACT

Extraction of metallic and non-metallic minerals has played a significant role in Montana's development over the last 100 years, and continues today. Mining and milling processes are major components of such resource development that produces waste by-products requiring disposal. Many of these by-products contain substantial concentrations of heavy metals, i.e., copper, lead, zinc, cadmium, etc., which if not handled properly have the potential for contamination of surface waters, ground water and soils.

Contamination or its potential for of surface waters, ground water, and soils from mining and its ancillary facilities are an area of concern throughout the mining industry and among governmental agencies. Current or proposed mines and facilities must spend considerable time and money to maintain or design elaborate facilities for the treatment of the generated wastes.

Similarly, wastes and contamination left from abandoned-inactive mine sites requires remediation, which can also require elaborate engineering practices. A method or mechanism for inhibiting the transport of selected heavy metals from mine sites and mine wastes could prove to be very helpful (beneficial) to the mining industry, governmental agencies, and local citizens.

One of several methods used for treatment of metal-laden wastewater is ion exchange, where one cation (usually a heavy metal, e.g., copper, lead, cadmium etc.) is exchanged for another cation (calcium, sodium, magnesium, or potassium) on a filter media. Zeolites are a group of naturally occurring minerals that have cation exchange properties available, and have the potential for use in treating mine wastes. Naturally occurring and synthetic zeolites have been used in various water treatment applications (Mumpton 1977); however, only small-scale laboratory studies have been made using naturally occurring zeolites in treatment of waters from mining operations (Zamzow and Murphy 1991).

Montana has thousands of acres of land not permitted (no responsible party) that need various levels of reclamation as a result of past mining activities. The Montana Department of Environmental Quality–Abandoned Mine Land Bureau has identified several hundred of the worst sites state wide to begin reclamation activities, while the U.S. Forest Service (USFS) and U.S. Bureau of Land Management (BLM) are currently in the process of inventorying or preparing reclamation plans for abandoned-inactive mine sites either on or affecting federal lands. Work to date has identified thousands of sites with potential problems. The Deerlodge National Forest, for instance, has over 1,050 abandoned-inactive mine sites, with almost 800 on or affecting USFS–administered lands (Metesh et al. 1994).

This project was undertaken two questions: 1) Can naturally occurring zeolites be used as an alternative, low-cost method of treating waste waters or contaminated soils from current or abandoned mine operations, and 2) Can Montana zeolite deposits be economically developed to provide material for such reclamation activities?

The findings from this study indicate that Montana has numerous zeolite occurrences; Montana zeolite deposits have the potential for economic development; and Montana zeolites' metal-attenuation ability compares favorably with that of zeolites available from out-of-state producers.

INTRODUCTION

The contamination potential for surface waters, groundwater, and localized soils from mining operations and their ancillary facilities are areas of concern throughout the mining industry and among governmental agencies. A combination of both Federal and State legislation such as the Comprehensive Environmental Response, Compensation and Liability Act (CERCLA, also referred to as Superfund) and the Montana Metal Mining Act have helped to increase the awareness of problems associated with both existing, future and past mining activities. Along with the increased need for reclamation and mitigation measures, comes the need for simpler and more economic treatment alternatives. Naturally occurring zeolites have the potential for use in treating waters or effluents, from selected sites. It is also possible that zeolites can be incorporated into impacted soils to aid reclamation projects, can be incorporated into tailing ponds to passively treat metal-laden waters that might seep through such impoundments.

Before the current study, the Montana Bureau of Mines and Geology (MBMG) had already conducted limited testing of a specific zeolite which showed promising results for treatment of heavy metal-laden waters (Jordan et al 1988); the US Bureau of Mines had also conducted some laboratory studies with favorable results (Zamzow, M.J. and Murphy, J.E., 1991). The MBMG initiated the current work to look at the feasibility of using naturally occurring zeolites, specifically those found in Montana, in remediation of existing abandoned mine problems and mitigation of future problems. The MBMG also undertook a companion investigation to locate occurrences of zeolites throughout Montana and identify the type(s) of zeolite present at each occurrence. (Berg, R.B. and Lonn, J. 1993).

PURPOSE AND SCOPE

The principal purpose of this project was to determine the technical and financial feasibility of using naturally occurring zeolites, specifically those found in Montana, in reclamation activities relating to heavy metal-contaminated waters and soils. Feasibility was evaluated through a office, lab, and field studies that consisted of three phases: 1) literature search, 2) laboratory testing and economic evaluation, and 3) greenhouse/field studies. A companion study identifying zeolite occurrences and zeolite type throughout Montana also was undertaken.

Montana, with its rich mining history, contains thousands of potentially problematic areas that vary in magnitude and where information gained from this study could be useful. Activities undertaken during

this study focused on the more common problems, e.g., low flow (discharge) from abandoned mine adits and mine wastes intermixed with native soils, and avoided major problems such as high discharge abandoned coal mines south of Great Falls and the Berkeley Pit, which contains in excess of 25 billion gallons of heavy metal-contaminated water. The Montana Department of Environmental Quality (formerly the Montana Department of State Lands)—Abandoned Mine and Hardrock Bureaus and Water Quality Section (formerly the Montana Department of Health and Environmental Sciences-Water Quality Bureau), the U.S. Forest Service, and operators of current mining properties were contacted throughout this project to identify existing needs and problem areas that this study should address.

ZEOLITES—WHAT ARE THEY?

The zeolite group of minerals includes almost 50 distinct naturally occurring minerals. In addition, more than 100 different zeolites have been synthesized for industrial applications. Zeolites are silicate minerals that in addition to silicon and oxygen contain aluminum, sodium, calcium, potassium, magnesium, and water molecules. Unlike other minerals, where the atoms are tightly packed together, the arrangement of atoms that form the zeolite crystal structure results in channels and voids, somewhat of a cage-like structure (figure 1). If the zeolite is dehydrated to remove water molecules from these voids, other molecules can be absorbed into the zeolite structure. The size of the molecule determines whether it can be admitted to the zeolite structure. In this function as a molecular sieve, some zeolites have been used to produce a gas that consists mainly of oxygen by selectively absorbing nitrogen from the air. Zeolites also have been used to remove sulfur dioxide, carbon dioxide, and hydrogen sulfide from natural gas.

Because of natural substitution by trivalent aluminum ions (3+) for quadravalent silicon ions (4+), a zeolite crystal has a negative charge. To balance this negative charge, cations such as sodium, calcium, potassium, and magnesium are absorbed by the zeolite crystal and occupy sites in the channels and voids. These cations are loosely held by the zeolite, so they can be exchanged by other, more selective cations. This property is used in water softeners where the zeolite makes hard water softer by adsorbing calcium and magnesium ions and releasing sodium ions. Treating the zeolite with a solution containing a high concentration of sodium ions that displace the absorbed calcium and magnesium ions regenerates the water softener. When the regenerated zeolite is again exposed to the hard water, the sodium ions

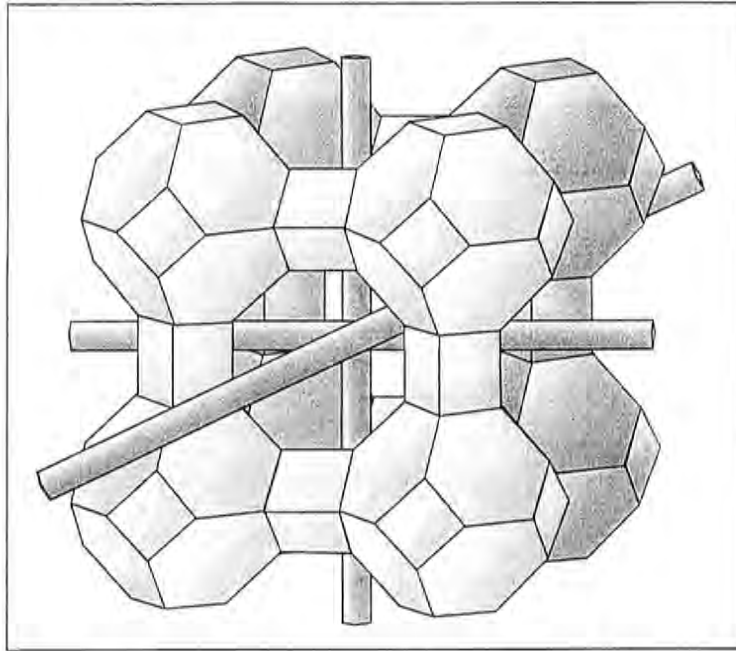


Figure 1. Example of zeolite structure.

are displaced by calcium and magnesium ions. This property of cation exchange is quantified and designated as cation exchange capacity (CEC). Metal cations such as lead, copper, cadmium, and zinc also can be absorbed by zeolites. In recent years, numerous investigations have focused on the possible use of zeolites to purify water by the removal of metal ions (Colella 1995; Colella et al. 1995; Zamaow and Schultz 1995; Feldmann 1995).

Zeolites can form by several different geologic processes. However, the largest deposits and those most important commercially are formed from volcanic ash. Volcanic ash consists of small glass shards that alter readily under certain conditions to form zeolites. The chemical composition of the volcanic ash is an important determinant in the formation of a zeolite or of bentonitic clay. Zeolites formed by the alteration of volcanic ash are in many instances associated with beds of bentonite. Because of abundant deposits of volcanic ash in the western states, large zeolite deposits occur in this region, in particular in California, Nevada, Arizona, Utah, Oregon, Idaho, and Wyoming. Although many species of zeolites have been reported to occur in these deposits, clinoptilolite is by far the most common and is the zeolite that has been mined in the largest quantity. Reports of zeolite deposits in Montana are more limited in extent than those in some of the other western states.

Alteration of a volcanic ash bed to a zeolite bed generally results in a harder and more durable rock that is less easily eroded than the unaltered volcanic ash. Zeolitized beds in numerous deposits can be recognized because they form erosion-resistant ridges and mesas. However, by compaction and cementation, some beds of volcanic ash also can become durable and are difficult to distinguish from zeolitized beds.

Zeolite crystals in these deposits are too small to be recognized microscopically. Most crystals are less than 20 micrometers (less than one-third the diameter of a human hair). The identification of zeolites is accomplished by x-ray diffraction analysis (figure 2a). This analytical method, which is commonly employed in mineral identification, uses a technique where x-ray beam is used to measure the distance between layers of atoms in the mineral. Because distances between atomic layers are different for different minerals, most minerals can be identified by this method that makes use of the distinctive "fingerprint" of the particular mineral. X-ray diffraction analysis of a sample suspected to contain a zeolite enables it to be identified as containing a zeolite and also enables the particular zeolite species to be identified. In addition, other minerals such as quartz, feldspar, and clays, often associated with zeolites, can be identified. Zeolite in the sample cannot be determined by routine x-ray diffraction analysis, but it can be quantified to a limited extent, such as inferring that the sample contains more than 90% clinoptilolite. Figure 2b is a micro-scanning electron microscope photo showing the blocky crystals of clinoptilolite samples from two locations.

Phase I - Literature Search

A literature search was conducted through the Montana University System, utilizing the Montana Tech library. Twelve major data bases were searched in addition to journals, magazines, and books contained within the library system.

A preliminary search keying on the word, ZEOLITE, produced over one-half million entries; subsequent searches used more specific key words: cabazite and clinoptilolite (two predominate zeolite types expected to be found in Montana), and copper, zinc, and lead (the major heavy metals of concern noted by regulatory agencies). The major data bases searched were as follows

- 1) NTIS - this data base contains reports from three major federal government agencies: DOE, DOD, and NASA. The subject range is broad and covers the period from 1964 to the present. The file contains over 1.4 million records and is updated biweekly.

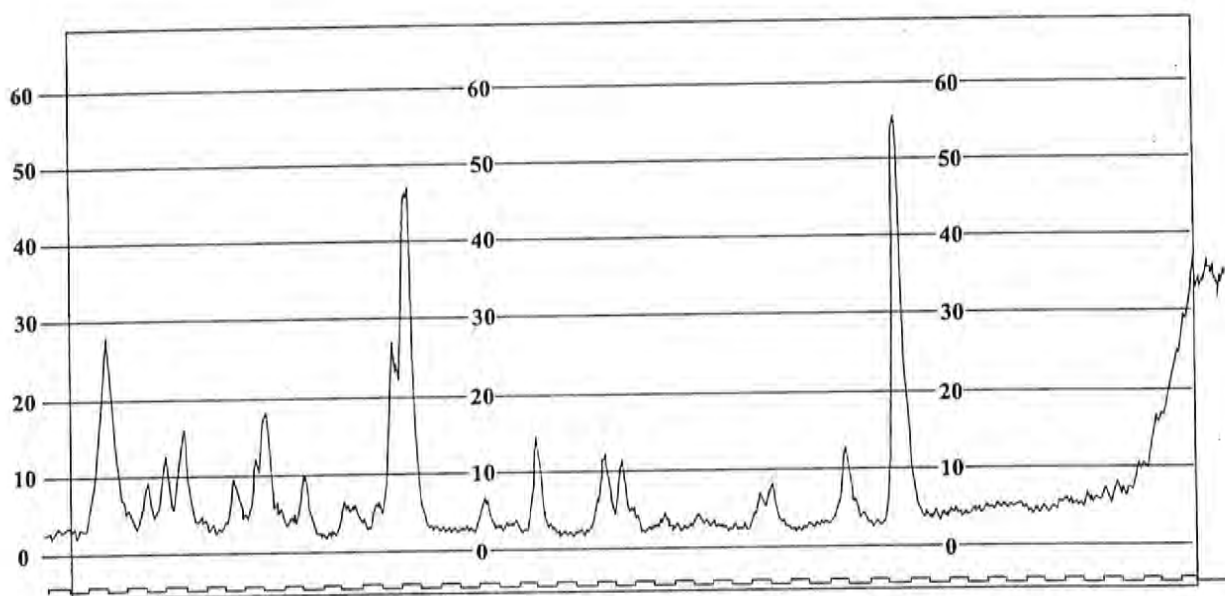
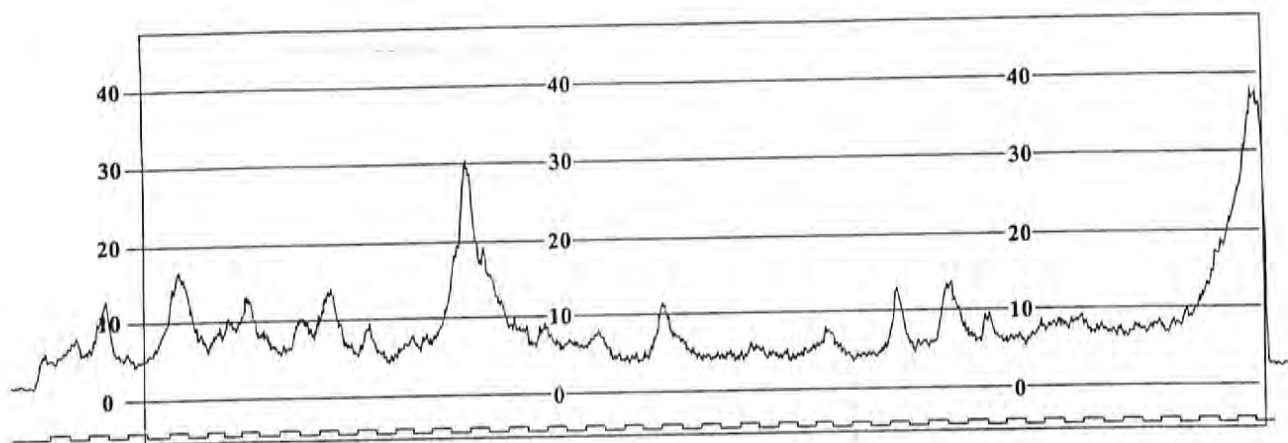


Figure 2a. X-ray diffraction traces.



Figure 2b. Blocky crystals of clinoptilolite samples from two locations.

- 2) COMPENDEX PLUS - this data base contains publications from around the world dealing with significant engineering and technological literature. It contains data from 1970 to the present with a file size of over 2.2 million records and is updated monthly.
- 3) ARIGICOLA - this data base contains publications broadly dealing with agriculture. It contains information from 1970 to the present and consists of over 1.3 million records. The data base is updated monthly.
- 4) PTS PROMPTS - this is a multi-industry data base that provides broad coverage of companies and technologies. It contains data from 1972 to the present and consists of over 2.0 million records. The file is updated daily.
- 5) PTS F&S INDEX - this is also a broad, multi-industry data base, with emphasis on trends (events) that might impact the business environment. It contains information from 1980 to the present and contains over 2 million records. The data base is updated weekly.
- 6) ASIS-PACIFIC - this data base covers industries related to the Pacific Rim nations and has a broad subject area. The data base contains information from 1985 to the present and consists of over 80,000 records. The data base is updated biweekly.

- 7) METADEX - this data base contains broad coverage of international metals literature. This file is broken into two general categories: 1) metals abstracts, and 2) alloys index. The data base contains data from 1966 through present and consists of over 770,000 records. The data base is updated monthly.
- 8) SCISEARCH - this data base is a multi-disciplinary index, which covers the broad fields of science, technology, and biomedicine. It contains information from 1974 to the present and consists of over 9 million records and is updated weekly.
- 9) DISSERTATION ABSTRACTS ONLINE - this data base contains virtually all American dissertations granted at accredited North American universities since 1861. Selected master's theses have been included since 1962. The data base contains over 1 million records and is updated monthly.
- 10) ENVIROLINE - this data base contains broad inter-disciplinary coverage of scientific and technical literature. It contains over 130,000 from 1971 to the present and is updated monthly.
- 11) GEOREF - this is the data base of the American Geological Institute and covers worldwide technical literature dealing with geology and geophysics. The data base contains 1.6 million files of data from 1785 to the present (North American material) and 1933 to the present (worldwide material). The data base is updated monthly.
- 12) AGRIS INTERNATIONAL - this is the international data base for agricultural sciences and technology. The data base contains over 700,000 files and covers the period from 1975 to the present. It is updated monthly.

Based on information gleaned from this literature search, a bibliographic data base was constructed. Articles or reports of potential relevance were acquired with the title, author and abstract and other pertinent information entered into the data base. The bibliographic data base consists of 84 entries and is contained in Appendix I.

The review of this literature found that zeolites 1) have been demonstrated to beneficially remove ammonia from waste waters, 2) are being used in the clean up of radioactive wastes at nuclear facilities, and 3) have shown positive results in removal of one or two metals in effluents. The review also found no substantial reports dealing with a complex matrix of metals as proposed in this study. This project would complement ongoing U.S. Bureau of Mines and other studies proposing to use zeolites to remove heavy metals from wastes. It is apparent that additional work investigating the ability of naturally occurring zeolites to remediate sites with heavy-metal contamination is justified. A limited

investigation of known zeolite occurrences in Montana also was undertaken simultaneously with the literature search. This investigation was quickly completed because the literature reported only a few occurrences of zeolites in Montana. Cretaceous and Tertiary beds in western Montana that contain a significant volcanic component were then examined. Beds near Dillon, White Sulphur Springs, Vaughn, Geyser, Helena, and Winston were sampled. Almost 200 samples of possible zeolitized ash were collected and analyzed by x-ray diffraction methods. A fusion technique for field use in identifying zeolite material was evaluated but was unreliable.

Phase I - Zeolite Occurrences in Montana

The Montana Bureau of Mines and Geology conducted a reconnaissance of bedded zeolite occurrences in Montana during 1991 and 1992. (Berg and Lonn 1993). Zeolite occurrences in western Montana are shown in figure 3. With the exception of two localities west of Great Falls (localities 1 and 2, figure 3), where analcime was found in a 4-8 inches thick bed, clinoptilolite was the dominant zeolite in all occurrences. The largest known zeolite deposit in Montana is 11-miles southwest of Dillon along Grasshopper Creek (locality 14, figure 3). Clinoptilolite was first identified from this locality by Robert Pearson of the U.S. Geological Survey during geologic mapping (Pearson 1989). Subsequent work by the Montana Bureau of Mines and Geology showed clinoptilolite to be the major zeolite with mordenite present in low concentrations in some samples. Many samples from this deposit have been made available to researchers investigating applications of zeolites in removing metals from water. Zeolitized beds also are exposed along Beaver Creek 20 miles southeast of Helena (locality 5, figure 3). Numerous samples collected from these beds contain clinoptilolite. However the quantity of clinoptilolite in this area is much less than at Grasshopper Creek because zeolitization is discontinuous, and the thickest bed is only four feet thick, whereas, at Grasshopper Creek masses of zeolitized rock are tens of feet thick.

In addition to these occurrences of clinoptilolite, there are several occurrences in the Bitterroot valley near Anaconda, Butte, and south and west of Dillon. On the basis of this reconnaissance, it seems unlikely that Montana has zeolite deposits as large as those found in some of the other western states, Montana does have zeolite deposits large enough to be developed if a local or regional market existed.

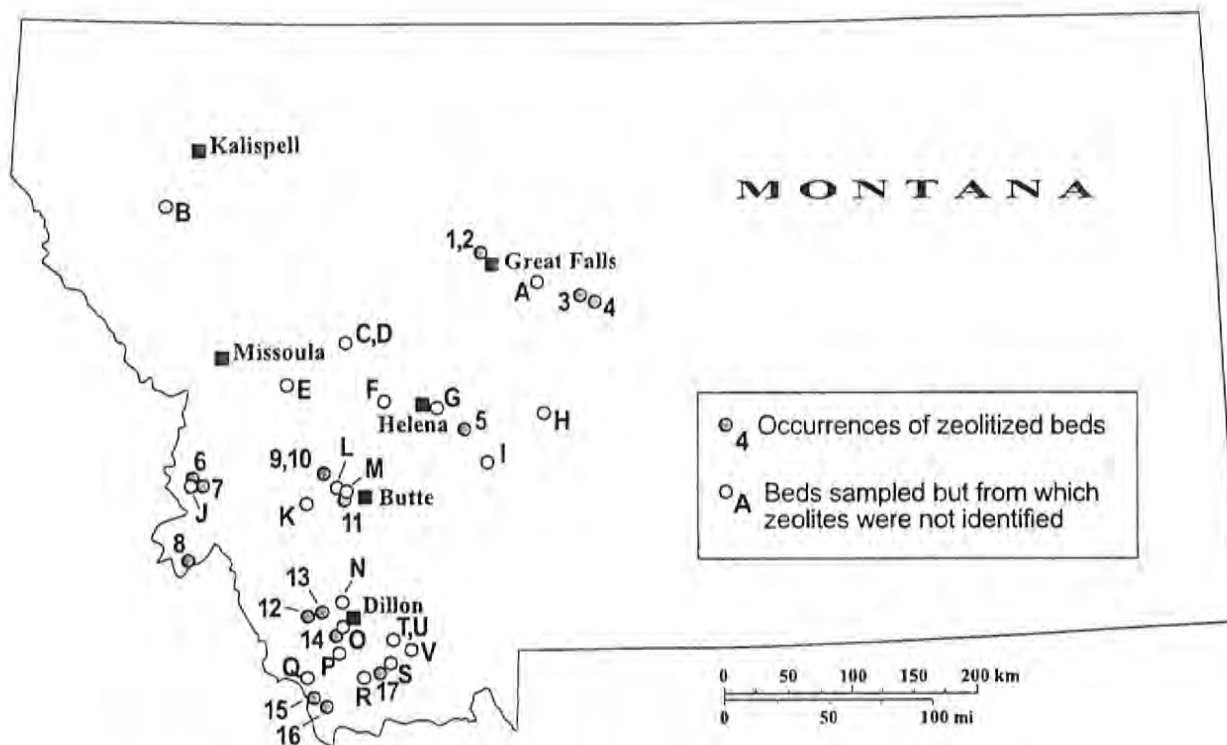


Figure 3. Zeolite occurrences in Montana (from Berg and Lonn 1993).

Phase II - Lab Studies

Laboratory studies consisted of several different activities: 1) sample characterization (zeolite mineralogy), 2) cation exchange capacity (CEC) determinations, and 3) metal attenuation testing (batch and column tests).

Sample Characterization (Zeolite Mineralogy)

The mineralogy of samples collected at each of the potential Montana zeolite occurrences, areas visited during the MBMG reconnaissance, were determined by x-ray diffraction. The x-ray diffraction analysis was made using a Norelco x-ray diffraction unit equipped with a diffracted beam monochromator yielding a CuK_2 diffracted beam. Routine identification of commonly encountered minerals was made by comparing the sample trace to traces of specific minerals. A total of 190 samples were collected and analyzed.

The most common zeolite in the samples was clinoptilolite. Ninety-five samples contained clinoptilolite in concentrations ranging from a trace (estimated to be <10%) to more than 90% (in a few samples). Only crude semi-quantitative estimates of the amount of clinoptilolite in these samples were

made. Figure 2a shows x-ray diffraction traces of two samples: one with strong peaks (Z-93) and the other with much less intense peaks (Z-466). Both samples consist essentially of the zeolite clinoptilolite. The peaks measured are cross hatched.

The difference in peak intensity of these two samples analyzed under identical conditions is probably related to crystallinity, i.e., the size of the individual zeolite crystals and the relative perfection of the crystals. Larger crystallites tend to produce more intense peaks than very small crystallites. Also the fewer imperfections in the crystal structure, the sharper and higher the x-ray diffraction peaks. The cation exchange capacity (CEC), or measure of suitability of zeolites for many applications, is considerably greater for sample Z-466 as compared to Z-93. It appears that there may be an inverse relationship between peak height (crystallinity) and CEC. If this relationship is found to be a consistent relationship, x-ray diffraction analysis could be a useful method for screening zeolite samples to identify those with high CEC. Because zeolite samples are routinely identified by x-ray diffraction, this method could be easily applied to this investigation of zeolites in Montana.

Cation Exchange Capacity (CEC)

Eighty-one of the zeolite samples collected from Montana occurrences were submitted for CEC determination. The CEC was determined by saturating the zeolite with sodium (Na) using a solution of 1M Na_2SO_4 , washing the sample with distilled water, drying, displacing the Na using a solution of 0.1M $(\text{NH}_4)_2\text{SO}_4$, and determining the Na concentration in the displacing solution by flame atomic absorption. Two samples of commercially available zeolites also were analyzed, Teague XY and Teague CH. Of these eighty-three (81 + 2) samples, seven were duplicate analyses as a check on lab quality. Table 1 contains the CEC results. Samples were analyzed by Steven Boese, Applied Analysis, Laramie, Wyoming.

It is apparent from the data shown in table 1 that the CEC of the samples collected and analyzed is quite variable. CEC's of the Montana zeolites ranged from a low of 0.08 meq/gm to a high of 1.90 meq/g. The average CEC of the Montana zeolites was 0.97 meq/gm, while the CEC from the Teague CH and XY zeolites was 1.33 meq/gm and 1.25 meq/gm, respectively.

Table 1. Zeolite ammonium ion exchange capacity.

Sample No.	CEC meq/g z	Sample	CEC meq/g z
XY*	1.25	Z-324	0.17
CH*	1.33	Z-328	0.18
Z-36	1.19	Z-329	0.37
Z-37	0.86	Z-340	0.79
Z-39	1.4	Z-341	0.08
Z-49	0.86	Z-342	0.58
Z-50	1.02	Z-343	0.76
Z-60	1.08	Z-344	1.04
Z-71-1	1.04	Z-346	1.44
Z-71-2	0.89	Z-349	1.54
Z-73	0.23	Z-351	1.5
Z-76	0.26	Z-353	1.24
Z-85	1.21	Z-354	1.8
Z-86	1.12	Z-364	0.94
Z-93*	0.94	Z-365	1.15
Z-126	0.96	Z-366	0.89
Z-127*	0.93	Z-402	1.34
Z-131	0.76	Z-405	0.8
Z-133	1.29	Z-406	1.41
Z-134*	1.17	Z-408	1.1
Z-136	1.17	Z-416	0.77
Z-137	1.1	Z-417	0.29
Z-138	0.68	Z-421	0.96
Z-140	1.23	Z-428	0.51
Z-193	0.36	Z-429	0.49
Z-196	1.27	Z-433	0.5
Z-206	1	Z-444	1.22
Z-207	0.99	Z-445	1.22
Z-209	1.19	Z-446	1.09
Z-211	0.5	Z-458 Duplicate of Z60	1.06
Z-222	1.31	Z-459 Duplicate of Z127	0.91
Z-246	0.87	Z-460 Duplicate of Z134	0.93
Z-247	0.98	Z-461 Duplicate of Z319	0.5
Z-248	1.19	Z-462 Duplicate of Z342	0.56
Z-249	0.89	Z-463 Duplicate of Z344	1
Z-274	1.38	Z-466*	1.86
Z-276	0.65	Z-467	1.6
Z-277	1.21	Z-468	1.33
Z-278	0.65	Z-469	1.11
Z-313	0.52	Z-471	1.9
Z-319	0.52	Z-472	0.87
Z-320	0.86		

* Zeolite used in lab test

(Ammonium ion exchange capacity was determined by saturating the zeolite with Na using a solution of 1M Na₂SO₄, washing the sample with distilled water, drying, displacing the Na using a solution of 0.1M (NH₄)₂SO₄, and determining the Na concentration in the displacing solution by flame atomic absorption.) Analyses by Steven Boese, Applied Analysis, Laramie, Wyoming.

Metal Attenuation Tests

Four zeolites collected from Montana occurrences and two commercially available varieties of zeolites were used in the laboratory attenuation tests. The commercial zeolites were provided by Teague Mineral Products of Adrian, Oregon, and were designated XY and CH. The Montana zeolites were collected from Grasshopper Creek (2 samples), Tabor Mountain, and the McCleery Gulch. Two different attenuation testing methods were used, those being batch and column tests.

Batch Tests

Originally, only column tests were planned for this project, however, during discussions with Department of Natural Resources and Conservation personnel, it was decided to add limited batch testing of selected zeolites to the study. The primary purpose of the batch tests was to verify that selected Montana zeolites had comparable attenuation of heavy metals to those of zeolites commercially available. If the Montana zeolites showed little or no attenuation of the heavy metals, no further testing would occur, and the project was to be terminated.

Zeolites from three of the Montana occurrences were crushed using a 2-in. chipmunk crusher. The crushed samples were sieved using a #10 mesh (2.0 mm) upper sieve and a #20 (0.84 mm) lower sieve (10–20 mesh). The size fraction retained between the two sieves was stored in sample bags for use in the laboratory tests.

Single cation stock solutions of copper (Cu), cadmium (Cd), and zinc (Zn) were prepared by dissolving prepared weights of hydrated copper-sulfate, zinc-sulfate, and cadmium-sulfate in distilled water. Calculated amounts of the stock solutions were then diluted with approximately 20 L of distilled water to create initial (head) solutions of Cu, Cd, and Zn, each having concentrations of approximately 100 mg/L.

Each batch test was performed using 2.5 grams of a 10–20 mesh zeolite and one liter each of 100 mg/L Cu, Cd, and Zn solutions. Stir bars were used in conjunction with a magnetic stir plate to agitate the zeolites added to each solution. The samples were agitated to ensure that maximum contact and exchange of ions would occur. The tests were run in 2 L glass beakers covered with plastic wrap to ensure no foreign matter would enter the solution and to avoid evaporative losses. The stir rod was kept at a velocity where a slight vortex was noticeable. The time increments that the zeolites were kept in contact with the solution were 10, 30, 100, 300, and 1,000 minutes. At the conclusion of each batch test approximately 150 mL of solution were filtered through a 0.45-micron cellulose fiber filter.

Approximately 20 mL of the filtrate was placed in a 25-mL plastic bottle then acidified with 0.2 mL of nitric acid (HNO_3). Batch tests were repeated for each zeolite type/solution type combination at increments of 10, 100, and 1,000 minutes. The tests were not repeated for the 30- and 300-min. increments.

The batch tests were run using five of the six zeolites identified in table 1; those were the two commercial zeolites provided by Teague Minerals (XY and CH) and three Montana zeolites (Z-93, Z-127, and Z-134).

Results of the batch tests are summarized in tables 2 and 3. Table 2 shows attenuated concentrations of cadmium, copper, and zinc, in mg/L, after 1,000 minutes contact time. Table 3 shows the percent attenuated for each of the three analytes after 1,000 minutes contact time. Figures 4, 5, and 6 show the average percent of each analyte attenuated by zeolite at 0 min., 10 min., 30 min., 100 min., 300 min., and 1,000 min. of contact time. The average percent attenuation is based on two sample runs.

The two commercial zeolites (Teague CH-XY) attenuated (removed) the highest percent of all metals, ranging from over 45% removal of cadmium by zeolite CH, to just under 20% removal of zinc by zeolite XY.

The batch tests provided some general data on the CEC efficiency of the tested zeolites. Clearly the samples having the lower CEC values were the least efficient exchangers, and their performances were somewhat erratic and unpredictable. The two commercial zeolites and the best native Montana sample (Z-134) appear somewhat predictable in terms of ion exchange.

The Montana zeolites removed from less than 10% of zinc for zeolites Z-93 and Z-127 to greater than 20% removal of cadmium and copper by zeolite Z-134. The Montana zeolites removed 50% or less of the metals removed by the two commercial zeolites. However, the batch tests did confirm that the Montana zeolites were successful in attenuating metals, therefore, column testing was initiated. It is not surprising that the commercial zeolites outperformed the Montana zeolites, due to the method the Montana zeolite samples were collected. Exposure to surface water and ground water could change the exchangeable cation population but might not really affect the lattice. The Montana zeolites were collected from surface outcrops of the zeolite and without any determination of the purity of the material; however, purity was estimated from x-ray diffraction analyses. The commercial zeolites are selectively mined from beds several feet in thickness of known high purity.

Table 2. Batch tests—zeolite metal attenuation (mg/L).

Analyte	Zeolite	*Run # 1 (mg/L)	*Run # 2 (mg/L)	Ave (mg/L)
Cadmium	CH	47.1	34.9	41.0
	XY	30.3	28.9	29.6
	Z-93	12.1	17.1	14.6
	Z-127	9.2	19.2	14.2
	Z-134	17.4	24.7	21.1
Copper	CH	32.9	33.0	33.0
	XY	20.7	17.8	19.3
	Z-93	10.6	8.9	9.8
	Z-127	16.7	12.2	14.5
	Z-134	12.0	15.8	13.9
Zinc	CH	27.8	30.1	29.0
	XY	24.8	25.3	25.1
	Z-93	6.3	5.5	5.9
	Z-127	7.3	7.6	7.5
	Z134	11.6	14.1	12.9

* Value listed is the difference in concentration (mg/L) from the beginning (head) concentration and the concentration after 1,000 minutes contact time. Initial concentrations of the respective metals were approximately 100 mg/L.

Table 3. Batch tests—percent metal attenuation.

Analyte	Zeolite	Run #1 (%)	Run #2 (%)	Ave (%)
Cadmium	CH	47.0	45.5	46.2
	XY	30.2	28.8	29.5
	Z-93	13.6	18.0	15.8
	Z-127	10.3	20.2	15.4
	Z-134	19.4	26.0	22.8
Copper	CH	32.0	32.7	32.4
	XY	24.2	24.6	24.4
	Z-93	10.9	8.9	9.9
	Z-127	17.1	12.2	14.6
	Z-134	12.3	18.0	15.2
Zinc	CH	27.5	27.4	27.5
	XY	20.5	17.6	19.1
	Z-93	6.6	5.6	6.1
	Z-127	7.6	7.8	7.7
	Z-134	12.1	14.4	13.3

Values were calculated based on a beginning (head) solution of 100 mg/L per metal.

Attenuation vs Contact Time

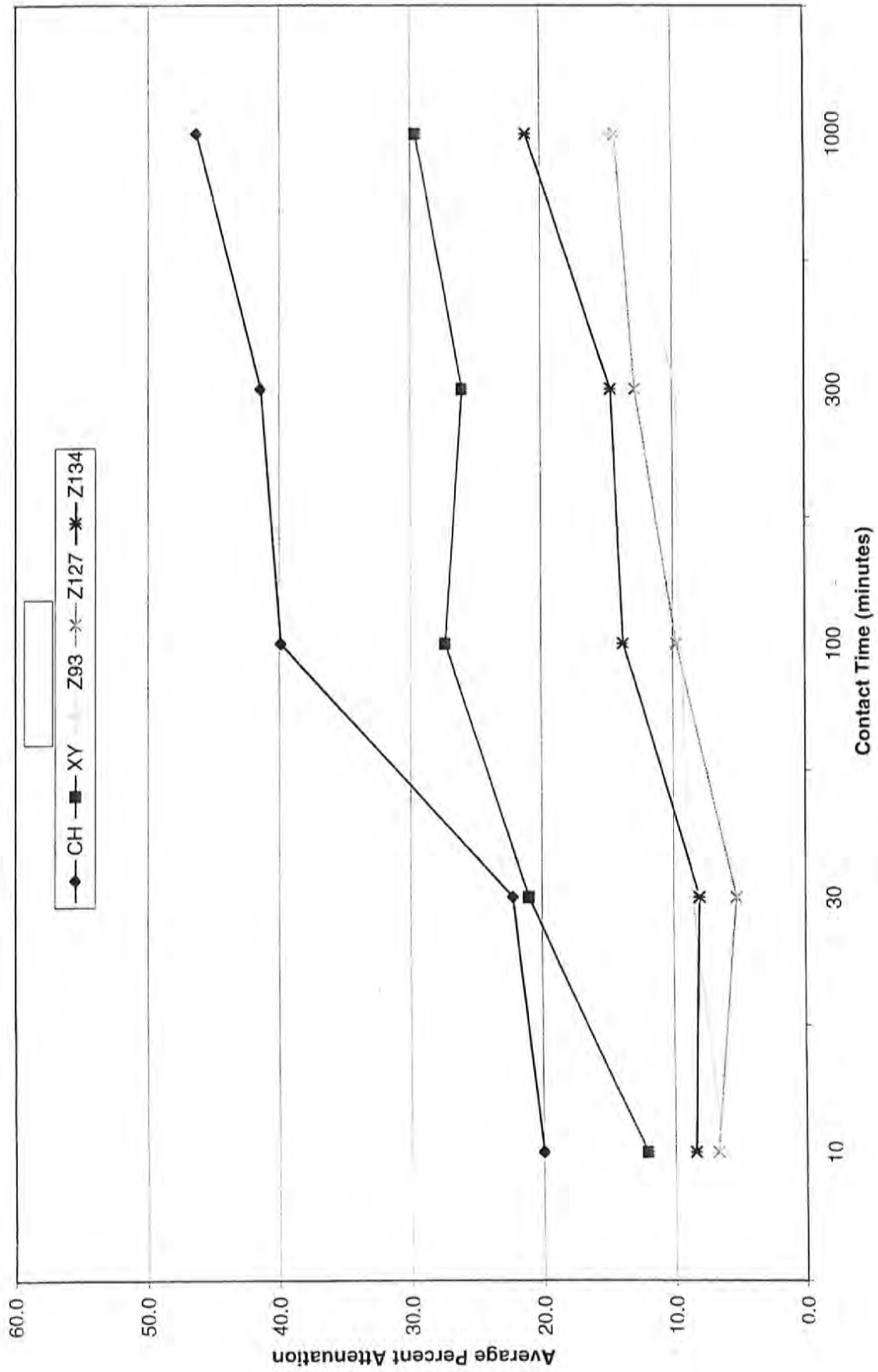


Figure 4. Average percent cadmium attenuation.

Attenuation vs Contact Time (minutes)

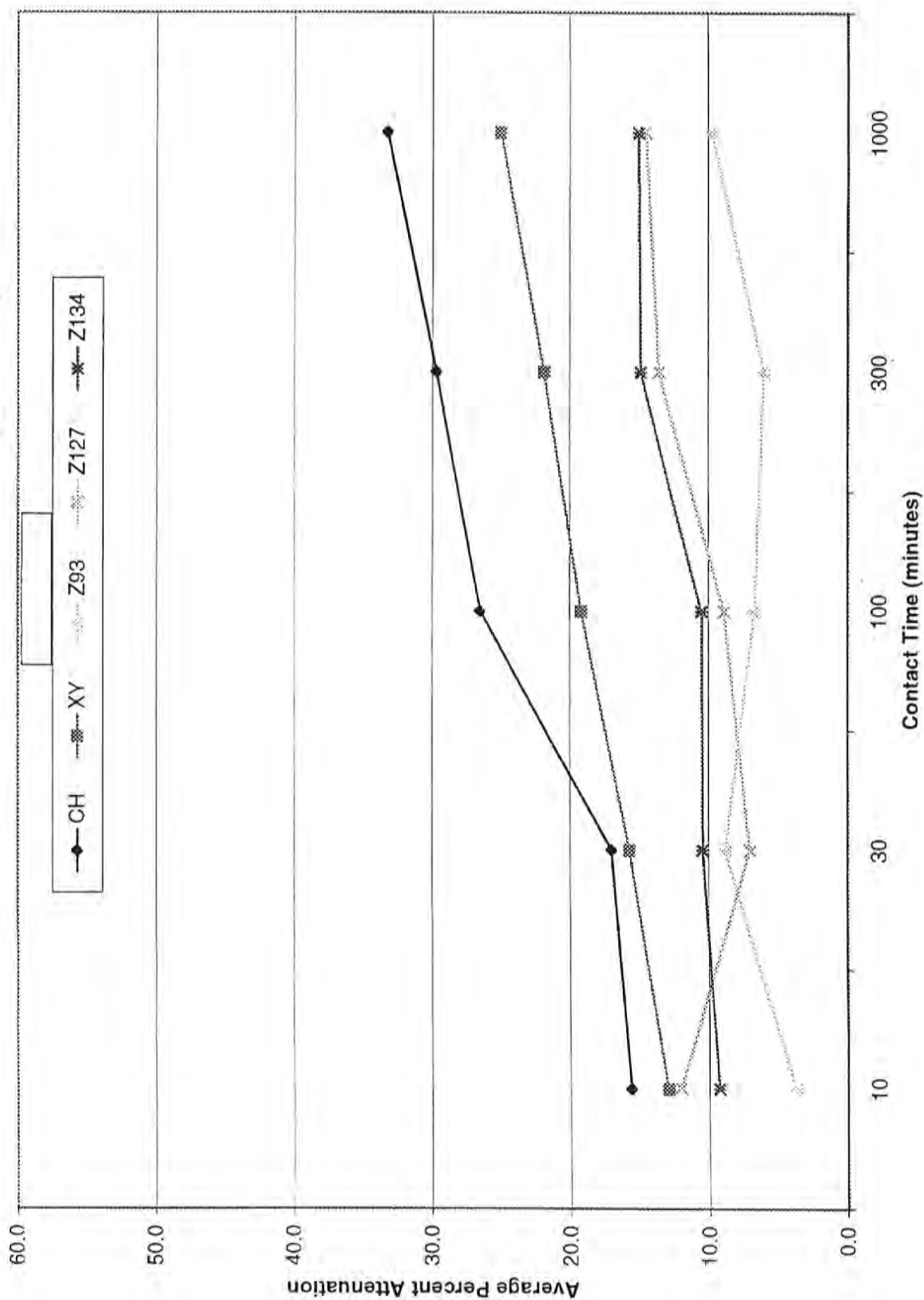


Figure 5. Average percent copper attenuation.

Attenuation vs Contact Time

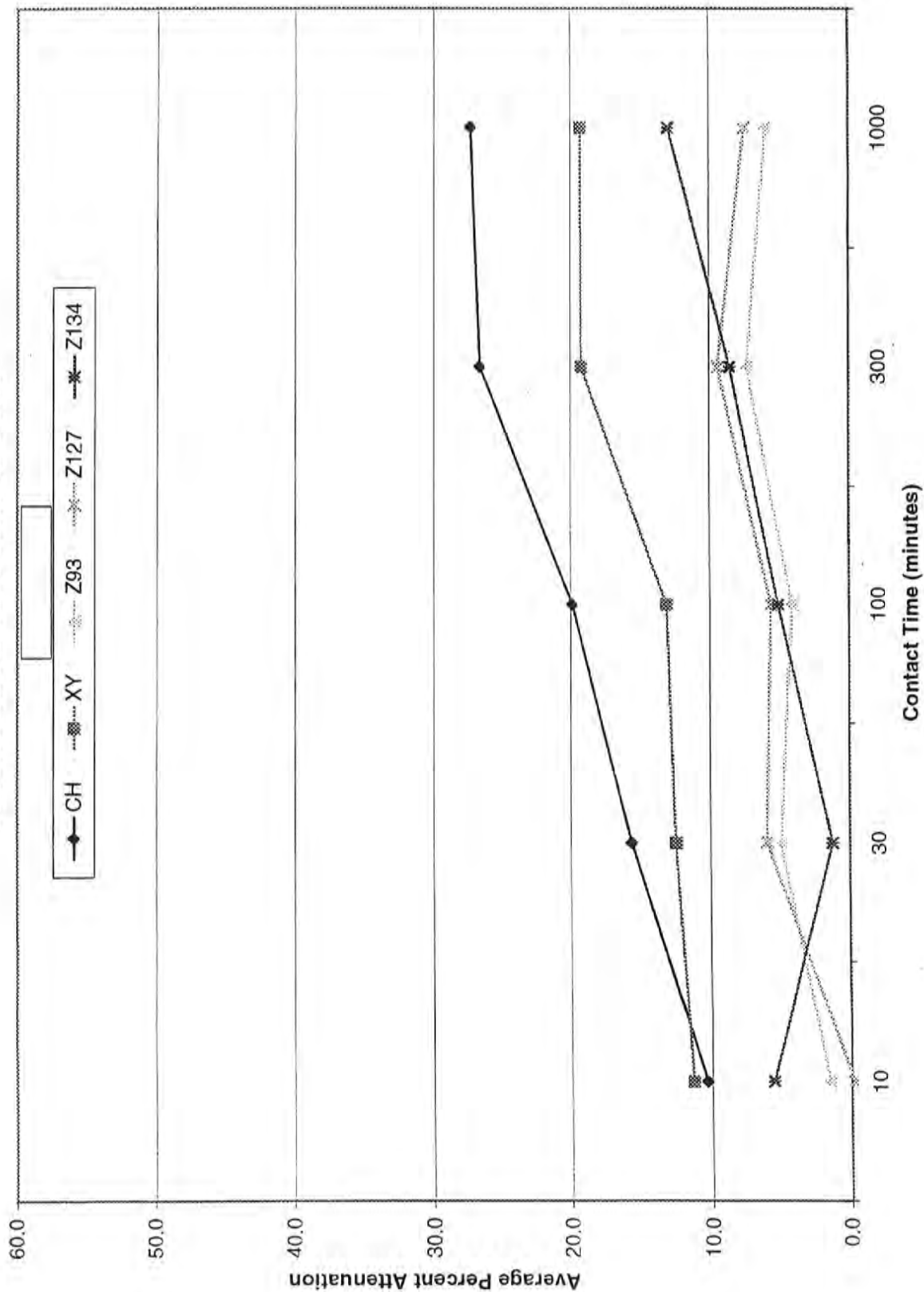


Figure 6. Average percent zinc attenuation.

Column Tests

Column tests involved the packing of 500 m of selected zeolite material into translucent acrylic cylinders 3 in. (7.5 cm) in diameter and 27.5 in. (70 cm) long. Prior to loading each column, a fine nylon mesh screen was placed in the bottom of the column, followed by the packing of 7 in.³ (117 cm³) of fine Ottawa sand. After the column was packed, the contents were gently tapped with a large wooden dowel to insure there would not be any preferential fluid flow through the column or along the column sides. The volume occupied by the 500 m of zeolite was measured and recorded.

Sample solution was pumped through each column from the bottom-up using a peristaltic pump. The pumping rate was kept constant at 10 mL/min. Effluent water discharged through an upper side port in the column and into a graduated cylinder. Filtered acidified samples of 125 mL each were collected at selected volume intervals. The pH and specific conductance of the effluent was periodically monitored by placing the instrument probes in the water between the top of the zeolite column and the discharge outlet. Samples were collected based on a selected sample volume schedule or until the effluent pH and specific conductance equaled that of the head solution in which case the test was terminated.

The column tests were run utilizing water from sites with heavy-metal contamination problems. Late spring snowstorms prevented the collection of test water from selected abandoned mines in the Deerlodge National Forest. Therefore, water was collected from a monitoring well within the Colorado Tailings area, located on the west end of Butte, Montana. The well that was chosen to collect test waters was highly contaminated with heavy metals as a result of historical mining operations (table 4, Head Sol. CTr 84-10). Approximately 10 gal (40 L) of water were collected either the afternoon prior to the column tests or early on the morning of the tests. Water samples (head solution) were collected for lab analysis before the start of each test and occasionally at the end of each test to determine if water quality of the head solution changed during testing.

Column tests were run initially using five of the six zeolites identified in table 1. Subsequent column tests were run using a zeolite from one other Montana occurrence, as well as using test water from an active mine discharge. Table 4 contains water quality results (concentrations) from selected column tests while table 5 shows the percent concentration removed during each test.

A review of the data presented in table 4 shows two distinct trends: 1) a substantial concentration reduction occurred in the first sample volume for all of the analytes and each type of zeolite, and 2) breakthrough in metal attenuation occurred first in zinc removal. (Breakthrough was considered to be where the percent metal attenuation, or removal, is less than 80%.) Figures 7a through 12d show analyte

Table 4. Zeolite test column leachate results selected concentration data.

Zeolite Type	Sample No.	Volume (mL)	Iron (mg/L)	Aluminum (ug/L)	Arsenic (ug/L)	Cadmium (ug/L)	Copper (ug/L)	Lead (ug/L)	Zinc (ug/L)	pH	SC (umhos/cm)	Comments
Z-93	0	0	11.30	2540	NA	106.0	7760	462.0	48060	4.08	1500	Head Sol. CT84-10 10ml/min
	1	500	0.08	15	NA	1.0	26	1.0	2440	7.34	1490	
	2	1220	0.04	25	NA	20.0	190	1.0	25830	6.50	1630	
	3	2750	0.42	25	NA	60.0	1070	1.0	45380	6.13	1675	
	4	6650	3.74	200	NA	110.0	5000	1.0	48090	5.63	1620	
	5	7750	5.87	370	NA	120.0	6450	1.0	47950	5.54	1590	
	6	9100	7.00	450	NA	120.0	6800	1.0	47690	5.43	1585	
	7	10600	7.77	600	NA	116.0	7440	1.0	47320	5.24	1575	
	8	12750	8.69	920	NA	120.0	7620	1.0	46830	5.09	1570	
	9	18650	0.07	2700	NA	110.0	7760	1.0	46590	4.68	1560	
	10	21500	0.03	2530	NA	109.0	7460	1.0	48580	4.55	1566	
	11	0	0.85	2530	NA	120.0	7570	440.0	47880	3.52	1630	Head Solution
Z-127	0	0	11.20	2240	599.0	111.5	7110	465.0	49700	3.96	1500	Head Sol. CT84-10 10ml/min
	1	276	0.05	50		5.0	80	1.0	380	7.31	1630	
	2	525	0.00	50		5.0	50	1.0	1110	6.87	1640	
	3	740	0.00	50		5.0	80	1.0	2700	6.73	1655	
	4	1050	0.04	50		5.0	110	1.0	6020	6.33	1630	
	5	2100	0.24	50	8.3	30.1	339	1.0	17650	6.12	1570	
	6	2700	0.56	50		53.0	717	1.0	27070	6.08	1565	
	7	3700	0.89	50		66.0	1165	1.0	34360	6.11	1560	
	8	4500	0.94	50	2.2	74.7	1500	1.0	38430	6.12	1535	
	9	6050	1.68	75		90.0	2234	1.0	43960	6.05	1515	
	10	7150	1.95	90		97.0	2660	1.0	45630	6.08	1510	
	11	8500	2.53	50		110.0	3350	1.0	46460	6.06	1440	
	12	9550	2.39	15	1.1	101.0	3530	1.0	46920	6.00	1485	
	13	13050	2.06	50		110.0	3820	1.0	48000	5.89	1460	
	14	15950	1.60	50		100.0	4320	1.0	48430	5.91	1450	
	15	23800	0.02	136		106.0	5720	1.0	48660	5.71	1485	
	16	0	3.96	2260		114.0	6980	445.0	50000	3.97	1480	Head Solution
Z-134	0	0	9.34	2160	NA	163.0	11230	673.0	61330	4.03	1410	Head Sol. CT84-10 10ml/min
	1	325	0.13	-80	NA	-10.0	50	-100.0	375	6.70	1560	
	2	525	0.08	-80	NA	-10.0	20	-100.0	290	6.63	1550	
	3	725	0.01	-80	NA	-10.0	24	-100.0	901	6.41	1530	
	4	825	0.03	-80	NA	-10.0	47	-100.0	2090	6.08	1510	
	5	1925	0.34	-80	NA	21.0	247	-100.0	8700	5.55	1450	
	6	2125	1.20	-80	NA	45.0	976	-100.0	18460	5.50	1440	
	7	3125	2.46	-80	NA	78.0	2460	-100.0	31290	5.22	1410	
	8	4125	3.98	-80	NA	109.0	4440	-100.0	39160	5.14	1390	
	9	6525	6.25	183	NA	137.0	7550	-100.0	55690	5.08	1380	
	10	8125	7.23	283	NA	150.0	8870	-100.0	58810	4.99	1370	
	11	10500	7.38	376	NA	148.0	9240	-100.0	63270	4.90	1360	
	12	12900	7.84	503	NA	154.0	10080	-100.0	63310	4.81	1360	
	13	14700	8.58	611	NA	170.0	10910	-100.0	62150	4.75	1360	
	14	15900	8.30	613	NA	159.0	10440	-100.0	60950	4.71	1360	
	15	17750	8.71	728	NA	163.0	11060	-100.0	60900	4.67	1360	
	16	27900	8.57	1115	NA	275.0	11470	-100.0	63320	4.42	1370	Last sample
Teague CH	0	0	11.10	2580	497.0	118.0	8270	429.0	51630	3.90	1880	Head Sol. CT84-10 10ml/min
	1	650	0.30	260		5.0	20	1.0	100	5.81	1880	
	2	950	0.38	320		5.0	20	1.0	50	5.87	1920	
	3	1800	0.13	50		5.0	20	1.0	80	5.57	1890	
	4	4850	0.12	75		20.0	170	1.0	3660	5.13	1845	
	5	6350	0.60	105	38.6	23.3	262	1.0	8060	4.98	1810	
	6	7450	1.14	180		40.0	710	1.0	13100	4.80	1810	
	7	8950	2.09	290		40.0	840	1.0	14700	4.70	1750	
	8	11050	3.95	520		70.0	1410	1.0	20200	4.52	1735	
	9	12900	5.14	610		80.0	1910	1.0	24400	4.50	1700	

Table 4. Zeolite test column leachate results selected concentration data.

Zeolite Type	Sample No.	Volume (mL)	Iron (mg/L)	Aluminum (ug/L)	Arsenic (ug/L)	Cadmium (ug/L)	Copper (ug/L)	Lead (ug/L)	Zinc (ug/L)	pH	SC (umhos/cm)	Comments
Teague XY	10	20200	0.02	900	<1	112.0	4520	2.3	37040	3.65	1690	
	11	23850	0.18	1170		110.0	5020	1.0	37170	4.22	1690	
	12	27850	0.11	1410		110.0	5550	1.0	38140	4.08	1690	
	13	38850	0.07	1860	18.0	115.0	6460	1.0	41570	3.93	1760	
	14	0	1.10	2490	2.7	118.0	8040	396.0	52400	3.53	1750	Head Solution
	0	0	10.10	2210	649.0	113.0	6820	451.0	48720	3.95	1420	Head Sol. CT84-10
	1	400	0.03	86		9.0	43	1.0	150	6.34	3220	10ml/min
	2	750	0.02	50		9.0	54	1.0	441	6.29	2970	
	3	1050	0.02	50		9.0	73	1.0	1097	6.20	2725	
	4	2100	0.03	50	22.8	13.8	200	1.0	4490	6.20	2500	
	5	2650	0.12	80		24.0	493	1.0	8110	5.62	1910	
Z-466	6	3700	0.32	90		36.0	802	1.0	11370	5.58	1760	
	7	4500	0.62	145	27.2	44.2	1391	3.4	17300	5.47	1775	
	8	6150	2.10	300		66.0	2760	1.0	28040	5.34	1685	
	9	7400	2.95	372		73.0	3325	1.0	31560	5.27	1660	
	10	9550	3.91	494	37.0	82.7	4150	33.3	36660	5.54	1600	
	11	0	8.10	2180		107.0	6870	441.0	49210	4.00	1630	
	0	0	8.11	1963	33.1	91.1	8175	588.9	39700	3.85	1300	Head Sol. CT84-10
	1	200	0.03	86	13.6	-2.0	9.4	41.8	17.8	5.93	1820	10ml/min
	2	400	0.02	118	12.6	-2.0	8.3	25.8	9.9	5.89	1810	
	3	600	0.02	128	12.7	-2.0	7.8	10.2	8.7	5.86	1800	
	4	800	0.02	124	12.4	-2.0	8.1	3.1	8.8	5.81	1790	
	5	1000	0.03	76	12.3	-2.0	6.1	-2.0	5.7	5.78	1780	
	6	1400	0.05	81	12.5	-2.0	7.5	-2.0	10.3	5.70	1760	
	7	1800	0.02	53	11.9	-2.0	5.8	-2.0	4.9	5.69	1750	
	8	2200	0.02	53	11.9	-2.0	5.5	-2.0	3.9	5.63	1740	
	9	3000	0.02	33	11.7	-2.0	5.3	-2.0	3	5.60	1720	
	10	3400	0.01	32	11.7	-2.0	5.4	-2.0	3.6	5.56	1710	
	11	13250	0.01	141	9.1	2.6	28.1	-2.0	343	4.95	1630	
	12	15250	0.01	233	8.9	5.3	54	-2.0	753.1	4.83	1590	
	13	17300	0.01	313	9.0	8.9	95.5	-2.0	1385	4.76	1570	Last sample

(-) A minus sign denotes that the analyte concentration was below the instrument detection limit.

Table 5. Zeolite test column leachate results percent concentration removed.

Zeolite Type	Sample No.	Volume (ml)	Iron (%)	Aluminum (%)	Arsenic (%)	Cadmium (%)	Copper (%)	Lead (%)	Zinc (%)	Comments
Z-93	0	0	0.0	0.0	NA	0.0	0.0	0.0	0.0	Head Sol. CT84-10 10ml/min
	1	500	99.3	99.4	NA	99.1	99.7	99.8	94.9	
	2	1220	99.6	99.0	NA	81.1	97.6	99.8	46.3	
	3	2750	96.3	99.0	NA	43.4	86.2	99.8	5.6	
	4	6650	66.9	92.1	NA	-3.8	35.6	99.8	-0.1	
	5	7750	48.1	85.4	NA	-13.2	16.9	99.8	0.2	
	6	9100	38.1	82.3	NA	-13.2	12.4	99.8	0.8	
	7	10600	31.2	76.4	NA	-9.4	4.1	99.8	1.5	
	8	12750	23.1	63.8	NA	-13.2	1.8	99.8	2.6	
	9	18650	99.4	-6.3	NA	-3.8	0.0	99.8	3.1	
	10	21500	99.7	0.4	NA	-2.8	3.9	99.8	-1.1	
	11	0	92.5	0.4	NA	-13.2	2.4	4.8	0.4	Head Solution
Z-127	0	0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	Head Sol. CT84-10 10ml/min
	1	275	99.6	97.8		95.5	98.9	99.8	99.2	
	2	525	100.0	97.8		95.5	99.3	99.8	97.8	
	3	740	100.0	97.8		95.5	98.9	99.8	94.6	
	4	1050	99.6	97.8		95.5	98.5	99.8	87.9	
	5	2100	97.9	97.8	98.6	73.0	95.2	99.8	64.5	
	6	2700	95.0	97.8		52.5	89.9	99.8	45.5	
	7	3700	92.1	97.8		40.8	83.6	99.8	30.9	
	8	4500	91.6	97.8	99.6	33.0	78.9	99.8	22.7	
	9	6050	85.0	96.7		19.3	68.6	99.8	11.5	
	10	7150	82.6	96.0		13.0	62.6	99.8	8.2	
	11	8500	77.4	97.8		1.3	52.9	99.8	6.5	
	12	9550	78.7	99.3	99.8	9.4	50.4	99.8	5.6	
	13	13050	81.6	97.8		1.3	46.3	99.8	3.4	
	14	15950	85.7	97.8		10.3	39.2	99.8	2.6	
	15	23800	99.8	93.9		4.9	19.5	99.8	2.1	
	16	0	64.6	-0.9		-2.2	1.8	4.3	-0.6	Head Solution
Z-134	0	0	0.0	0.0	NA	0.0	0.0	0.0	0.0	Head Sol. CT84-10 10ml/min
	1	325	98.6	103.7	NA	106.1	99.6	114.9	99.4	
	2	525	99.2	103.7	NA	106.1	99.8	114.9	99.5	
	3	725	99.9	103.7	NA	106.1	99.8	114.9	98.5	
	4	825	99.7	103.7	NA	106.1	99.6	114.9	96.6	
	5	1925	96.4	103.7	NA	87.1	97.8	114.9	85.8	
	6	2125	87.2	103.7	NA	72.4	91.3	114.9	69.9	
	7	3125	73.7	103.7	NA	52.1	78.1	114.9	49.0	
	8	4125	57.4	103.7	NA	33.1	60.5	114.9	36.1	
	9	6525	33.1	91.5	NA	16.0	32.8	114.9	9.2	
	10	8125	22.6	86.9	NA	8.0	21.0	114.9	4.1	
	11	10500	21.0	82.6	NA	9.2	17.7	114.9	-3.2	
	12	12900	16.1	76.7	NA	5.5	10.2	114.9	-3.2	
	13	14700	8.1	71.7	NA	-4.3	2.8	114.9	-1.3	
	14	15900	11.1	71.6	NA	2.5	7.0	114.9	0.6	
	15	17750	6.7	66.3	NA	0.0	1.5	114.9	0.7	
	16	27900	8.2	48.4	NA	-68.7	-2.1	114.9	-3.2	Last sample
Teague CH	1	0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	Head Sol. CT84-10 10ml/min
	2	650	97.3	89.9		95.8	99.8	99.8	99.8	
	3	950	96.6	87.6		95.8	99.8	99.8	99.9	
	4	1800	98.8	98.1		95.8	99.8	99.8	99.8	
	5	4850	98.9	97.1		83.1	97.9	99.8	92.9	
	6	6350	94.6	95.9	92.2	80.3	96.8	99.8	84.4	
	7	7450	89.7	93.0		66.1	91.4	99.8	74.6	
	8	8950	81.2	88.8		66.1	89.8	99.8	71.5	
	9	11050	64.4	79.8		40.7	83.0	99.8	60.9	
	10	12900	53.7	76.4		32.2	76.9	99.8	52.7	
	11	20200	99.8	65.1	100.0	5.1	45.3	99.5	28.3	
	12	23850	98.4	54.7		6.8	39.3	99.8	28.0	
	13	27850	99.1	45.3		6.8	32.9	99.8	26.1	
	14	38850	99.4	27.9	96.4	2.5	21.9	99.8	19.5	
	15	0	90.1	3.5	99.5	0.0	2.8	7.7	-1.5	Head Solution

Table 5. Zeolite test column leachate results percent concentration removed.

Zeolite Type	Sample No.	Volume (ml)	Iron (%)	Aluminum (%)	Arsenic (%)	Cadmium (%)	Copper (%)	Lead (%)	Zinc (%)	Comments
Z-93 Teague XY	0	0	0.0	0.0	NA	0.0	0.0	0.0	0.0	Head Sol. CT84-10
	1	0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	Head Sol. CT84-10
	2	400	99.7	96.1		92.0	99.4	99.8	99.7	10ml/min
	3	750	99.9	97.7		92.0	99.2	99.8	99.1	
	4	1050	99.9	97.7		92.0	98.9	99.8	97.7	
	5	2100	99.7	97.7	96.5	87.8	97.1	99.8	90.8	
	6	2650	98.8	96.4		78.8	92.8	99.8	83.4	
	7	3700	96.8	95.9		68.1	88.2	99.8	76.7	
	8	4500	93.9	93.4	95.8	60.9	79.6	99.2	64.5	
	9	6150	79.2	86.4		41.6	59.5	99.8	42.4	
	10	7400	70.8	83.2		35.4	51.2	99.8	35.2	
	11	9550	61.3	77.6	94.3	26.8	39.1	92.6	24.8	
	12	0	19.8	1.4		5.3	-0.7	2.2	-1.0	
Z-466	0	0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	Head Sol. CT84-10
	1	200	99.7	95.6	58.9	102.2	99.9	92.9	100.0	10ml/min
	2	400	99.8	94.0	61.9	102.2	99.9	95.6	100.0	
	3	600	99.8	93.5	61.6	102.2	99.9	98.3	100.0	
	4	800	99.8	93.7	62.5	102.2	99.9	99.5	100.0	
	5	1000	99.7	96.1	62.8	102.2	99.9	100.3	100.0	
	6	1400	99.4	95.9	62.2	102.2	99.9	100.3	100.0	
	7	1800	99.8	97.3	64.0	102.2	99.9	100.3	100.0	
	8	2200	99.8	97.3	64.0	102.2	99.9	100.3	100.0	
	9	3000	99.8	98.3	64.7	102.2	99.9	100.3	100.0	
	10	3400	99.9	98.4	64.7	102.2	99.9	100.3	100.0	
	11	13250	99.9	92.8	72.5	97.1	99.7	100.3	99.1	
	12	15250	99.9	88.1	73.1	94.2	99.3	100.3	98.1	
	13	17300	99.9	84.1	72.8	90.2	98.8	100.3	96.5	Last sample

concentrations in relation to the volume of water passed through the test column for each of the six zeolites tested. A discussion of each of the zeolites metal attenuation is presented below.

Z-93

Zeolite Z-93 is from a zeolite occurrence located southwest of Butte named McCleery Gulch. Berg and Lonn (1993) referred to the samples from this site as being the closest to pure clinoptilolite of any they found during their investigation. However, this zeolite was the poorest of all the samples tested for metal removal. As seen in table 1, it also had one of the lowest CEC values of the tested samples. Breakthrough occurred between the 1st and 2nd (500 and 1,200 mL) sample volumes for zinc, and between the 2nd and 4th sample volume for all but one of the other metals (figures 7a–7d). The percent removal of lead (table 6) is comparable to that of the other zeolites tested.

Z-127

Zeolite Z-127 is one of several samples from the zeolite deposit described as the Grasshopper Creek Deposit by Berg and Lonn (1993) and R. C. Pearson (1989). Clinoptilolite was identified as the predominant zeolite in a majority of samples collected at this site (15 out of 19). This was the largest zeolite occurrence examined during the MBMG's field work. Its size is large enough to be considered a deposit, and the property owners are planning future development of the site. The CEC of this sample was the lowest of those tested but comparable to that of sample Z-93 (table 1). Zinc was the 1st analyte to exhibit breakthrough, occurring between the 4th and 5th (1,050 and 2,100 mL) sample volume (figures 8a–8d). The volume of water treated was from double to four times that of Z-93. This sample showed the same excellent removal of lead as Z-93 while also having a similar high removal level for aluminum (table 6).

Z-134

Zeolite Z-134 is also a sample of material from the Grasshopper Creek deposit. However, the CEC value of 1.17 meq/g is considerably higher than that of Z-127. A reduction in metal removal by this zeolite followed previously described trends, with zinc breakthrough occurring 1st between the 5th and 6th (1,925 and 2,125 mL) sample volumes (figures 9a–9d). The volume of water treated by this zeolite varied from no increase to twice that observed for Z-127. Z-134 had excellent lead removal, along with a high rate of aluminum removal (table 6).

**Montana Bureau of Mines and Geology
Test Column Results**

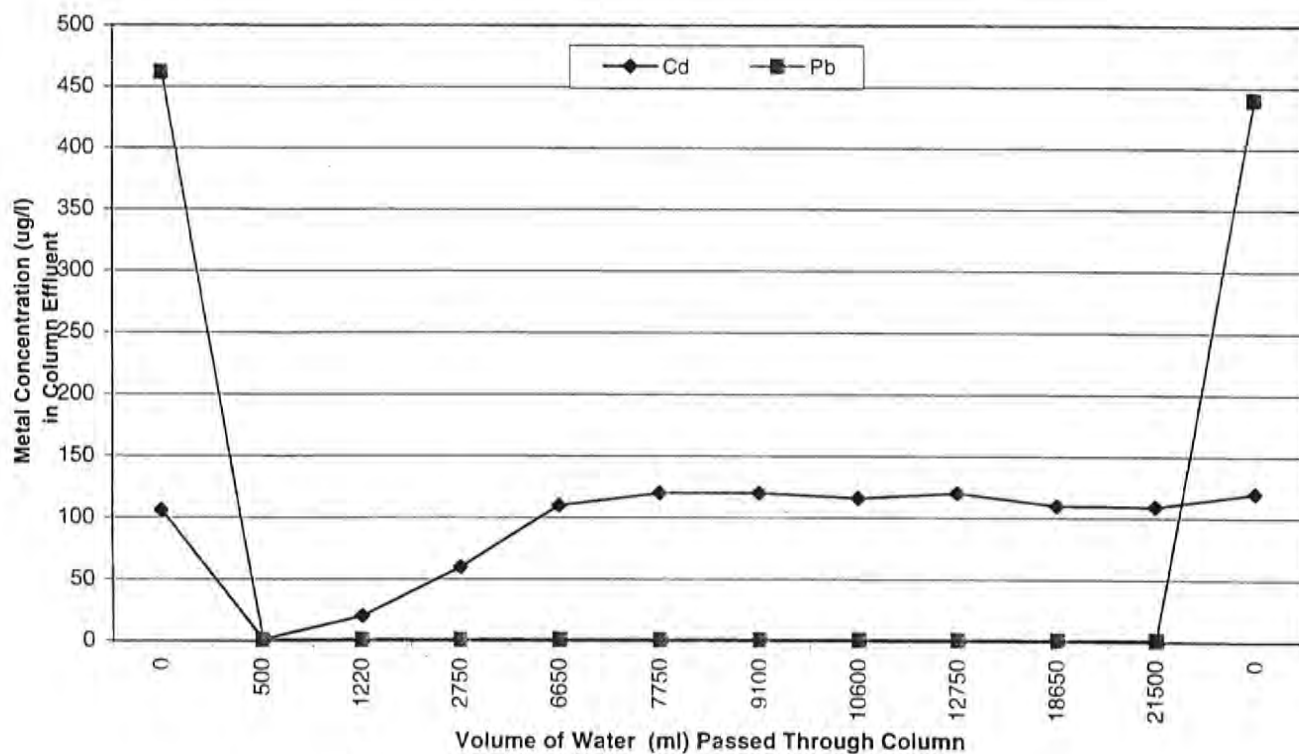
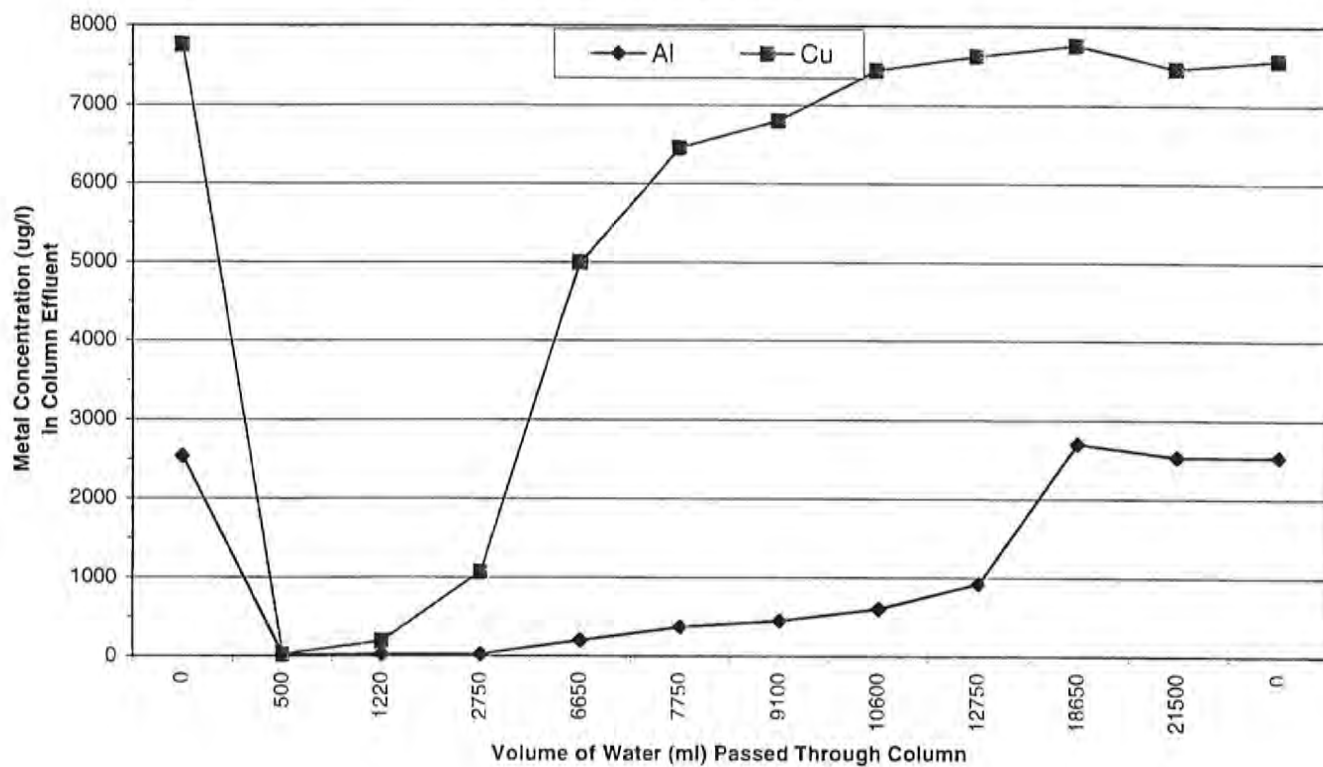


Figure 7. Zeolite Z-93, column test results (7a) aluminum and copper and (7b) cadmium and lead.

Montana Bureau of Mines and Geology
Test Column Results

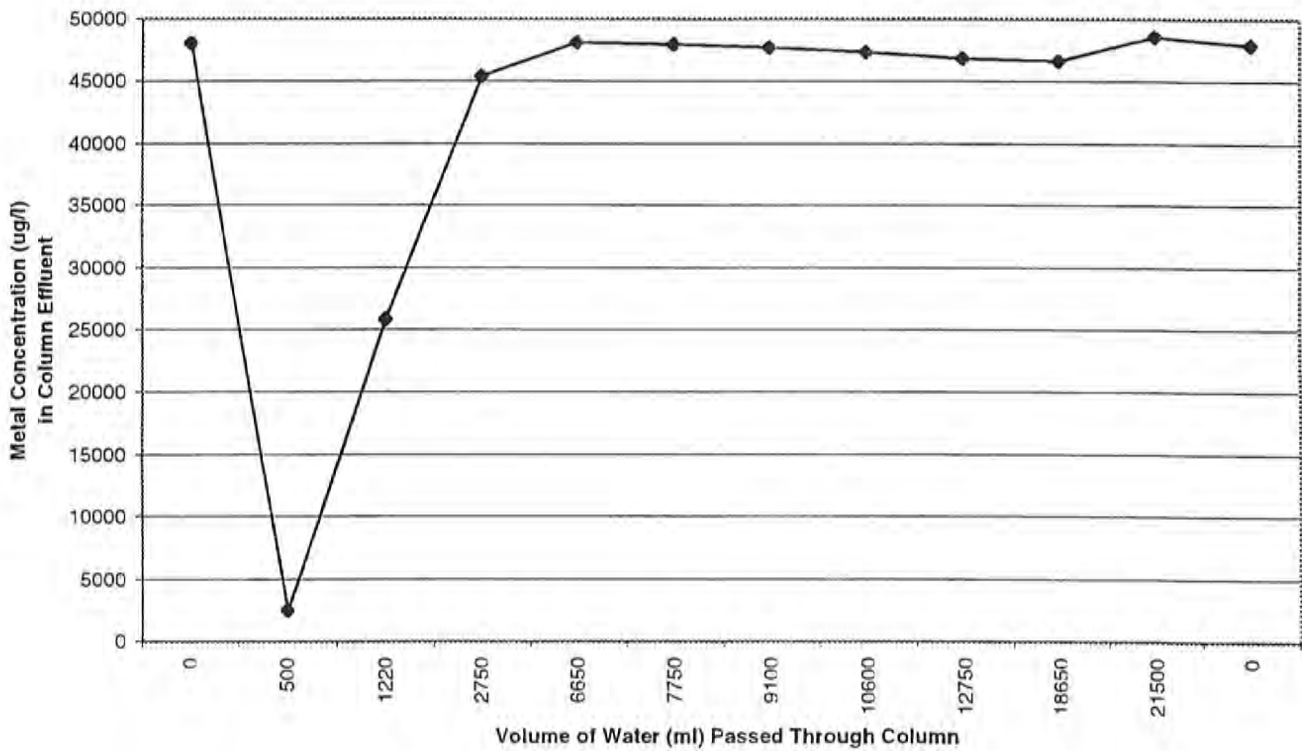
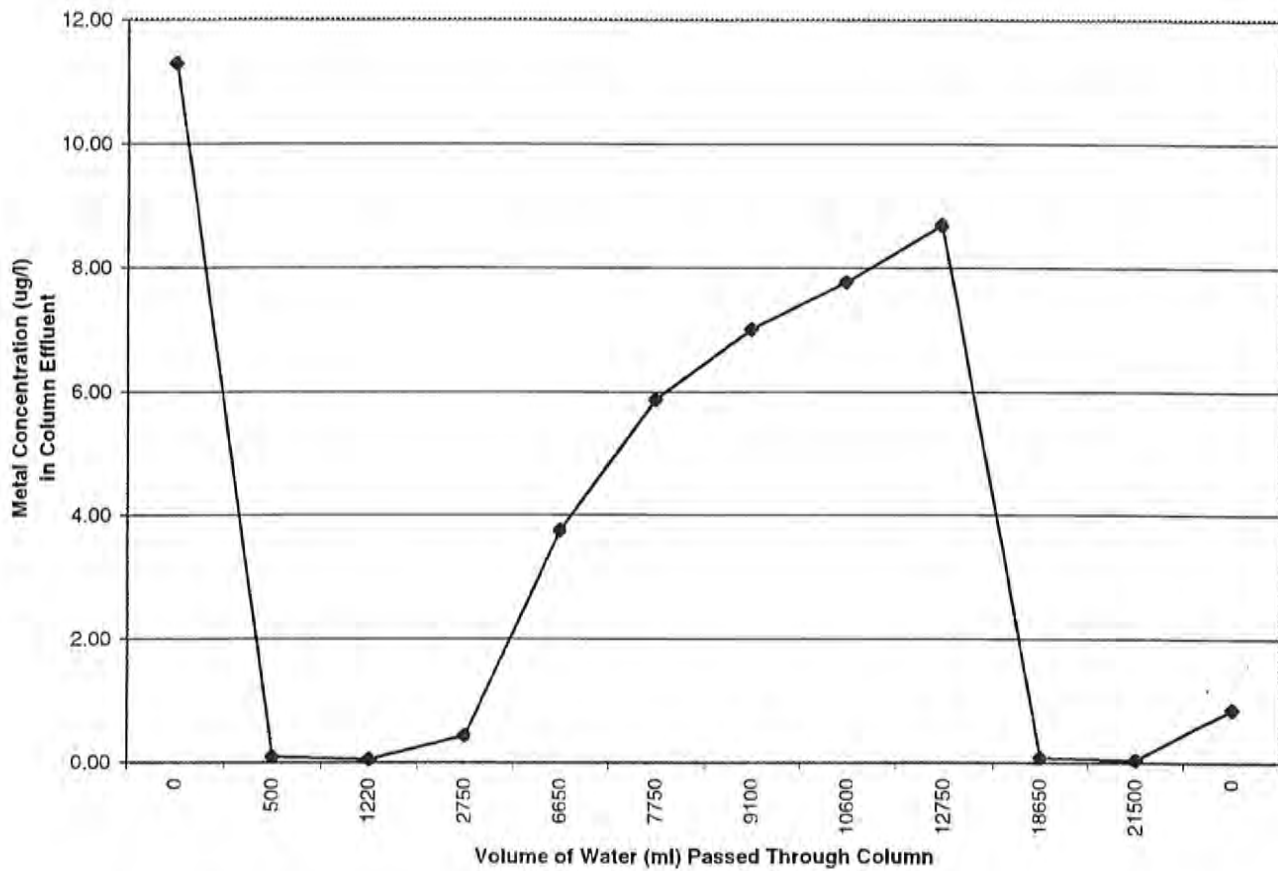


Figure 7. Zeolite Z-93, column test results (7c) iron and (7d) zinc.

Table 6. Zeolite test column leachate results concentration in milliequivalents per liter (meq/L).

Volume (mL)	Ca	Mg	Sum (Ca+Mg)	Na	K	Sum (NA+K)	Al	As	Cd	Cu	Fe	Mn	Ph	Zn	SiO ₂	Sum (T.M.)
Zeolite Z-03																
0	7.53	2.50	10.04	4.17	0.10	4.27	0.282	0.000	0.002	0.244	0.608	0.441	0.004	1.460	0.000	1.46
500	7.78	2.02	9.80	6.39	0.56	6.95	0.002	0.000	0.000	0.001	0.004	0.045	0.000	0.074	0.140	0.21
1220	1.12	2.90	4.02	5.35	0.46	5.80	0.003	0.000	0.000	0.006	0.002	0.372	0.000	0.783	-0.007	0.78
2750	9.28	2.58	11.87	5.13	0.47	5.60	0.003	0.000	0.001	0.034	0.023	0.455	0.000	1.378	0.022	1.40
6650	8.08	2.49	10.57	4.74	0.46	5.19	0.022	0.000	0.002	0.157	0.201	0.448	0.000	1.460	0.053	1.51
7750	8.18	2.59	10.78	4.70	0.45	5.14	0.041	0.000	0.002	0.203	0.316	0.452	0.000	1.457	0.015	1.47
9100	7.98	2.49	10.48	4.52	0.43	4.95	0.050	0.000	0.002	0.214	0.376	0.434	0.000	1.448	0.038	1.49
10600	7.58	2.54	10.13	4.43	0.45	4.88	0.067	0.000	0.002	0.234	0.418	0.434	0.000	1.436	-0.013	1.42
12750	8.08	2.64	10.73	4.61	0.47	5.08	0.102	0.000	0.002	0.240	0.467	0.455	0.000	1.420	-0.025	1.40
18650	8.18	2.59	10.78	4.48	0.45	4.92	0.300	0.000	0.002	0.244	0.404	0.444	0.000	1.414	-0.022	1.39
21500	7.63	2.43	10.06	4.18	0.43	4.61	0.281	0.000	0.002	0.235	0.402	0.423	0.000	1.475	0.012	1.49
Head	7.83	2.58	10.42	4.29	0.11	4.40	0.281	0.000	0.002	0.238	0.446	0.437	0.004	1.454	-0.010	1.44
Zeolite Z-127																
0	7.58	2.47	10.05	4.03	0.11	4.13	0.249	0.024	0.002	0.224	0.602	0.426	0.004	1.508	0.948	2.46
276	11.13	1.13	12.26	5.09	0.44	5.53	0.011	0.000	0.000	0.003	0.003	0.005	0.001	0.012	0.948	0.96
525	12.72	1.41	14.13	5.26	0.47	5.73	0.011	0.000	0.000	0.002	0.001	0.030	0.001	0.034	0.948	0.98
740	13.17	1.56	14.73	5.13	0.47	5.60	0.011	0.000	0.000	0.003	0.001	0.060	0.001	0.082	0.948	1.03
1050	12.23	1.65	13.87	4.83	0.43	5.26	0.011	0.000	0.000	0.003	0.002	0.109	0.001	0.183	0.948	1.13
2100	11.78	1.98	13.76	4.48	0.42	4.90	0.011	0.000	0.001	0.011	0.013	0.231	0.000	0.536	0.948	1.48
2700	11.23	2.23	13.46	4.43	0.41	4.85	0.011	0.000	0.001	0.023	0.030	0.321	0.001	0.822	0.948	1.77
3700	10.78	2.39	13.17	4.35	0.41	4.76	0.011	0.000	0.001	0.037	0.048	0.366	0.001	1.043	0.948	1.99
4500	10.13	2.39	12.52	4.22	0.40	4.62	0.003	0.000	0.001	0.047	0.051	0.393	0.000	1.166	0.948	2.11
6050	10.23	2.49	12.72	4.22	0.40	4.62	0.011	0.000	0.002	0.070	0.090	0.430	0.001	1.334	0.948	2.28
7150	10.08	2.55	12.63	4.13	0.39	4.52	0.010	0.000	0.002	0.084	0.105	0.441	0.001	1.385	0.948	2.33
8500	10.18	2.64	12.82	4.27	0.40	4.67	0.011	0.000	0.002	0.106	0.136	0.466	0.001	1.410	0.948	2.36
9550	9.38	2.58	11.97	3.91	0.40	4.31	0.003	0.000	0.002	0.111	0.128	0.463	0.000	1.424	0.948	2.37
13050	9.78	2.63	12.41	4.28	0.42	4.71	0.011	0.000	0.002	0.120	0.111	0.463	0.001	1.457	0.948	2.41
15950	9.18	2.50	11.68	4.07	0.40	4.47	0.011	0.000	0.002	0.136	0.086	0.426	0.001	1.470	0.948	2.42
23800	9.38	2.55	11.93	4.04	0.41	4.45	0.015	0.000	0.002	0.180	0.001	0.441	0.001	1.477	0.948	2.43
Head	7.78	2.53	10.32	4.09	0.11	4.20	0.251	0.000	0.002	0.220	0.213	0.432	0.004	1.517	0.948	2.47

Table 6. Zeolite test column leachate results concentration in milliequivalents per liter (meq/L).

Volume (mL)	Ca	Mg	Sum (Ca+Mg)	Na	K	Sum (NA+K)	Al	As	Cd	Cu	Fe	Mn	Pb	Zn	SiO ₂	Sum (T.M.)
Zeolite Z-134																
0	6.79	2.21	8.99	4.11	0.12	4.23	0.240	0.000	0.003	0.354	0.502	0.395	0.007	1.861	0.948	2.81
325	10.93	1.98	12.90	5.57	0.32	5.88	0.009	0.000	0.000	0.002	0.007	0.002	0.001	0.011	0.948	0.96
525	10.68	1.98	12.66	5.39	0.31	5.70	0.009	0.000	0.000	0.001	0.004	0.009	0.001	0.009	0.948	0.96
725	10.93	1.99	12.92	5.22	0.31	5.53	0.009	0.000	0.000	0.001	0.001	0.020	0.001	0.027	0.948	0.98
825	10.68	1.98	12.66	5.13	0.31	5.44	0.009	0.000	0.000	0.001	0.001	0.036	0.001	0.063	0.948	1.01
1925	10.28	2.11	12.39	5.04	0.30	5.35	0.009	0.000	0.000	0.008	0.018	0.104	0.001	0.264	0.948	1.21
2125	9.33	2.12	11.45	4.78	0.29	5.07	0.009	0.000	0.001	0.031	0.065	0.179	0.001	0.560	0.948	1.51
3125	8.58	2.23	10.81	4.61	0.28	4.89	0.009	0.000	0.001	0.077	0.132	0.258	0.001	0.950	0.948	1.90
4125	8.23	2.35	10.58	4.61	0.28	4.89	0.009	0.000	0.002	0.140	0.214	0.325	0.001	1.188	0.948	2.14
6525	7.73	2.33	10.06	4.43	0.28	4.71	0.020	0.000	0.002	0.238	0.336	0.382	0.001	1.690	0.948	2.64
8125	7.53	2.33	9.86	4.35	0.27	4.62	0.031	0.000	0.003	0.279	0.389	0.391	0.001	1.785	0.948	2.73
10500	6.94	2.18	9.12	4.10	0.25	4.36	0.042	0.000	0.003	0.291	0.397	0.375	0.001	1.920	0.948	2.87
12900	6.94	2.22	9.16	4.14	0.26	4.40	0.056	0.000	0.003	0.317	0.422	0.374	0.001	1.921	0.948	2.87
14700	7.49	2.37	9.86	4.39	0.27	4.66	0.068	0.000	0.003	0.344	0.461	0.415	0.001	1.886	0.948	2.83
15900	7.04	2.22	9.26	4.21	0.27	4.47	0.068	0.000	0.003	0.329	0.446	0.387	0.001	1.850	0.948	2.80
17750	7.29	2.30	9.59	4.35	0.28	4.63	0.081	0.000	0.003	0.348	0.468	0.408	0.001	1.848	0.948	2.80
27900	7.29	2.37	9.66	4.39	0.28	4.67	0.124	0.000	0.005	0.361	0.461	0.413	0.001	1.922	0.948	2.87
Zeolite Z-466																
0	6.49	2.19	8.68	4.00	0.12	4.12	0.218	0.001	0.002	0.257	0.436	0.397	0.006	1.205	0.948	2.15
200	0.61	0.01	0.62	14.77	0.32	15.09	0.010	0.001	0.000	0.000	0.001	0.000	0.000	0.001	0.948	0.95
400	0.59	0.01	0.60	14.30	0.30	14.61	0.013	0.001	0.000	0.000	0.001	0.000	0.000	0.000	0.948	0.95
600	0.60	0.01	0.61	14.60	0.31	14.91	0.014	0.001	0.000	0.000	0.001	0.000	0.000	0.000	0.948	0.95
800	0.61	0.01	0.62	14.41	0.32	14.73	0.014	0.000	0.000	0.000	0.001	0.000	0.000	0.000	0.948	0.95
1000	0.63	0.01	0.64	14.94	0.32	15.27	0.008	0.000	0.000	0.000	0.001	0.000	0.000	0.000	0.948	0.95
1400	0.66	0.01	0.67	15.25	0.32	15.58	0.009	0.001	0.000	0.000	0.002	0.000	0.000	0.000	0.948	0.95
1800	0.54	0.01	0.55	13.29	0.28	13.57	0.006	0.000	0.000	0.000	0.001	0.000	0.000	0.000	0.948	0.95
2200	0.55	0.01	0.56	13.59	0.28	13.88	0.006	0.000	0.000	0.000	0.001	0.000	0.000	0.000	0.948	0.95
3000	0.55	0.01	0.56	13.59	0.28	13.87	0.004	0.000	0.000	0.000	0.001	0.000	0.000	0.000	0.948	0.95
3400	0.53	0.01	0.54	13.00	0.27	13.27	0.004	0.000	0.000	0.000	0.001	0.000	0.000	0.000	0.948	0.95
13250	0.89	0.46	1.35	12.27	0.29	12.56	0.016	0.000	0.000	0.001	0.000	0.015	0.000	0.010	0.948	0.96
15250	1.08	0.83	1.91	11.37	0.29	11.67	0.026	0.000	0.000	0.002	0.001	0.029	0.000	0.023	0.948	0.97
17300	1.50	1.35	2.85	11.40	0.34	11.74	0.035	0.000	0.000	0.003	0.000	0.051	0.000	0.042	0.948	0.99

Table 6. Zeolite test column leachate results concentration in milliequivalents per liter (meq/L).

Volume (mL)	Ca	Mg	Sum (Ca+Mg)	Na	K	Sum (NA+K)	Al	As	Cd	Cu	Fe	Mn	Pb	Zn	SiO ₂	Sum (T.M.)
Zeolite CH																
0	7.68	2.53	10.21	4.09	0.10	4.20	0.287	0.020	0.002	0.260	0.597	0.444	0.004	1.567	0.948	2.52
650	2.99	0.26	3.26	12.17	2.29	14.47	0.029	0.000	0.000	0.001	0.016	0.001	0.001	0.003	1.035	1.04
950	3.04	0.27	3.32	11.91	2.32	14.24	0.036	0.000	0.000	0.001	0.020	0.001	0.001	0.002	1.017	1.02
1800	3.29	0.32	3.61	12.04	2.36	14.40	0.011	0.000	0.000	0.001	0.007	0.003	0.001	0.002	1.043	1.05
4850	4.95	1.23	6.18	9.78	2.34	12.12	0.011	0.000	0.000	0.005	0.006	0.086	0.001	0.111	1.163	1.27
6350	5.39	1.80	7.19	8.13	2.12	10.25	0.012	0.000	0.000	0.008	0.032	0.160	0.000	0.245	0.992	1.24
7450	5.64	2.20	7.84	7.04	2.04	9.08	0.020	0.000	0.001	0.022	0.076	0.223	0.001	0.398	0.952	1.35
8950	5.49	2.37	7.86	6.57	2.20	8.77	0.032	0.000	0.001	0.026	0.112	0.256	0.001	0.446	0.970	1.42
11050	5.84	2.63	8.47	5.91	2.35	8.27	0.058	0.000	0.001	0.044	0.212	0.320	0.001	0.613	0.995	1.61
12900	6.09	2.76	8.85	5.48	2.40	7.88	0.068	0.000	0.001	0.060	0.276	0.358	0.001	0.741	1.002	1.74
20200	6.94	2.72	9.66	4.35	2.45	6.79	0.100	0.000	0.002	0.142	0.001	0.419	0.000	1.124	1.045	2.17
23850	6.74	2.49	9.23	4.03	2.37	6.41	0.130	0.000	0.002	0.158	0.010	0.383	0.001	1.128	0.948	2.08
27850	6.79	2.50	9.29	3.95	2.36	6.31	0.157	0.000	0.002	0.175	0.006	0.386	0.001	1.158	0.967	2.12
38850	6.84	2.61	9.45	3.95	2.16	6.11	0.207	0.000	0.002	0.203	0.004	0.404	0.000	1.262	0.988	2.25
Head	7.98	2.59	10.58	4.20	0.10	4.30	0.277	0.001	0.002	0.253	0.059	0.444	0.004	1.590	0.988	2.58
Zeolite XY																
0	7.39	2.44	9.83	3.93	0.11	4.04	0.246	0.026	0.002	0.215	0.543	0.411	0.004	1.479	0.948	2.43
400	7.44	2.50	9.94	19.22	0.29	19.51	0.010	0.000	0.000	0.001	0.002	0.009	0.001	0.005	0.948	0.95
750	7.04	2.35	9.38	17.09	0.27	17.35	0.011	0.000	0.000	0.002	0.001	0.015	0.001	0.013	0.948	0.96
1050	7.04	2.35	9.39	15.39	0.24	15.63	0.011	0.000	0.000	0.002	0.001	0.026	0.001	0.033	0.948	0.98
2100	6.89	2.38	9.26	12.09	0.20	12.28	0.011	0.000	0.000	0.006	0.002	0.073	0.000	0.136	0.948	1.08
2650	7.29	2.55	9.84	11.00	0.18	11.18	0.009	0.000	0.000	0.016	0.006	0.124	0.001	0.246	0.948	1.19
3700	7.39	2.55	9.94	10.22	0.17	10.39	0.010	0.000	0.001	0.025	0.017	0.164	0.001	0.345	0.948	1.29
4500	7.49	2.56	10.04	8.48	0.14	8.62	0.016	0.001	0.001	0.044	0.033	0.217	0.000	0.525	0.948	1.47
6150	7.73	2.72	10.45	7.43	0.14	7.57	0.033	0.000	0.001	0.087	0.113	0.332	0.001	0.851	0.948	1.80
7400	7.93	2.72	10.65	7.30	0.14	7.44	0.041	0.000	0.001	0.105	0.159	0.364	0.001	0.958	0.948	1.91
9550	7.58	2.57	10.15	6.48	0.13	6.60	0.055	0.001	0.001	0.131	0.210	0.379	0.000	1.113	0.948	2.06
Head	7.68	2.55	10.24	4.09	0.12	4.20	0.242	0.000	0.002	0.216	0.435	0.434	0.004	1.493	0.948	2.44

Montana Bureau of Mines and Geology Test Column Results

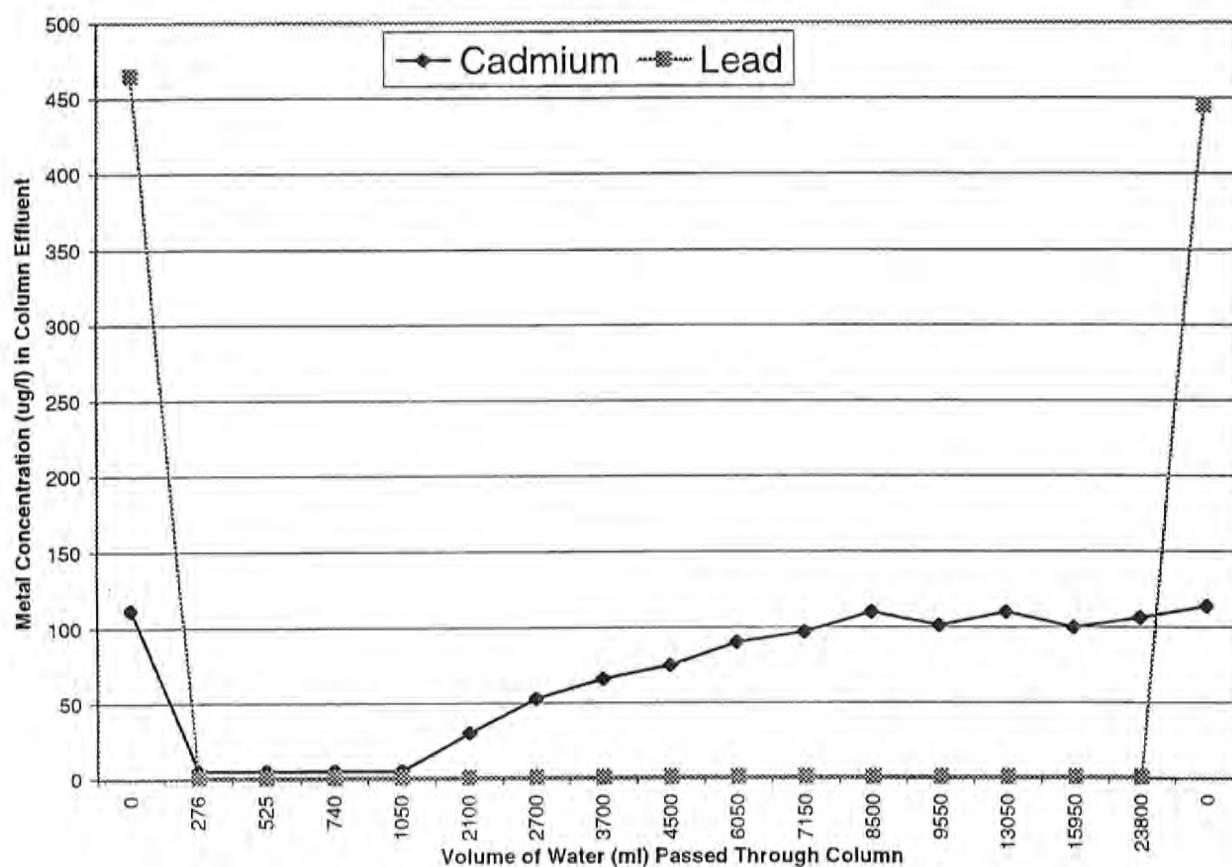
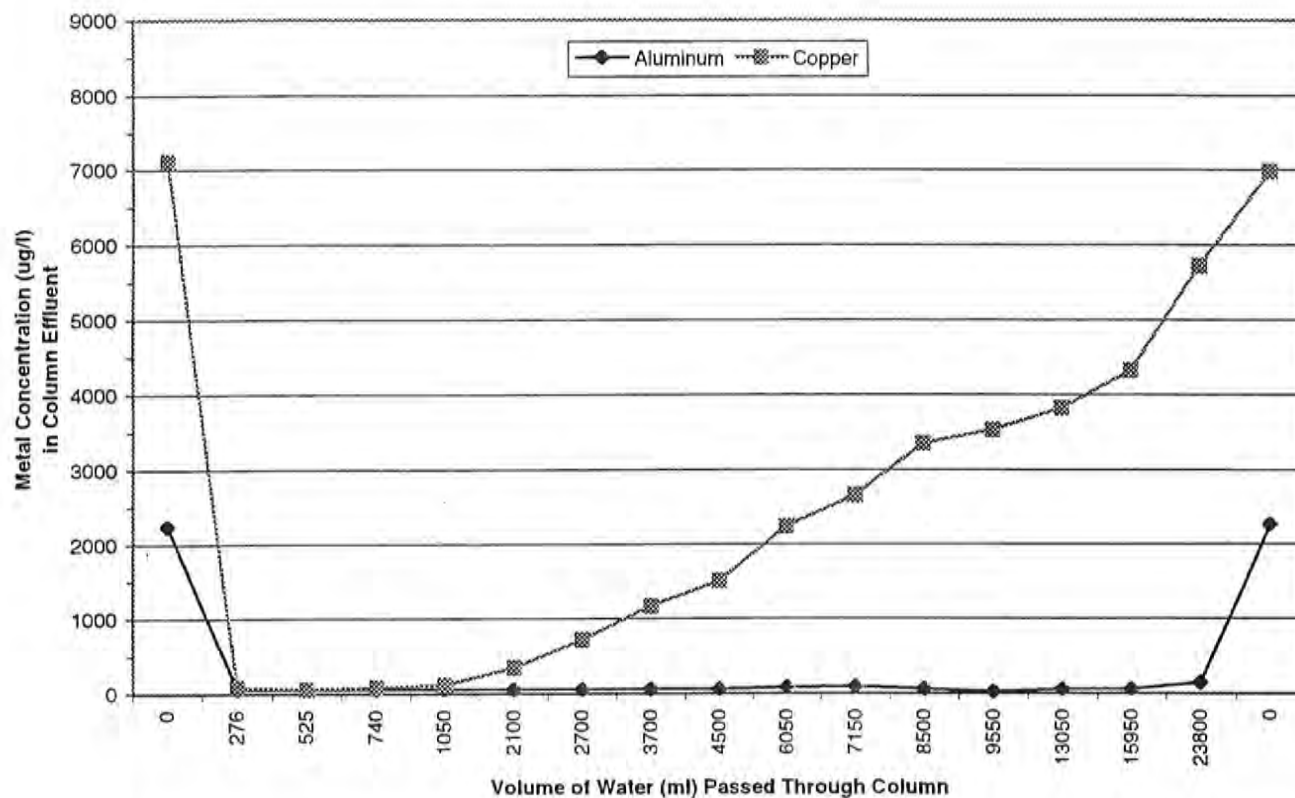


Figure 8. Zeolite Z-127, column test results (8a) aluminum and copper and (8b) cadmium and lead.

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Test Column Results

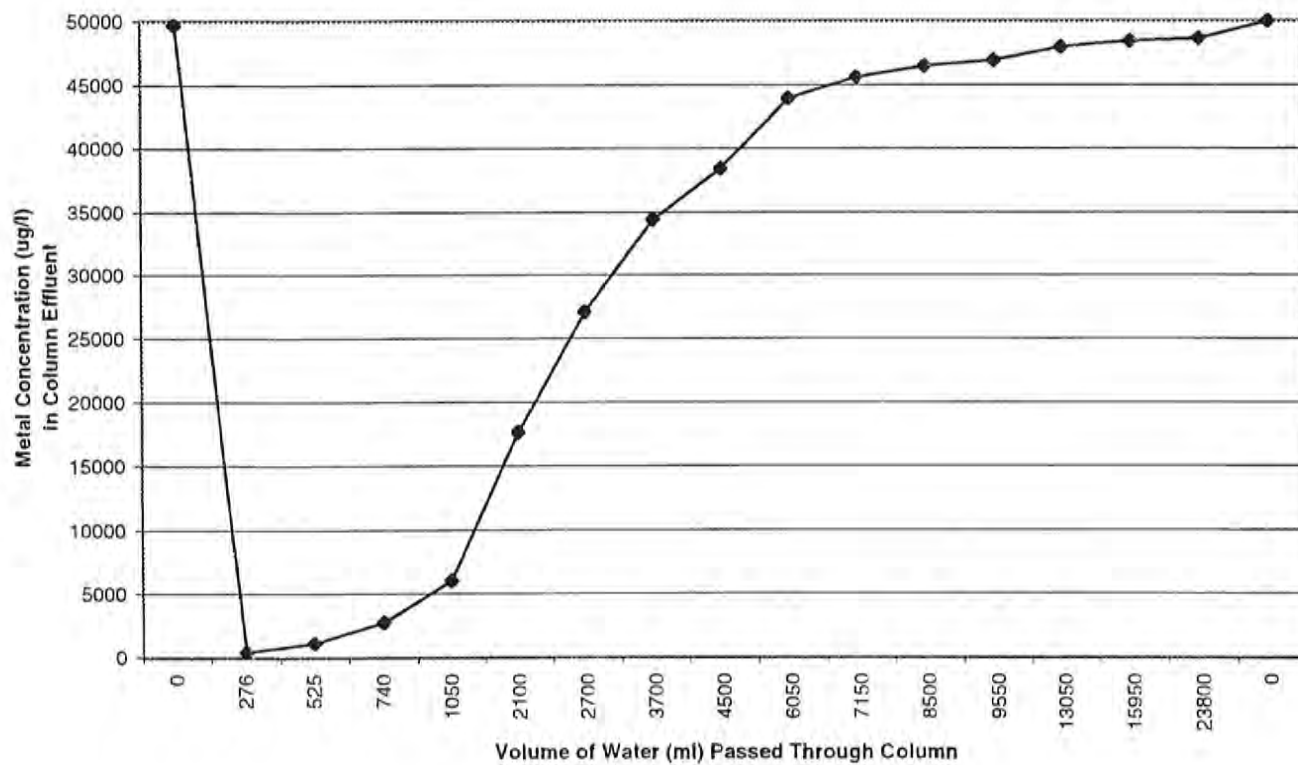
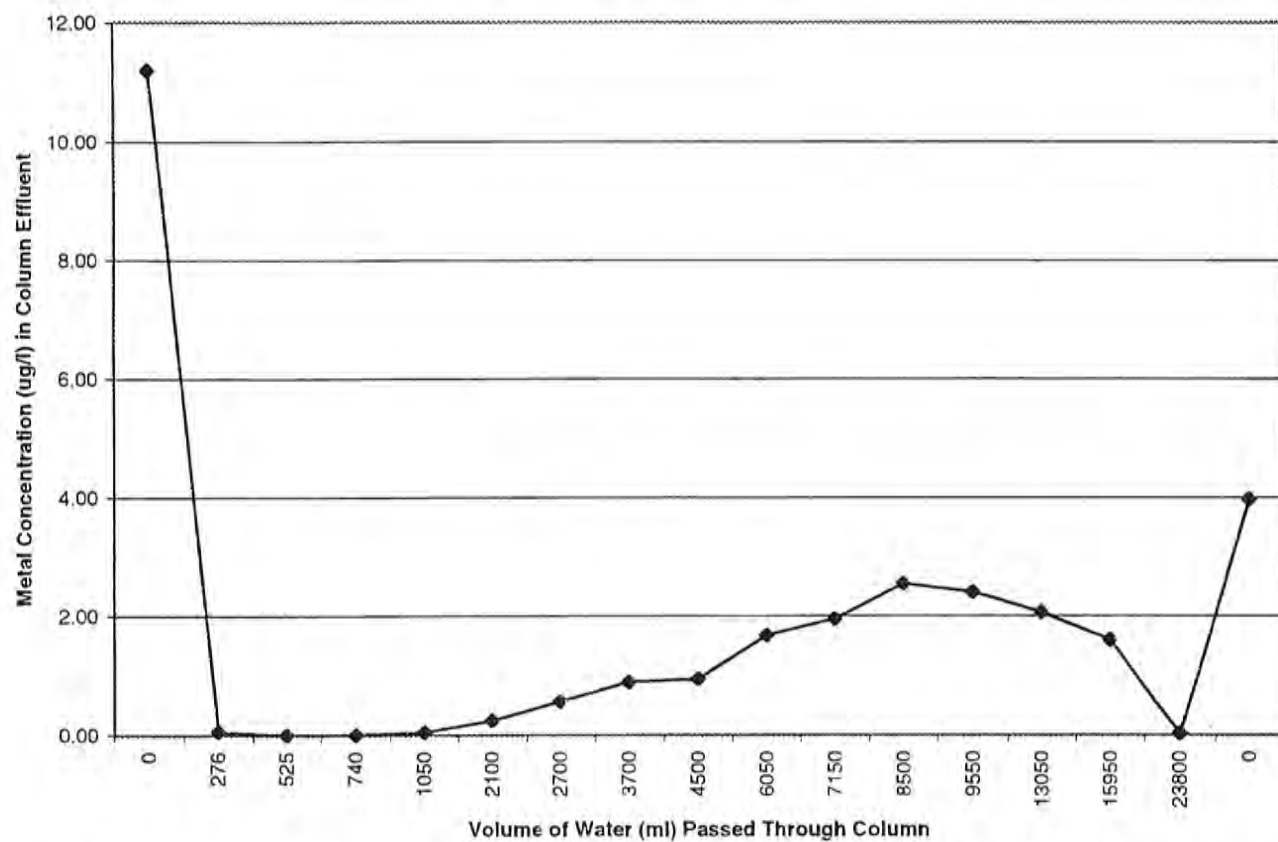


Figure 8. Zeolite Z-127, column test results (8c) iron and (8d) zinc.

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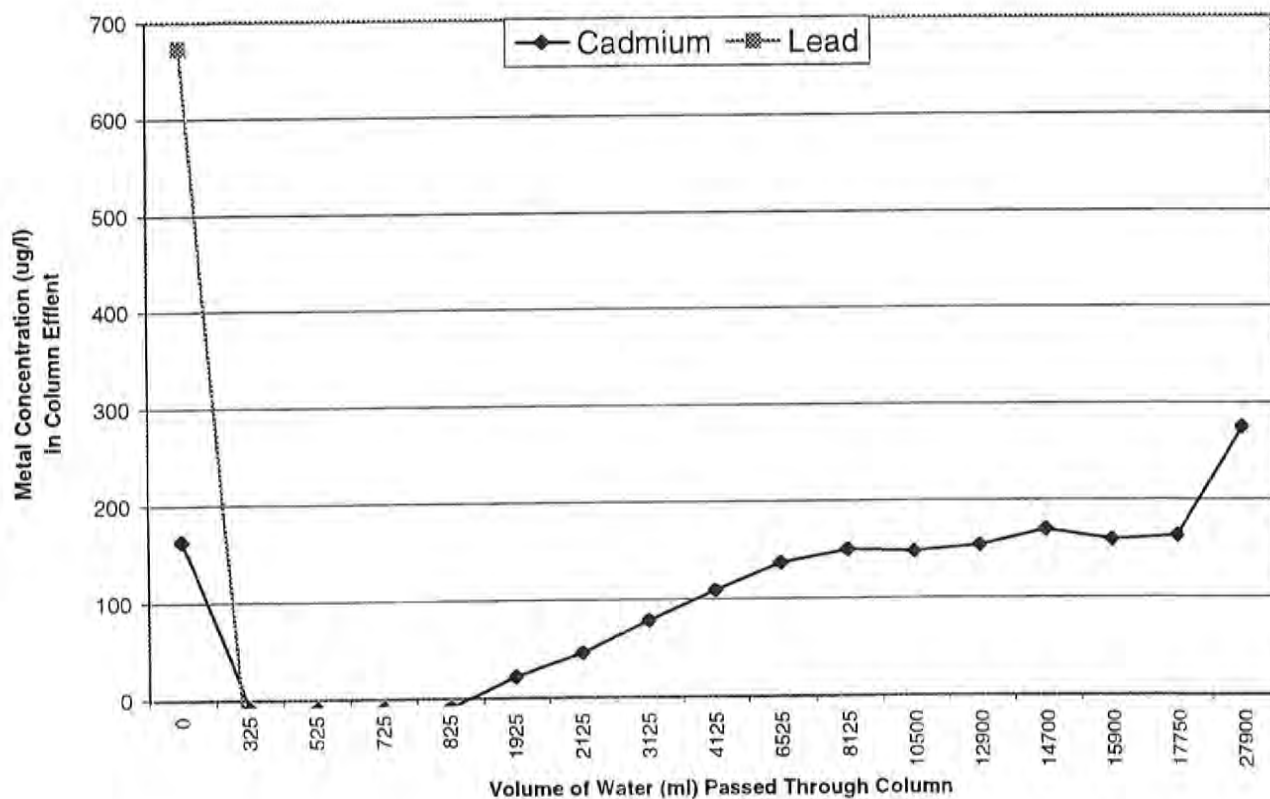
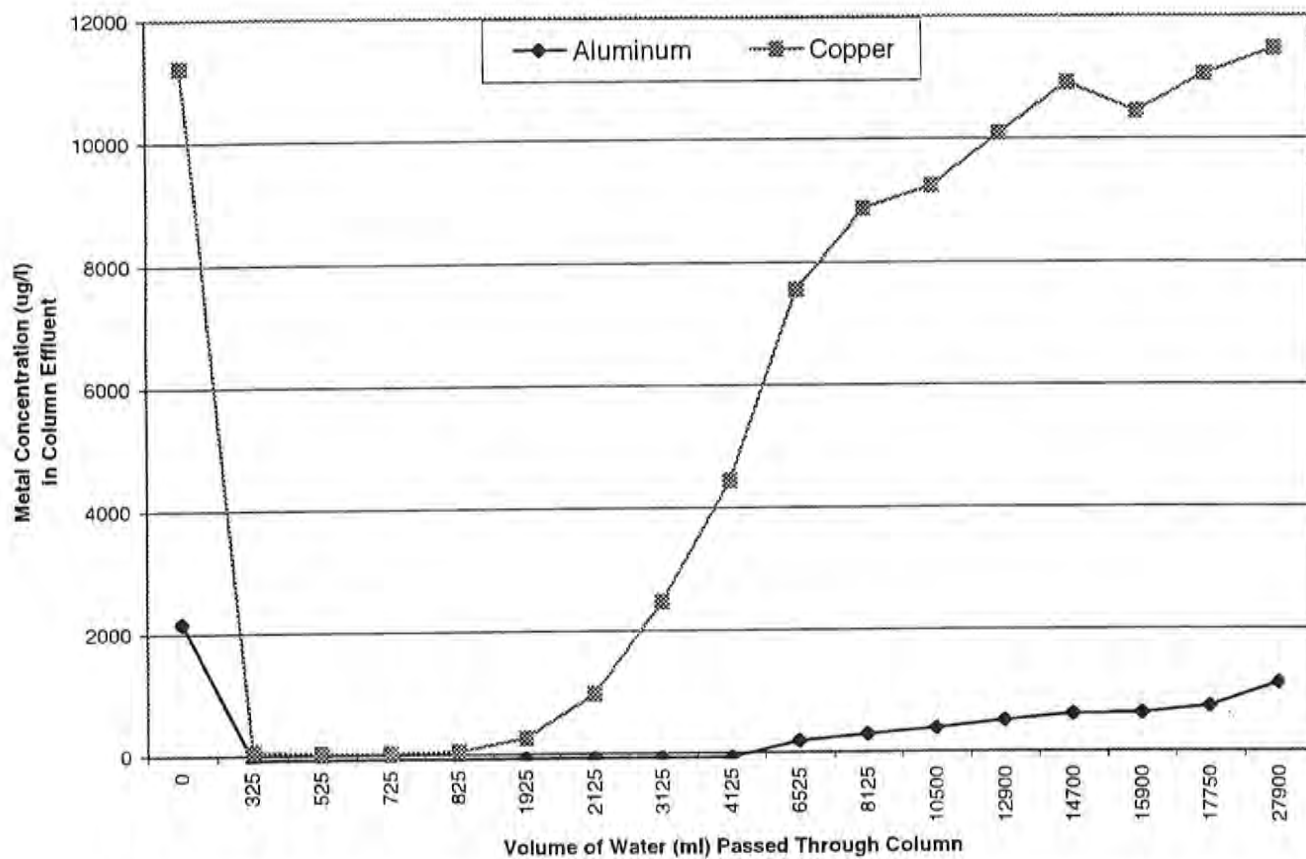


Figure 9. Zeolite Z-134, column test results (9a) aluminum and copper and (9b) cadmium and lead.

Montana Bureau of Mines and Geology
Test Column Results

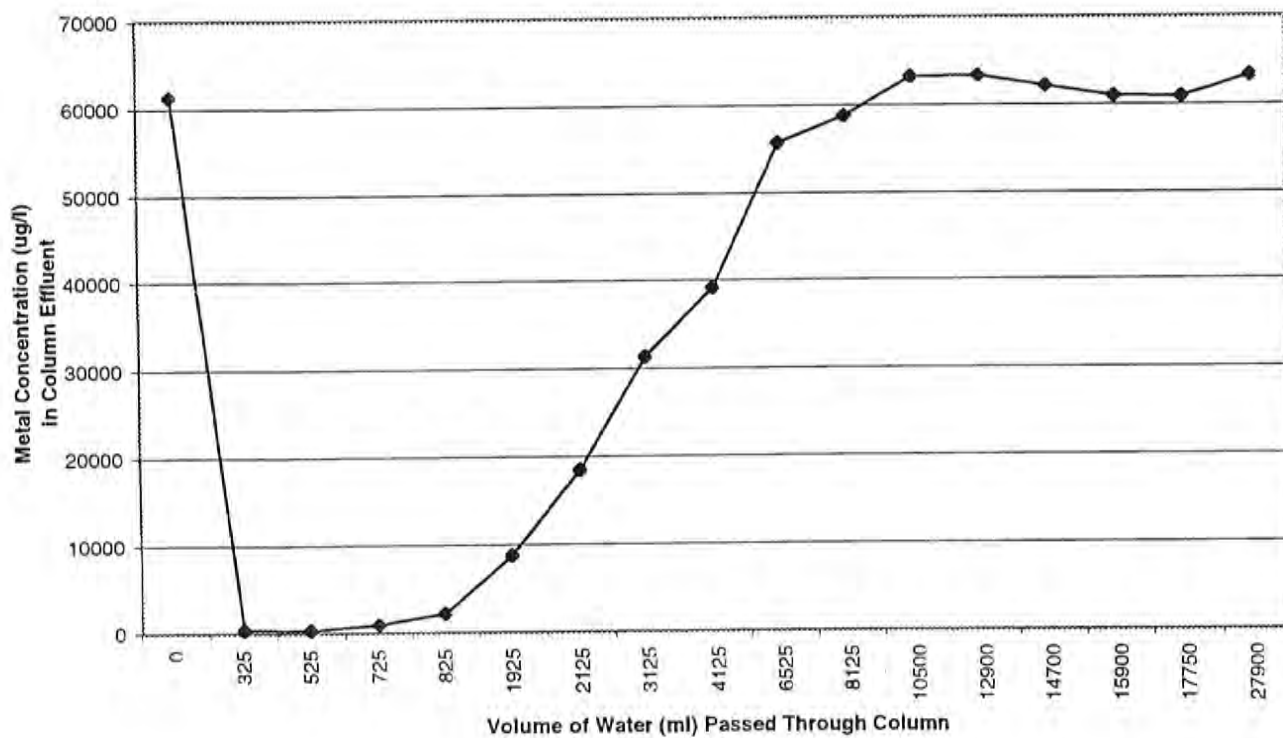
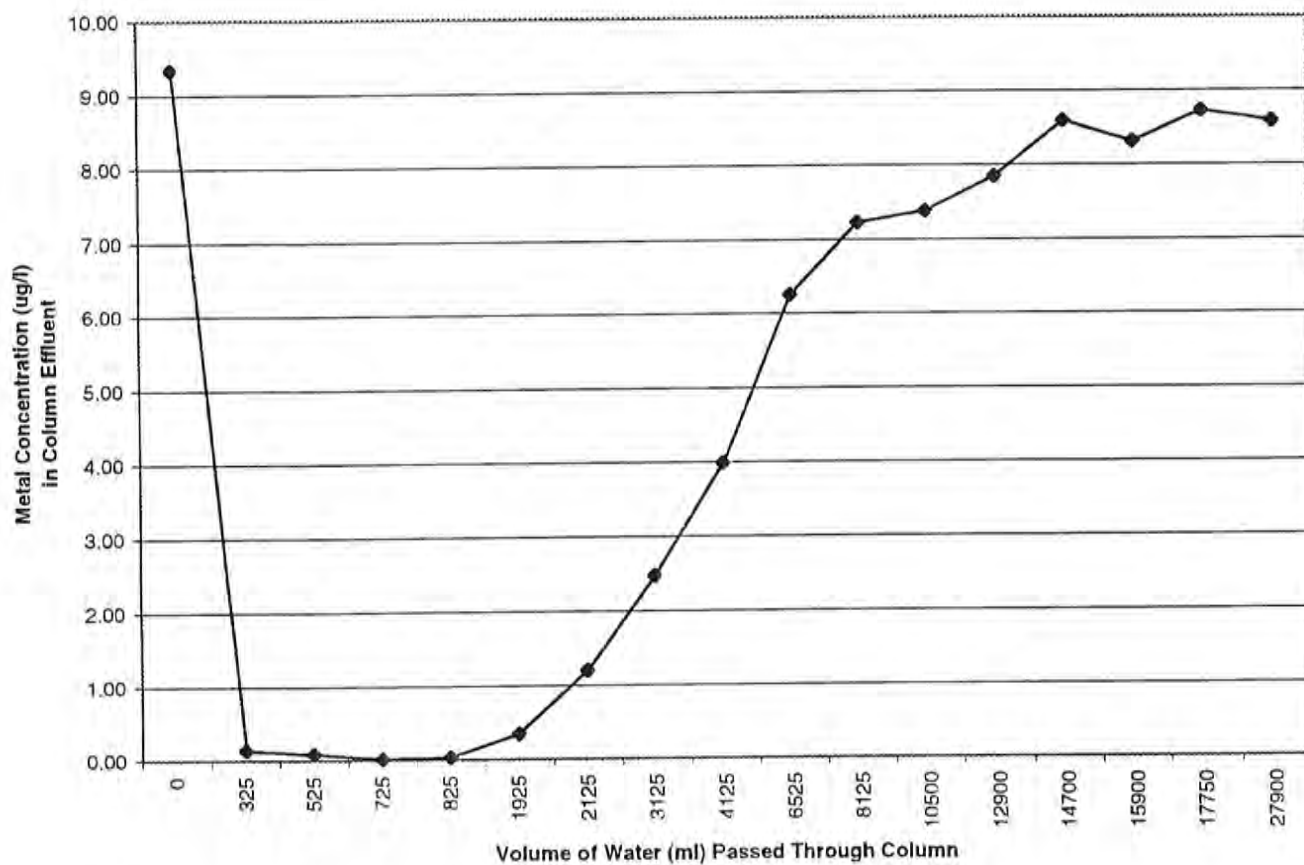


Figure 9. Zeolite Z-134, column test results (9c) iron and (9d) zinc.

Teague CH

The Teague CH zeolite, also a clinoptilolite, is one of two zeolites provided by Teague Minerals, Adrian, Oregon. The measured CEC of 1.33 meq/g is considerably greater than that for Z-93 and Z-127 and about 15% greater than Z-134. Breakthrough trends were similar to the other zeolites, with breakthrough occurring first in zinc and cadmium removal (figures 10a–10d). This zeolite had excellent removal of lead and iron plus good removal of aluminum.

Teague XY

Teague XY is the other zeolite sample provided by Teague Minerals, Adrian, Oregon. This zeolite is also classified as clinoptilolite. Its CEC of 1.25 meq/gm is slightly lower than that of the CH zeolite. Metal attenuation trends were similar to the other zeolites, with breakthrough occurring first in cadmium and in zinc attenuation (figures 11a–11d). Lead removal was very good for this zeolite, with a high removal of aluminum also occurring (table 6).

The Teague XY zeolite had somewhat better metal attenuation than the Teague CH zeolite, which would be somewhat unexpected based on their CEC values.

Z-466

Zeolite Z-466 is from a zeolite occurrence at Tabor Mountain, south of Hamilton, by Berg and Lonn (1993). Clinoptilolite was identified as the predominant zeolite in the collected samples. This zeolite had one of the highest CEC values of any analyzed during this study. Its CEC of 1.86 meq/gm is twice that of Z-93 and Z-127, and over 50% higher than Z-134. As might be expected, the level of metal removal was much greater than that of the other three Montana zeolites and exceeded that shown by both Teague zeolites. As shown in figures 12a–12d, no breakthrough was observed in any of the six metals analyzed for, over 17,000 mL of sample volume.

The column tests for each of the six zeolites were conducted in a similar manner. The flow rate of sample water was maintained at 10 mL/min. Based on the data presented in table 6 for the percent of each analyte's concentration removed, it appears that zeolite Z-466 performed the best of the six tested zeolites. While the other three Montana zeolites did not perform as well as Z-466 or the two Teague Mineral zeolites, zeolites Z-127 and Z-134 still removed substantial concentrations several analytes.

Column attenuation test results were reviewed for milliequivalents per liter changes. Because zeolites are cation exchangers for every meq/L of trace (heavy) metal removed from solution, an equal

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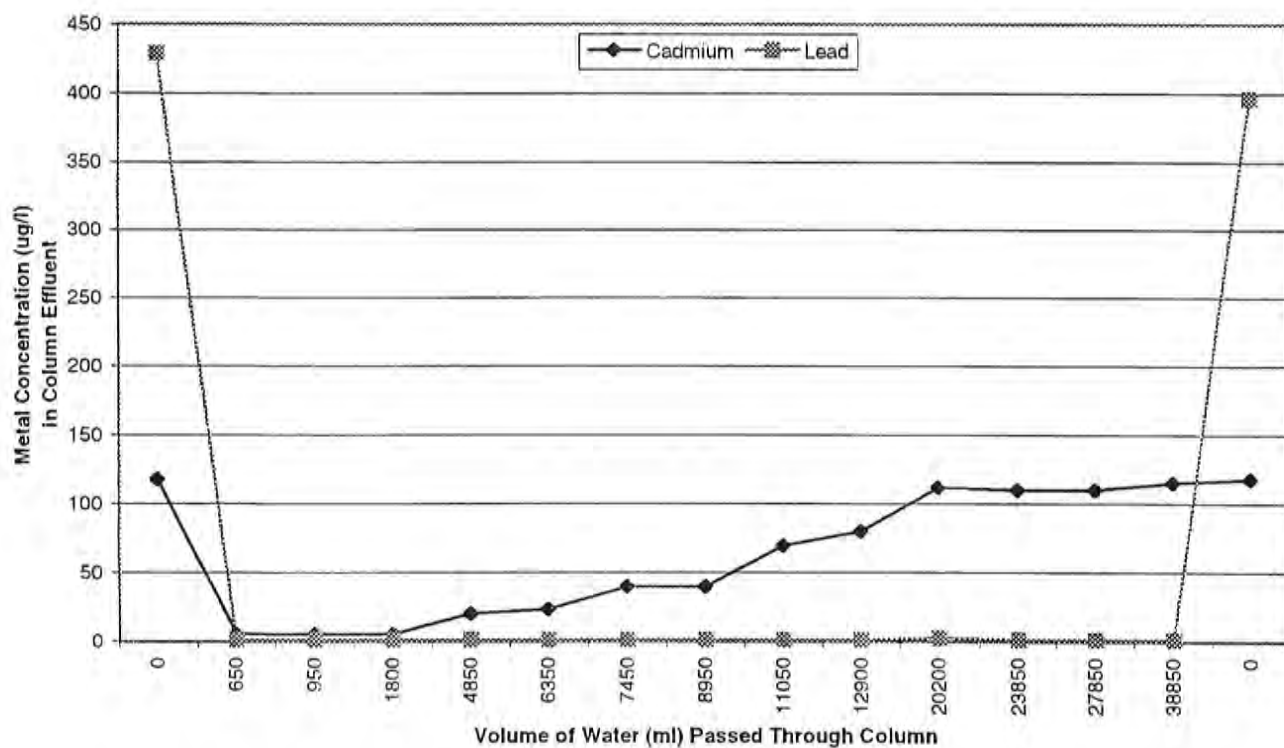
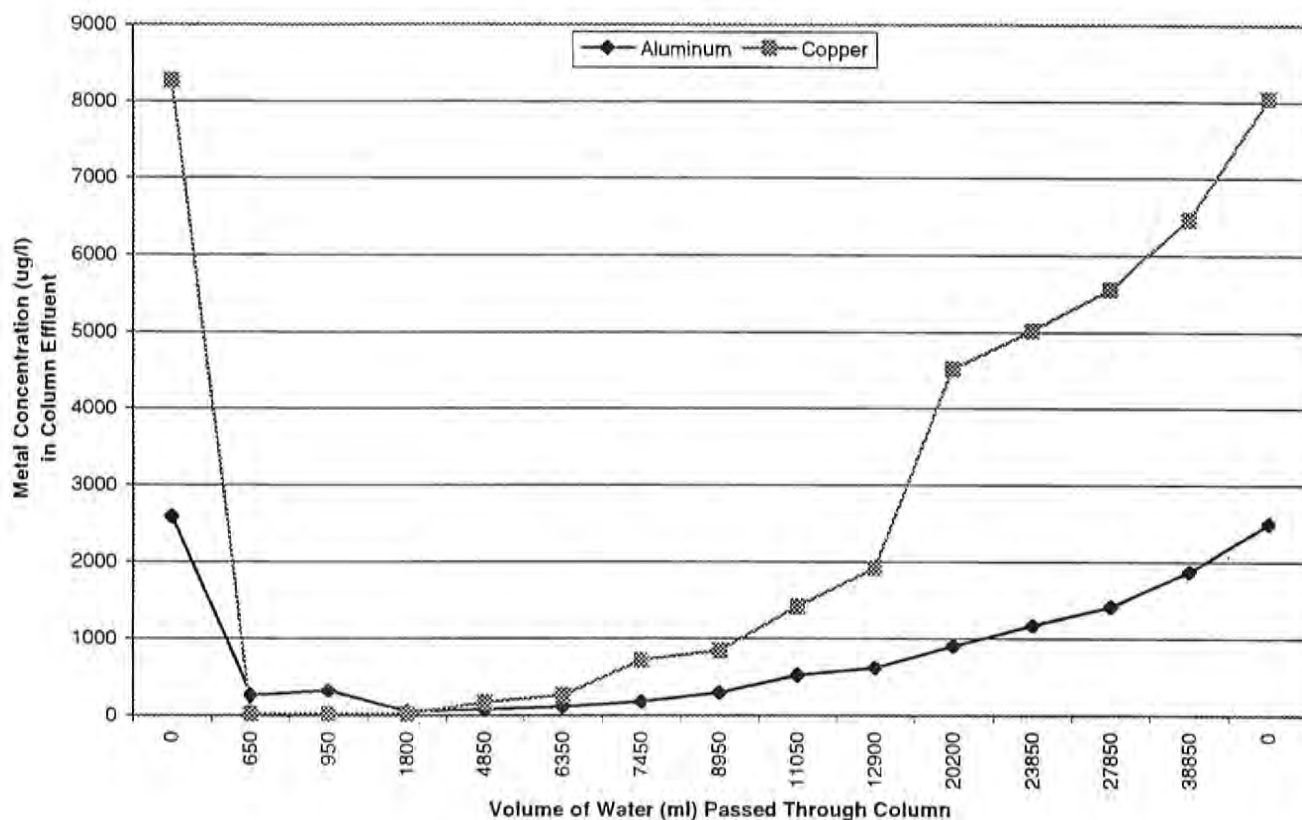


Figure 10. Zeolite CH, column test results (10a) aluminum and copper and (10b) cadmium and lead.

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Test Column Results

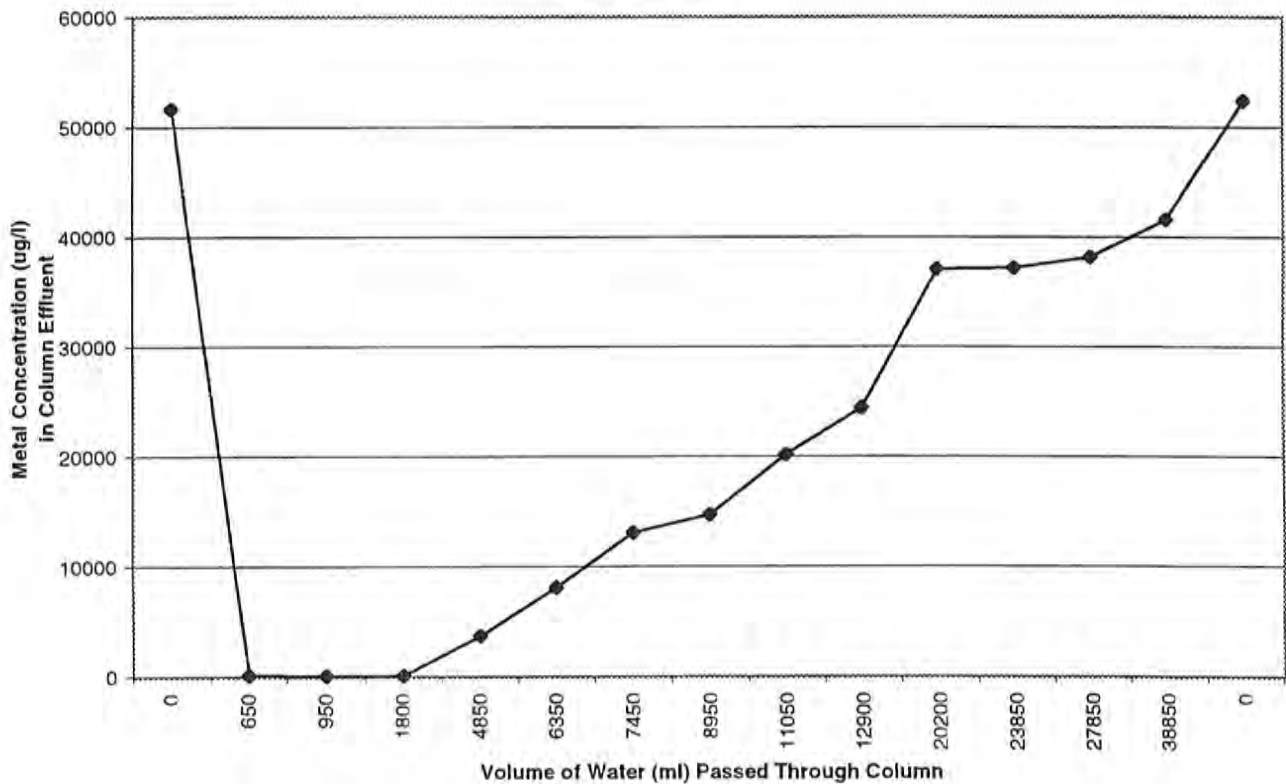
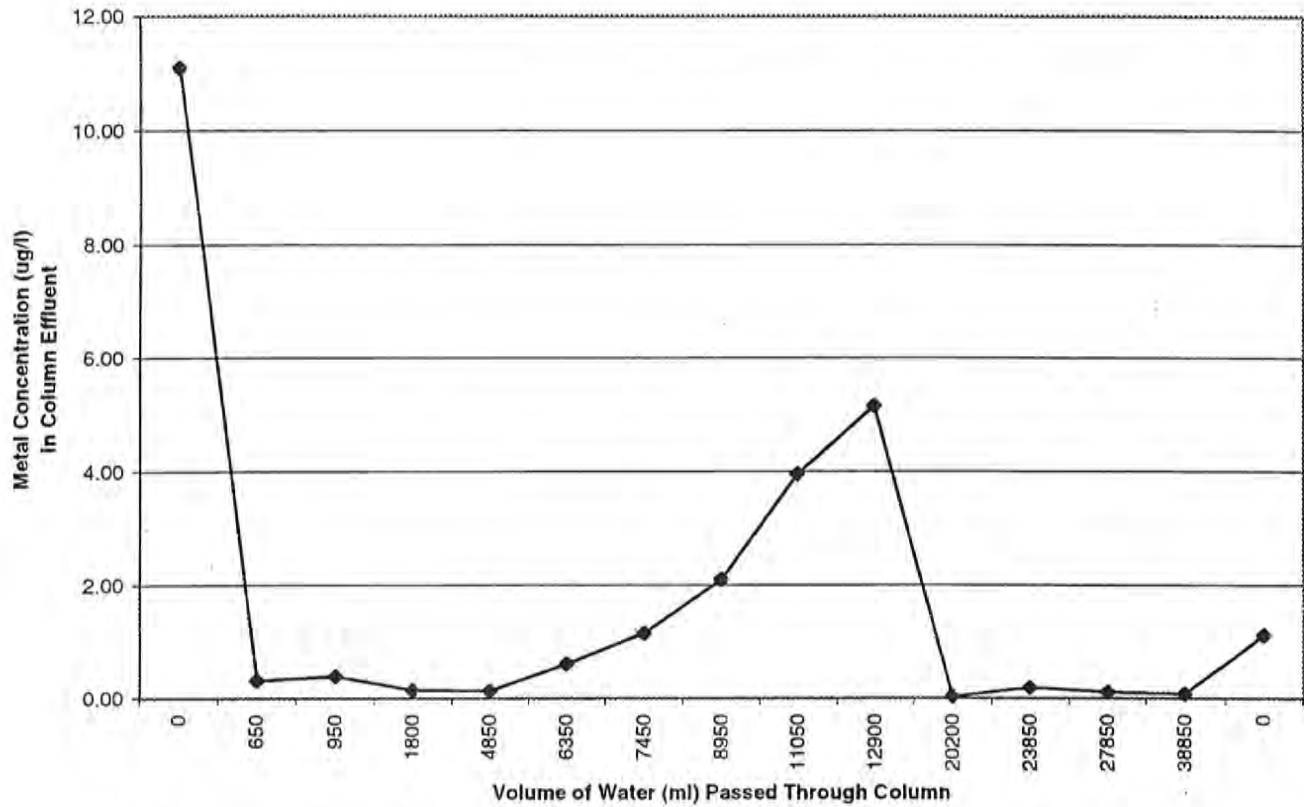


Figure 10. Zeolite CH, column test results (10c) iron and (10d) zinc.

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Test Column Results**

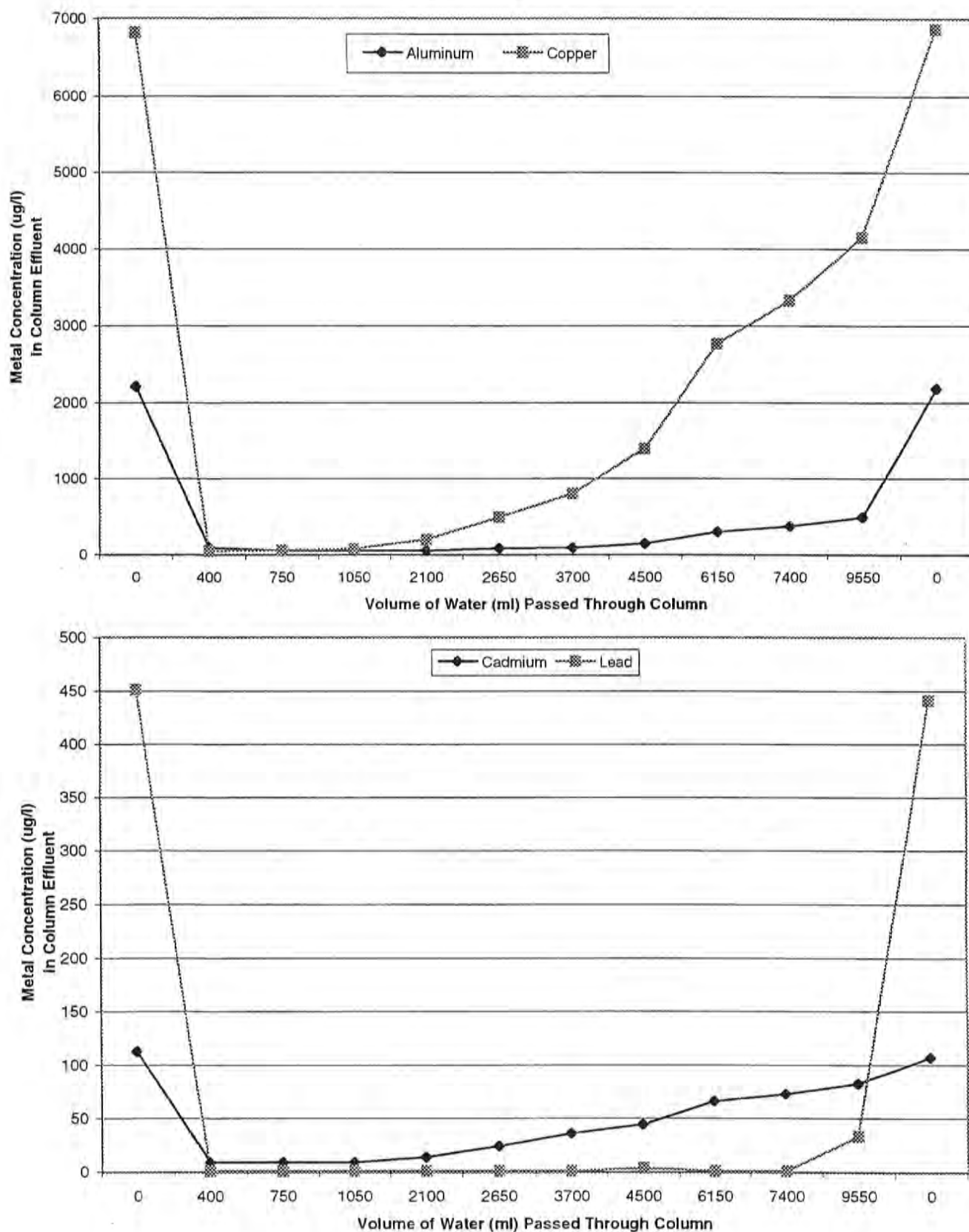


Figure 11. Zeolite XY, column test results (11a) aluminum and copper and (11b) cadmium and lead.

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Test Column Results

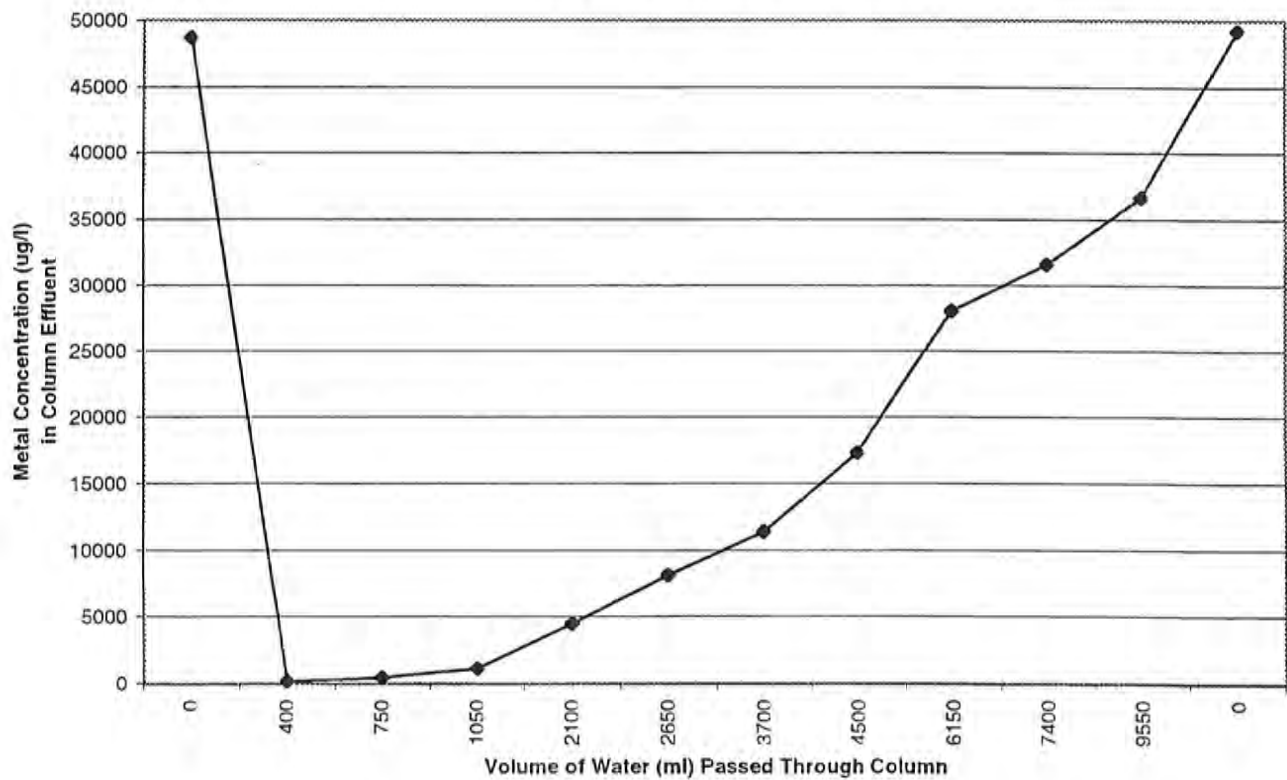
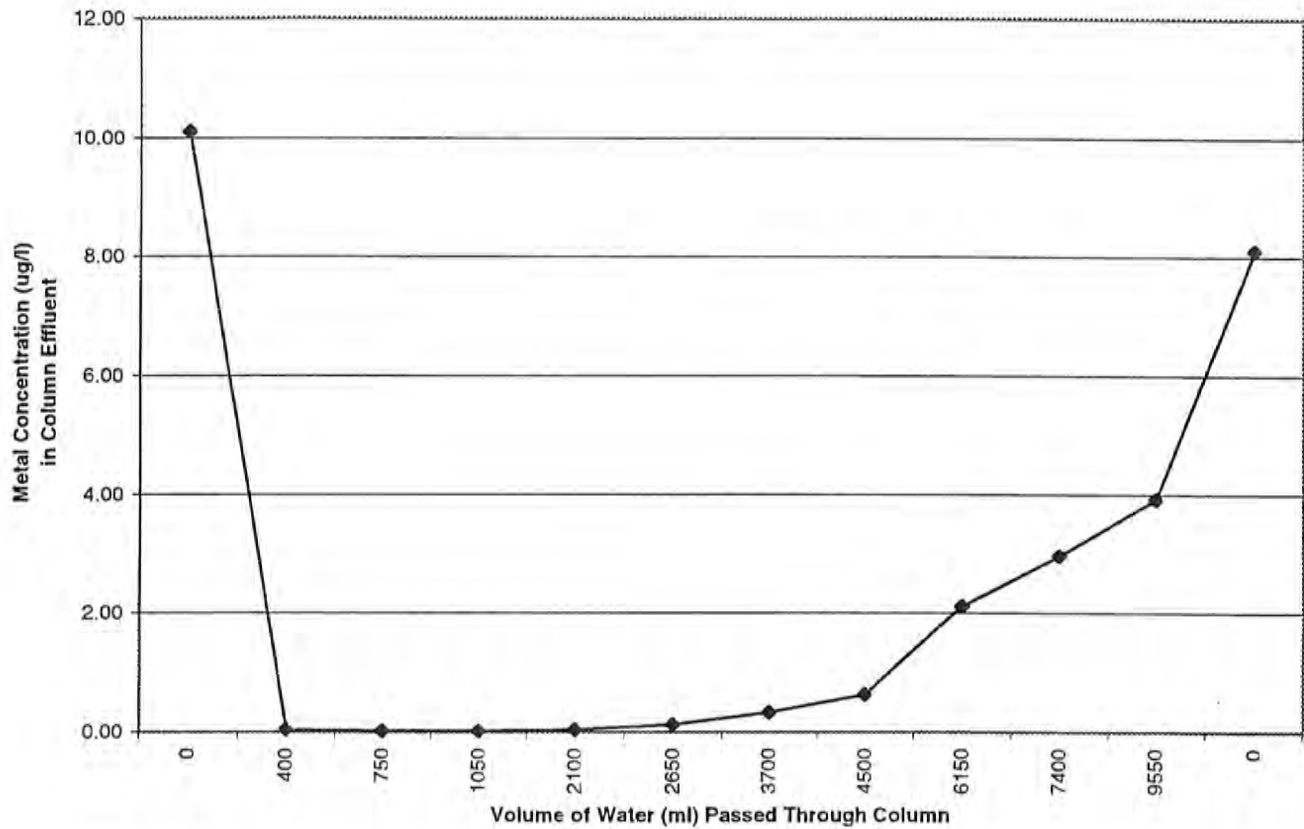


Figure 11. Zeolite XY, column test results (11c) iron and (11d) zinc.

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Test Column Results

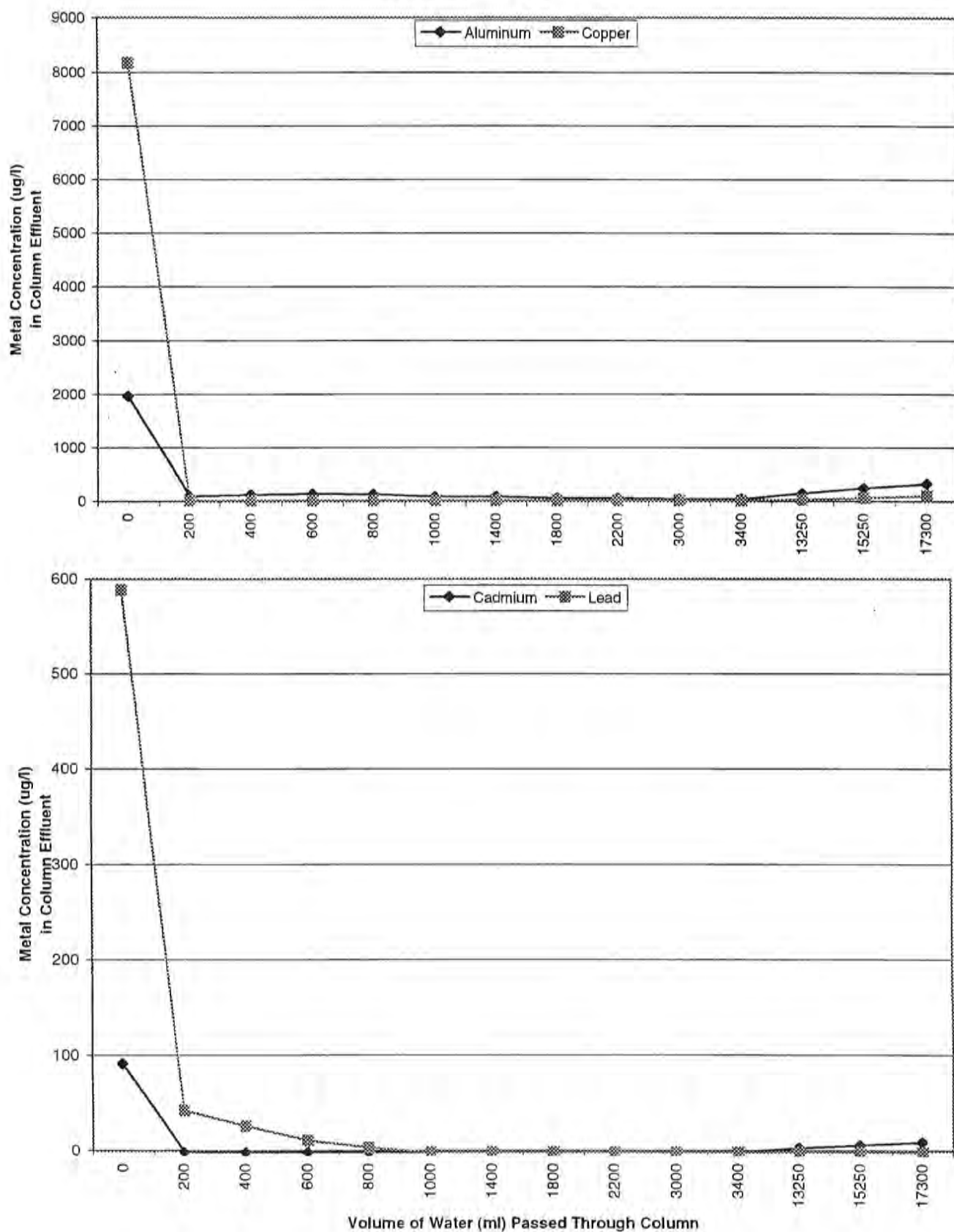


Figure 12. Zeolite Z-466, column test results (12a) aluminum and copper and (12b) cadmium and lead.

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Test Column Results

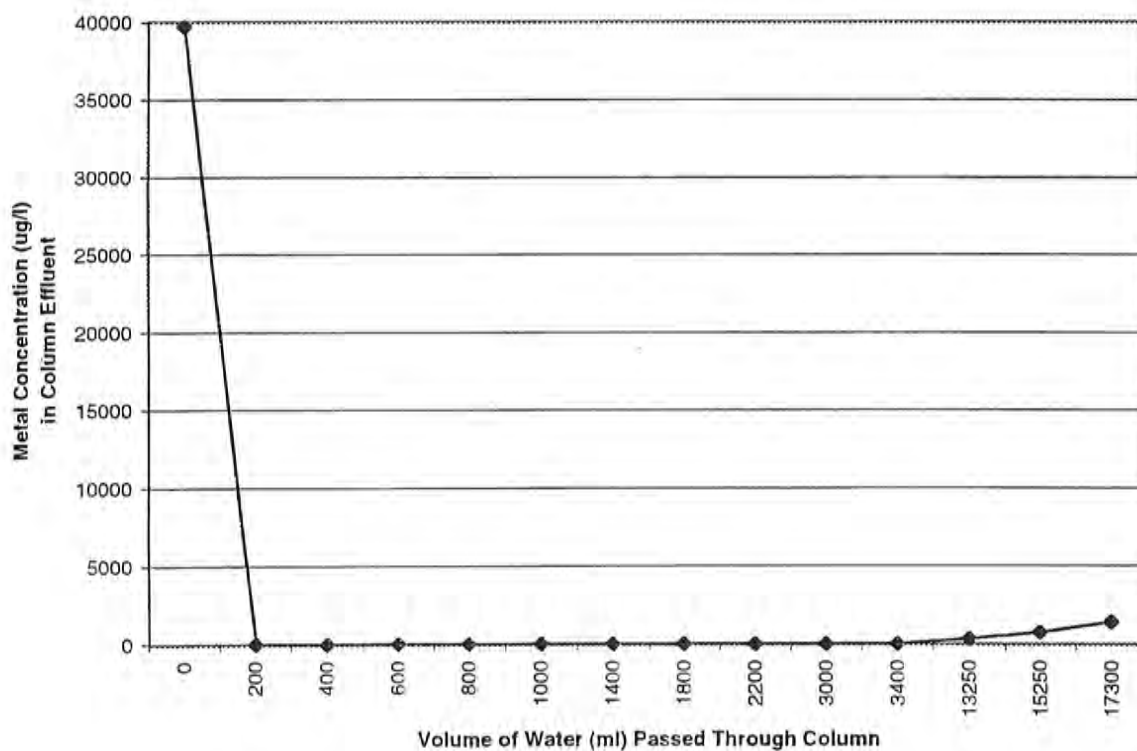
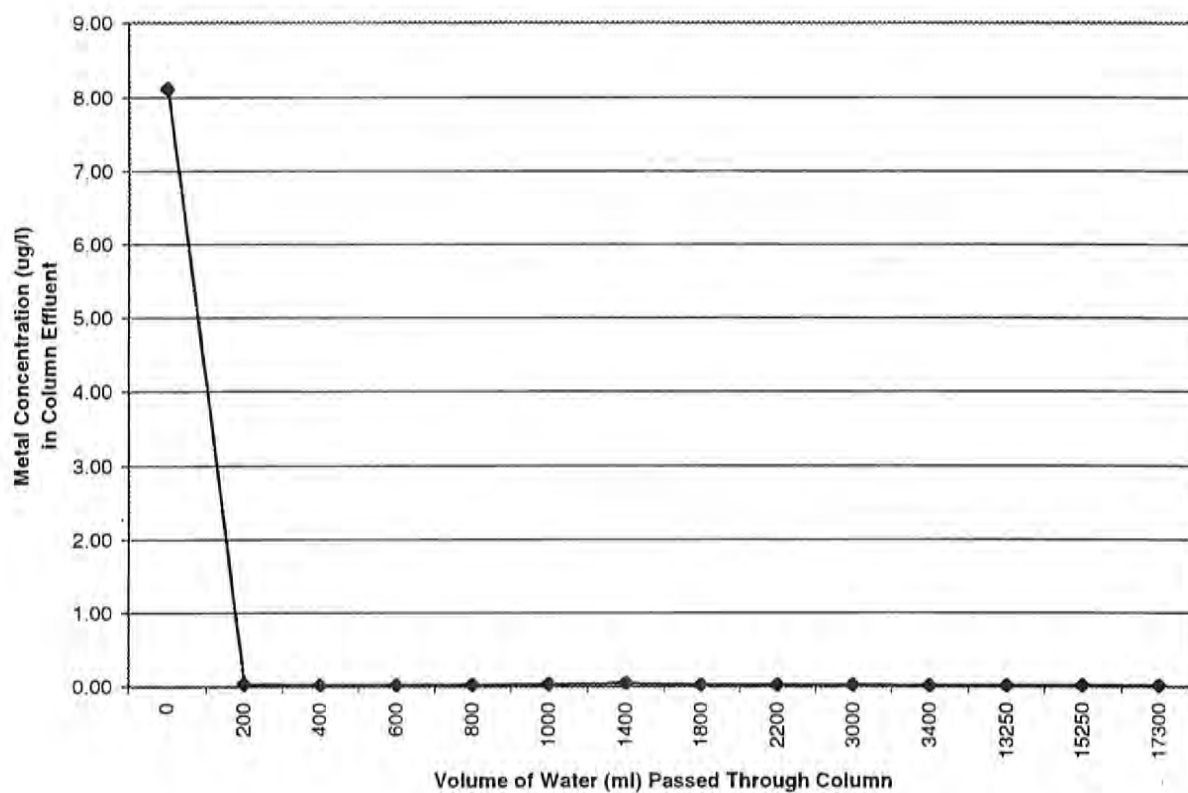


Figure 12. Zeolite, Z-466, Column Test Results (12c) Iron and (12d) Zinc.

amount of meq/L needs to be released from the zeolite. Table 6 contains meq data for selected parameters and tests. This table lists meq/L concentrations in three categories: 1) sum of calcium and magnesium (Ca+Mg), in meq/L; 2) sum of sodium and potassium (Na+K), in meq/L; and 3) sum of the major trace metals, e.g., aluminum, copper, lead, and zinc (Al+Cu+Pb+Zn+...), in meq/L, for the volume of solution passed through the column. The values at volume zero represent beginning meq/L concentrations of the test waters, prior to contact with the various zeolites. Meq/L concentrations at the following volumes represent the changes in concentrations as a result of cation exchange between the zeolites and test waters. Figures 13a–15b show those changes.

Figure 13a shows that Na+K concentrations increased immediately after contact with zeolite Z-93, with a decrease in Ca+Mg and trace-metal concentrations. As more water passed through the column, meq/L concentrations within the three categories gradually returned to levels approaching those at the start of the test (time zero). A decrease in attenuation or breakthrough in metal removal is apparent and is similar to that noted and shown in figures 7a–7d. Zeolite Z-93 is a sodium exchanger based on the high release of sodium.

Figure 13b shows meq/L concentration changes for zeolite Z-127. The Ca+Mg and Na+K cation categories increased in meq/L on contact with the sample water, with a resulting decrease in trace metal concentrations. Once again, a decrease in metal attenuation is shown as the meq/L concentrations gradually approach initial values. This zeolite is a Ca+Mg and Na+K group exchanger.

Figures 14a and 14b depict meq/L concentrations for zeolites Z-134 and Z466, respectively. Zeolite Z-134 behaves similar Z-127, exchanging Ca and Na in the attenuation of trace metals. Zeolites Z-127 and Z-134 are from the Grasshopper Creek deposit.

Zeolite Z-466 (figure 14b) responds differently from the other three previously described zeolites. There is a large increase in the Na+K categories (over a four-fold increase) with a resulting decrease in the Ca+Mg and trace metal groups. However, as attenuation lessens, the meq/L concentrations for all three groups starts to approach the concentrations observed at the begin of the test. Z-466 is a Na exchanger.

Figures 15a and 15b shows meq/L concentrations for the two commercial zeolites, CH and XY. The CH zeolite (figure 15a) responds similar to Z-466, releasing large concentrations of Na+K and attenuating the Ca+Mg and trace metal groups. This zeolite is a Na exchanger.

The other commercial zeolite, XY, had the largest release of meq/L from the Na+K group (figure 15b). Na+K group concentrations increased almost five-fold. The level of attenuation of the Ca+Mg group was also much less for this zeolite than either the CH or Z-466 zeolites. Attenuation was about

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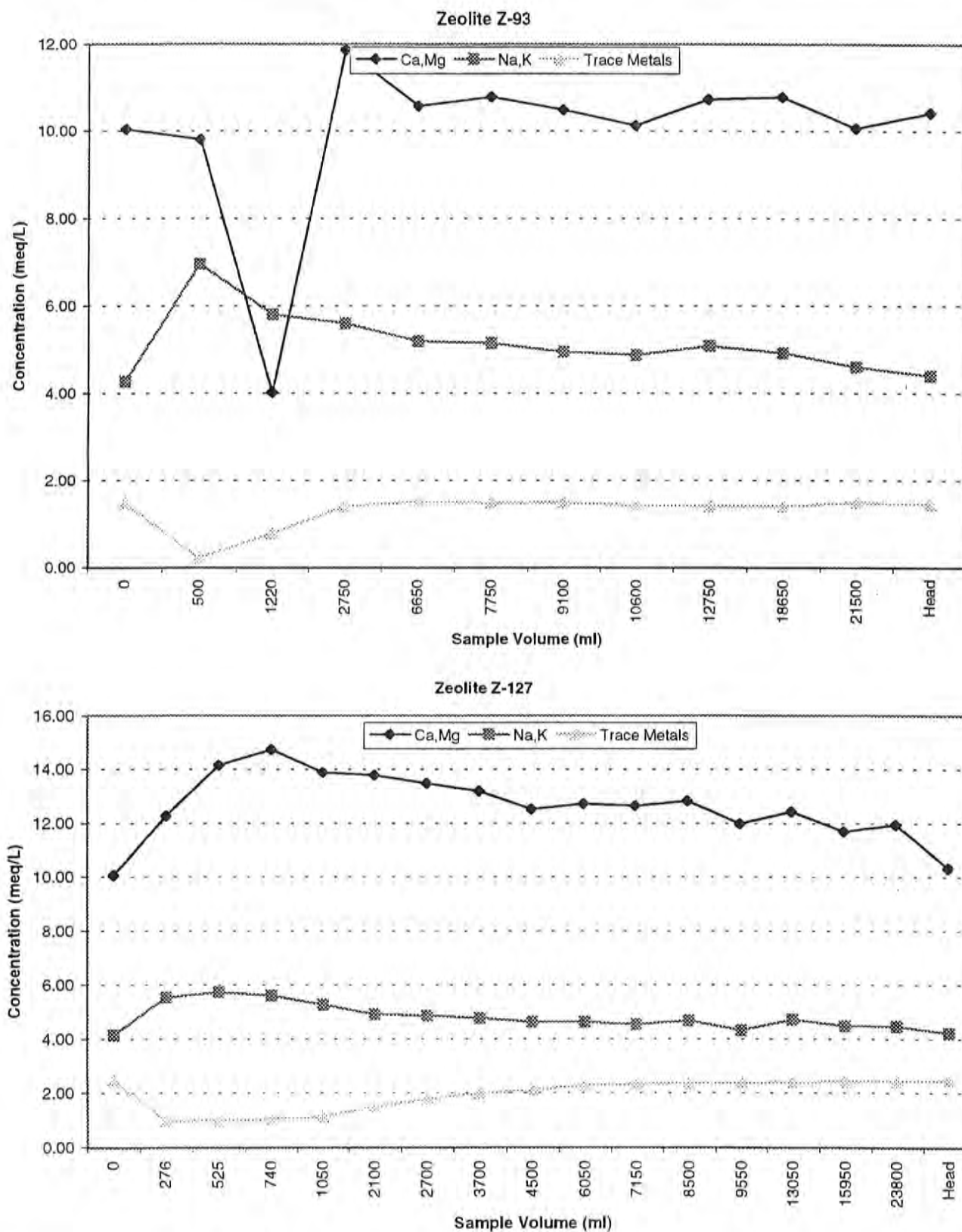


Figure 13. Zeolites (13a) Z-93: Ca, Mg, Na, K, and trace metals and (13b) Z-127: Ca, Mg, Na, K, and trace metals.

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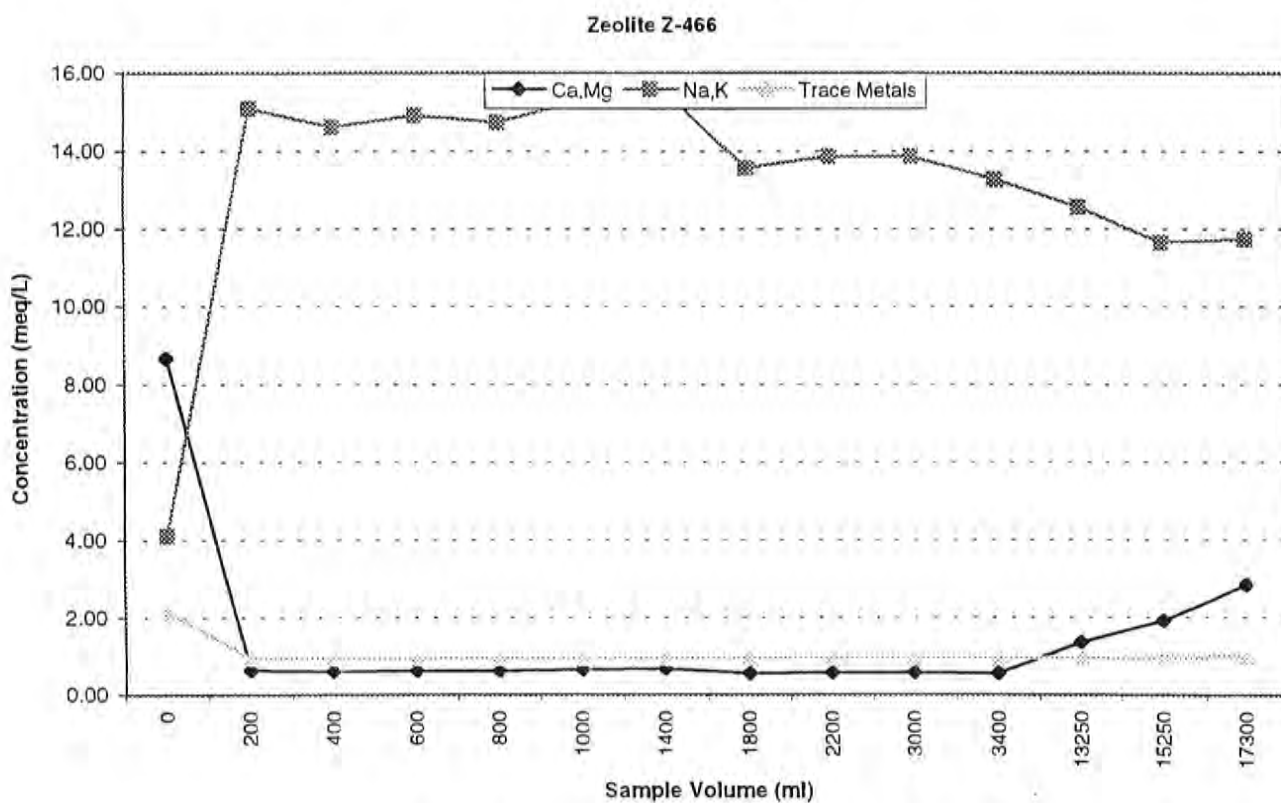
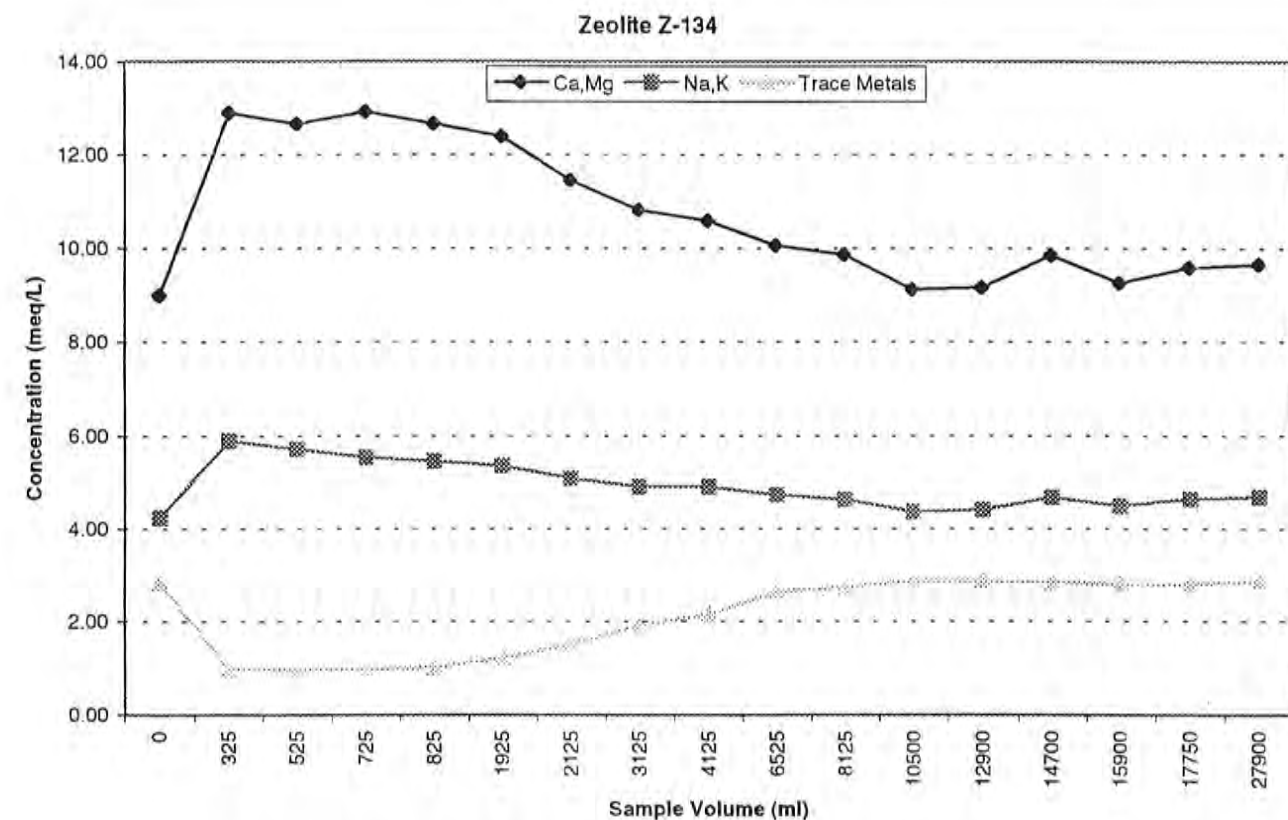


Figure 14. Zeolites (14a) Z-134: Ca, Mg, Na, K and trace metals and (14b) Z-466: Ca, Mg, Na, K and trace metals.

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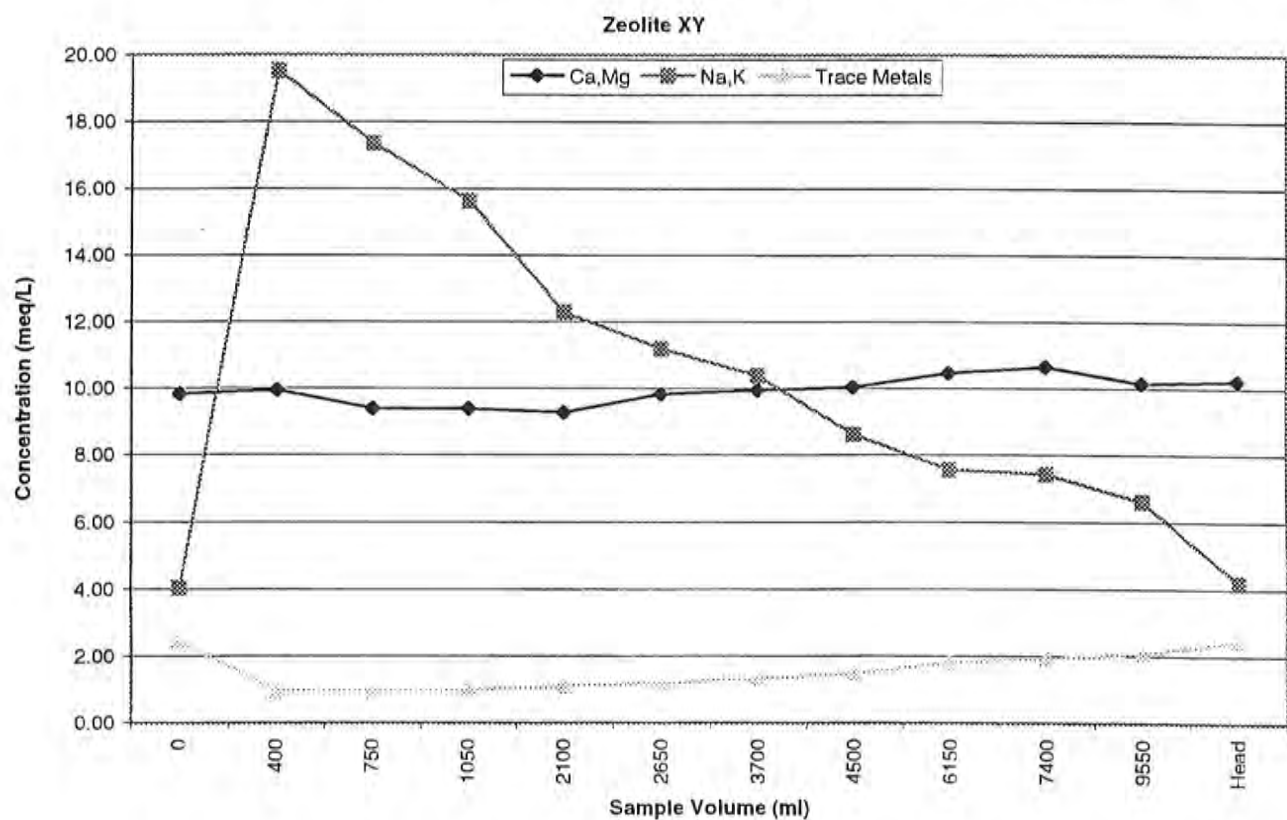
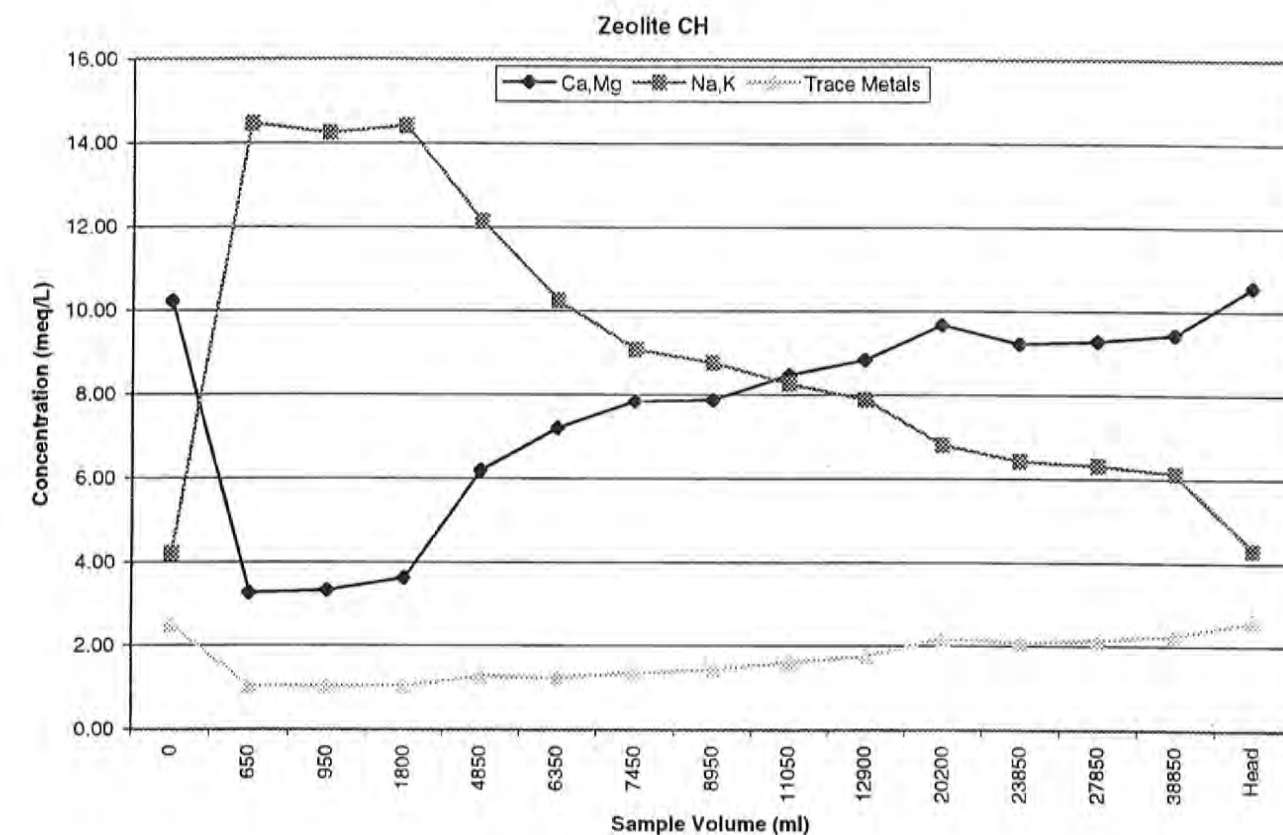


Figure 15. Zeolites, (15a) CH: Ca, Mg, Na, K, and trace metals and (15b) XY: Ca, Mg, Na, K, and trace metals.

three-fold of Ca+Mg for the XY Zeolite, while the CH and Z-466 zeolites had almost an eight-fold increase. The XY zeolite is a sodium exchanger.

Measuring a zeolite's ability to remove trace metals from solution can be estimated by looking at the total meq/L removed and added. However, this method does not identify which of the individual metals are being attenuated. As has been shown previously, the attenuation rate varies for different metals. While most of the six tested zeolites had reached breakthrough (less than 80% reduction in concentrations from initial levels) for Al, Cu, Cd, Fe, and Zn, none of them had reached that point for Pb attenuation. Therefore, the method used for determination of individual metal attenuation should be based on individual analyte concentrations. Comparing meq/L concentrations and changes would be best suited for an overall zeolite to zeolite comparison in their ability to remove metals in general and identifying the type of exchange taking place, i.e., if the zeolite is a Ca+Mg or Na+K ion exchanger.

Additional column tests were run using discharge water from an active mine near Lewiston, Montana (table 7). The Gies mine was entering the final stages of operation, and the operators were looking for a method of treating the mine's discharge water, which had an elevated zinc concentration from pre-mining conditions (Wilson 1994). Column tests were run on this discharge water utilizing Z-134 material. The Z-134 zeolite was chosen for use during the two column tests because of its availability and its level of success during previous testing.

Bulk water samples of the Gies mine adit discharge were collected on two occasions. Water quality analyses were run on these samples to characterize the adit discharge. The head solution values shown in table 7 represent the adit discharge. It is apparent that zinc was the only analyte, of those previously tested during the column tests, to be above or near detection concentrations. The sample water was moderately alkaline (pH 7.4–7.7) and of much better quality (lower trace metal concentrations) than that used during earlier tests. Figures 16a and 16b show zinc attenuation during the column tests. During the first test, over 5 gal (18 L) of water was passed through the zeolite column, with a zinc removal rate greater than 90%. While during the second test, over 5.5 gal (21 L) of water were passed through the column, still achieving over a 95% removal of zinc (table 8).

One problem noticed during the first Gies mine water test was the apparent flushing (leaching) of trace concentrations of arsenic from the zeolites used in the column. Shortly after the start of the test (20 min/200 mL), arsenic concentrations over 70 µg/L were noted; however, these concentrations steadily decreased throughout the test (figure 17a). A similar trend was observed during the second test, with beginning arsenic concentrations just above the detection limit, increasing in concentration to over 60

Table 7
Gies Mine Column Leachate Results

Zeolite Type	Sample No.	Volume (ml)	Iron (mg/l)	Aluminum (ug/l)	Arsenic (ug/l)	Cadmium (ug/l)	Copper (ug/l)	Lead (ug/l)	Zinc (ug/l)	pH	SC (umhos/cm)	Comments
Z-134 Gies Mine	0	0	0.01	-30	-1.0	-2.0	3.8	-2.0	195.5	7.40	800	Head Sol.-Adit Discharge Flow rate 10ml/min
	1	200	0.04	-30	76.4	-2.0	104.7	3.6	44.7	7.87	1540	
	2	400	0.034	-30	69.3	-2.0	65	2.8	28.1	7.87	1430	
	3	600	0.032	-30	59.5	-2.0	28.7	2.6	23.6	7.86	1330	
	4	800	0.029	-30	55.0	-2.0	26.4	2.3	23.3	7.85	1280	
	5	1000	0.024	-30	49.1	-2.0	18.4	2.3	19.6	7.85	1220	
	6	1400	0.020	-30	37.8	-2.0	17.1	-2.0	17.5	7.83	1120	
	7	1800	0.018	-30	33.8	-2.0	18.5	-2.0	14.8	7.81	1050	
	8	2200	0.013	-30	25.7	-2.0	13.5	-2.0	13.6	7.80	1000	
	9	2600	0.009	-30	20.3	-2.0	8.8	-2.0	12.6	7.78	960	
	10	3000	0.011	-30	16.6	-2.0	7.6	-2.0	11.7	7.78	930	
	11	3600	0.007	-30	13.6	-2.0	6.2	-2.0	11.8	7.76	890	
	12	4600	0.006	-30	9.8	-2.0	5.2	-2.0	9.1	7.75	860	
	13	7125	0.005	-30	7.2	-2.0	5.7	-2.0	12.4	7.75	820	
	14	12400	0.005	-30	5.4	-2.0	3.5	-2.0	18.8	7.73	800	
	15	18100	0.004	-30	5.1	-2.0	3.5	-2.0	11.7	7.73	800	Last sample
Z-134 Gies Mine	0	0	0.01	-30	1.8	-2.0	-2	-2.0	155.1	7.77	730	Head Sol.-Adit Discharge Flow rate 10ml/min
	1	200	0.04	-30	60.7	-2.0	15.8	-2.0	23.8	7.87	1260	
	2	400	0.04	-30	56.6	-2.0	13.8	-2.0	13.6	7.86	1180	
	3	600	0.02	-30	49.0	-2.0	9.9	-2.0	11.4	7.86	1120	
	4	800	0.02	-30	44.4	-2.0	9.3	-2.0	9.8	7.85	1070	
	5	1000	0.02	-30	39.3	-2.0	8.5	-2.0	10.3	7.85	1030	
	6	1400	0.02	-30	31.4	-2.0	7.1	-2.0	8.9	7.85	970	
	7	2000	0.01	-30	22.8	-2.0	5.3	-2.0	7.1	7.82	880	
	8	2800	0.01	-30	14.7	-2.0	4.1	-2.0	5.8	7.80	820	
	9	3600	0.01	-30	10.9	-2.0	8.0	-2.0	6.7	7.78	780	
	10	4600	0.01	-30	7.8	-2.0	2.6	-2.0	4.0	7.75	750	
	11	5800	0.01	-30	6.8	-2.0	2.1	-2.0	4.2	7.75	730	
	12	9450	<0.003	-30	3.4	-2.0	-2	-2.0	3.4	7.78	700	
	13	14800	<0.003	-30	2.7	-2.0	-2	-2.0	2.8	7.76	690	
	14	17500	0.01	-30	2.9	-2.0	-2	-2.0	4.4	7.76	680	
	15	21950	<0.003	-30	2.5	-2.0	2.1	-2.0	6.3	7.76	680	Last sample

(-) A minus sign denotes that analyte concentration was less than the instrument detection limit

Montana Bureau of Mines and Geology Test Column Results

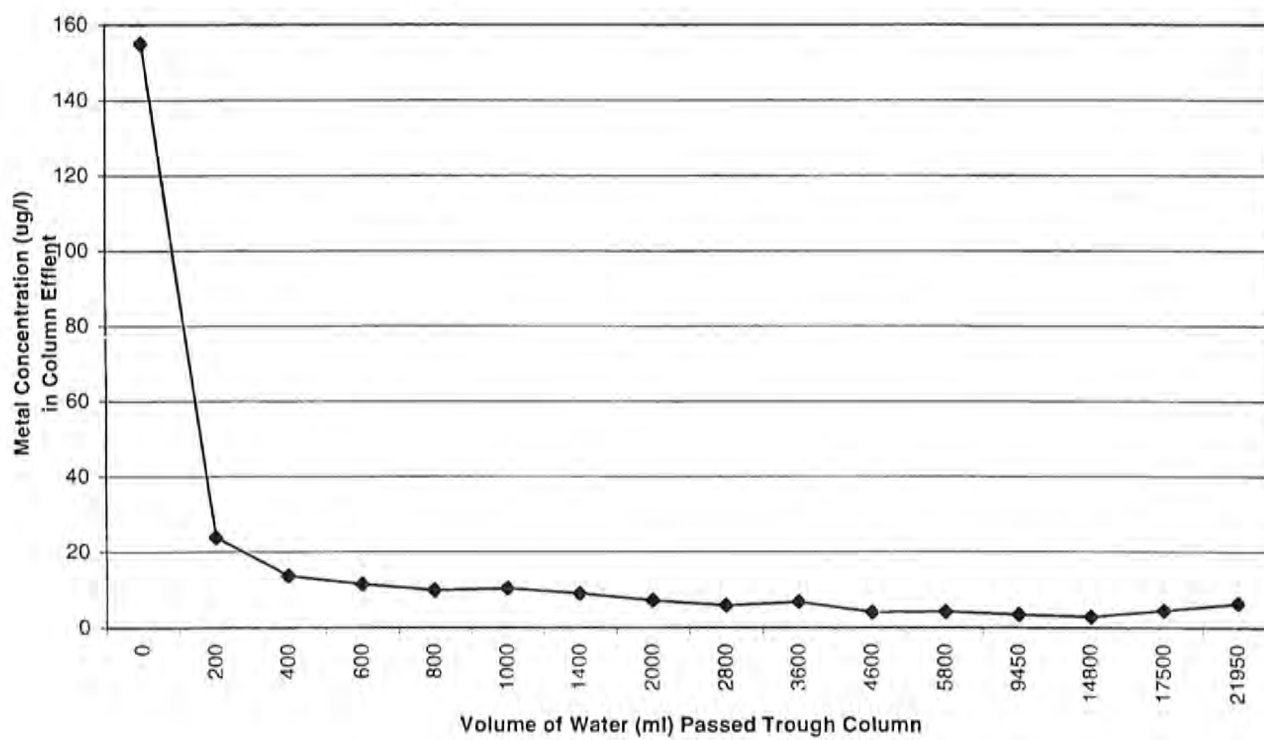
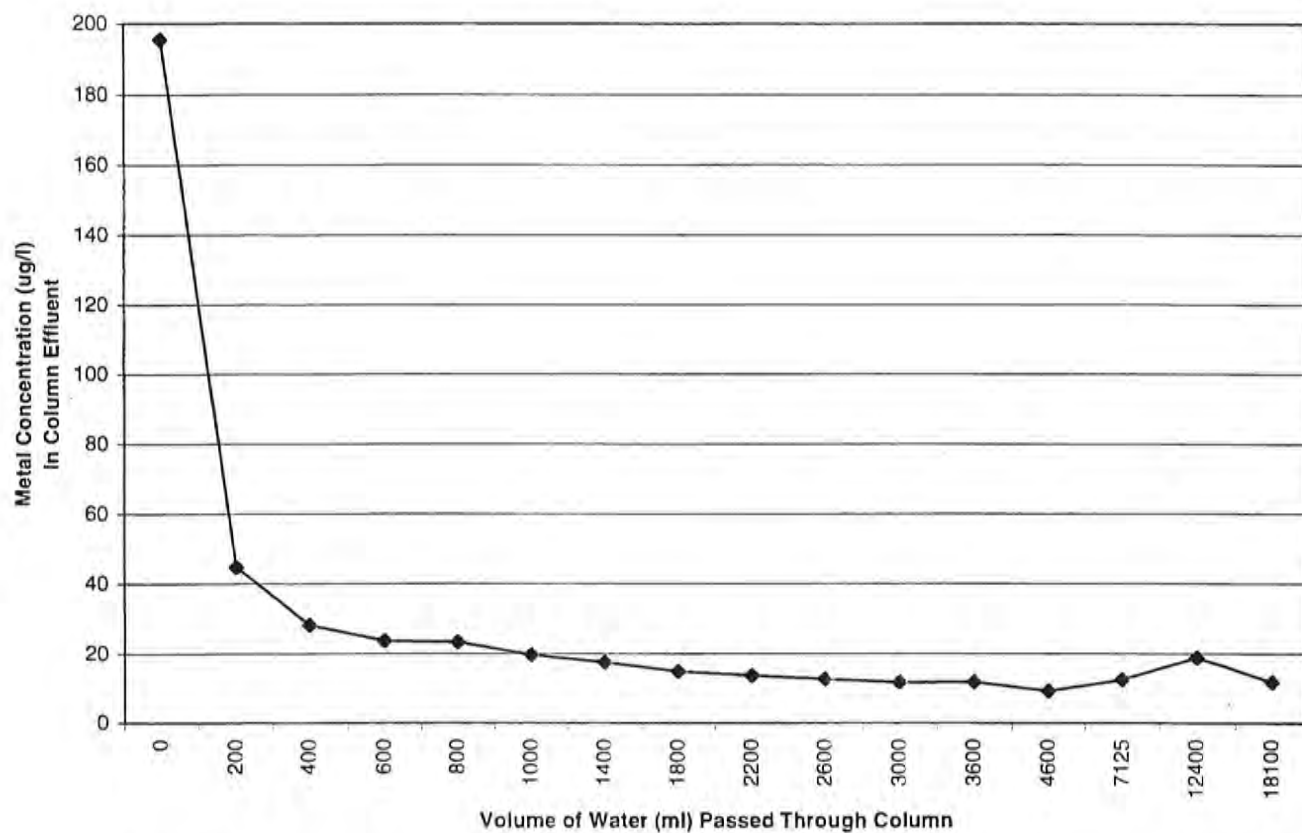


Figure 16. Gies mine zinc concentration Z-134, (16a) Test #1(16b) Test #2.

Table 8. Gies mine column leachate test results percent concentration removed.

Zeolite Type	Sample No.	Volume (ml)	Iron %	Aluminum %	Arsenic %	Cadmium %	Copper %	Lead %	Zinc %	Comments
Z-134 Gies Mine Test #1	0	0	0	NA	0	NA	0	NA	0	Head Sol.-Adit Discharge Flow rate 10ml/min
	1	200	-300	NA	-15180	NA	-2655	NA	77.1	
	2	400	-240	NA	-13760	NA	-1611	NA	85.6	
	3	600	-220	NA	-11800	NA	-655	NA	87.9	
	4	800	-190	NA	-10900	NA	-595	NA	88.1	
	5	1000	-140	NA	-972	NA	-384	NA	90	
	6	1400	-100	NA	-7460	NA	-350	NA	91	
	7	1800	-80	NA	-6660	NA	-387	NA	92.4	
	8	2200	-30	NA	-5040	NA	-255	NA	93	
	9	2600	10	NA	-3960	NA	-132	NA	93.6	
	10	3000	-10	NA	-3220	NA	-100	NA	94	
	11	3600	30	NA	-2620	NA	-63	NA	94	
	12	4600	40	NA	-1860	NA	-37	NA	95.3	
	13	7125	50	NA	-1340	NA	-50	NA	93.7	
	14	12400	50	NA	-980	NA	8	NA	90.4	
	15	18100	60	NA	-920	NA	8	NA	94	Last sample
Z-134 Gies Mine #2 Test #2	0	0	0.00	NA	0	NA	0	NA	0	Head Sol.-Adit Discharge Flow rate 10ml/min
	1	200	-366.70	NA	-3272	NA	-690	NA	84.7	
	2	400	-300.00	NA	-3044	NA	-590	NA	91.2	
	3	600	-166.70	NA	-2622	NA	-395	NA	92.6	
	4	800	-133.30	NA	-2367	NA	-365	NA	93.7	
	5	1000	-133.30	NA	-2083	NA	-325	NA	93.4	
	6	1400	-88.90	NA	-1644	NA	-255	NA	94.3	
	7	2000	-22.20	NA	-1167	NA	-165	NA	95.4	
	8	2800	22.20	NA	-717	NA	-105	NA	96.3	
	9	3600	0.00	NA	-506	NA	-300	NA	95.7	
	10	4600	-11.10	NA	-33	NA	-30	NA	97.4	
	11	5800	22.20	NA	-278	NA	-5	NA	97.3	
	12	9450	100.00	NA	-89	NA	200	NA	97.8	
	13	14800	100.00	NA	-50	NA	200	NA	98.2	
	14	17500	33.30	NA	-61	NA	200	NA	97.2	
	15	21950	100.00	NA	-39	NA	-5	NA	95.9	Last sample

* Test #1 initial arsenic concentration less than instrument detection limit. Assumed initial concentration to be 1/2 detection limit for calculating percent arsenic removed

(-) A minus sign denotes that analyte concentration in effluent was greater than the initial concentration.

Montana Bureau of Mines and Geology Test Column Results

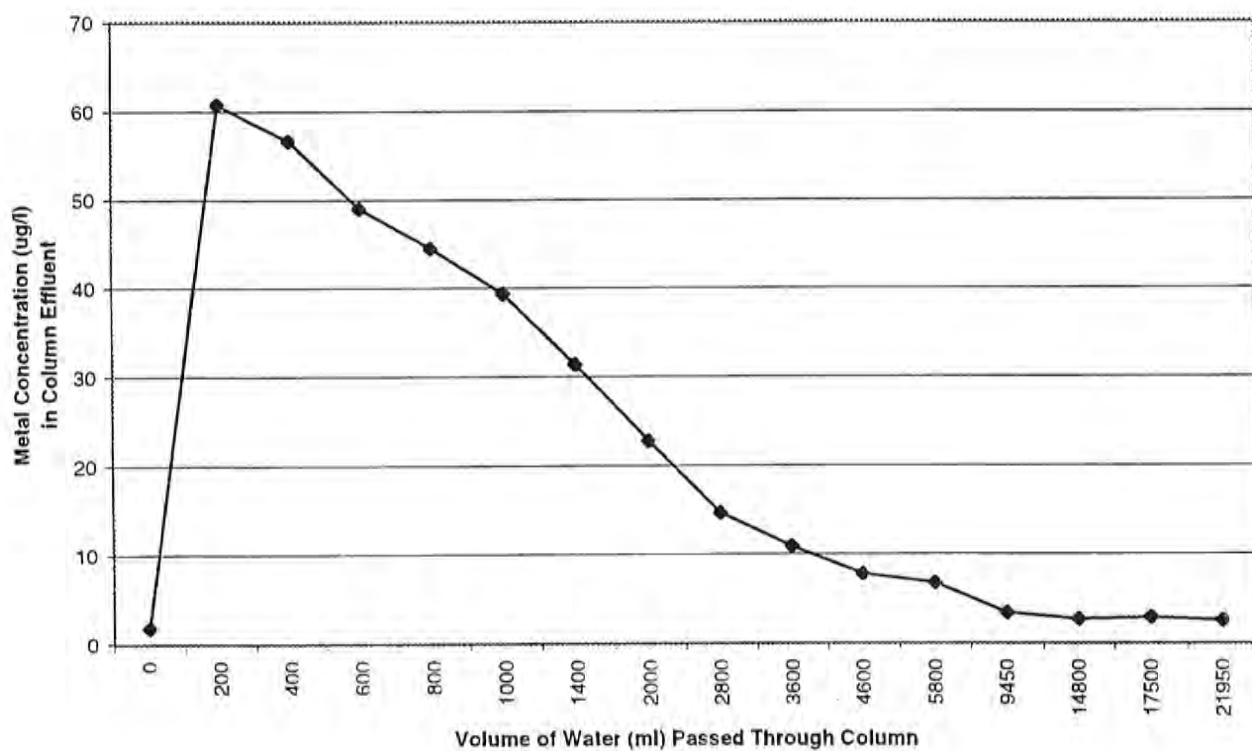
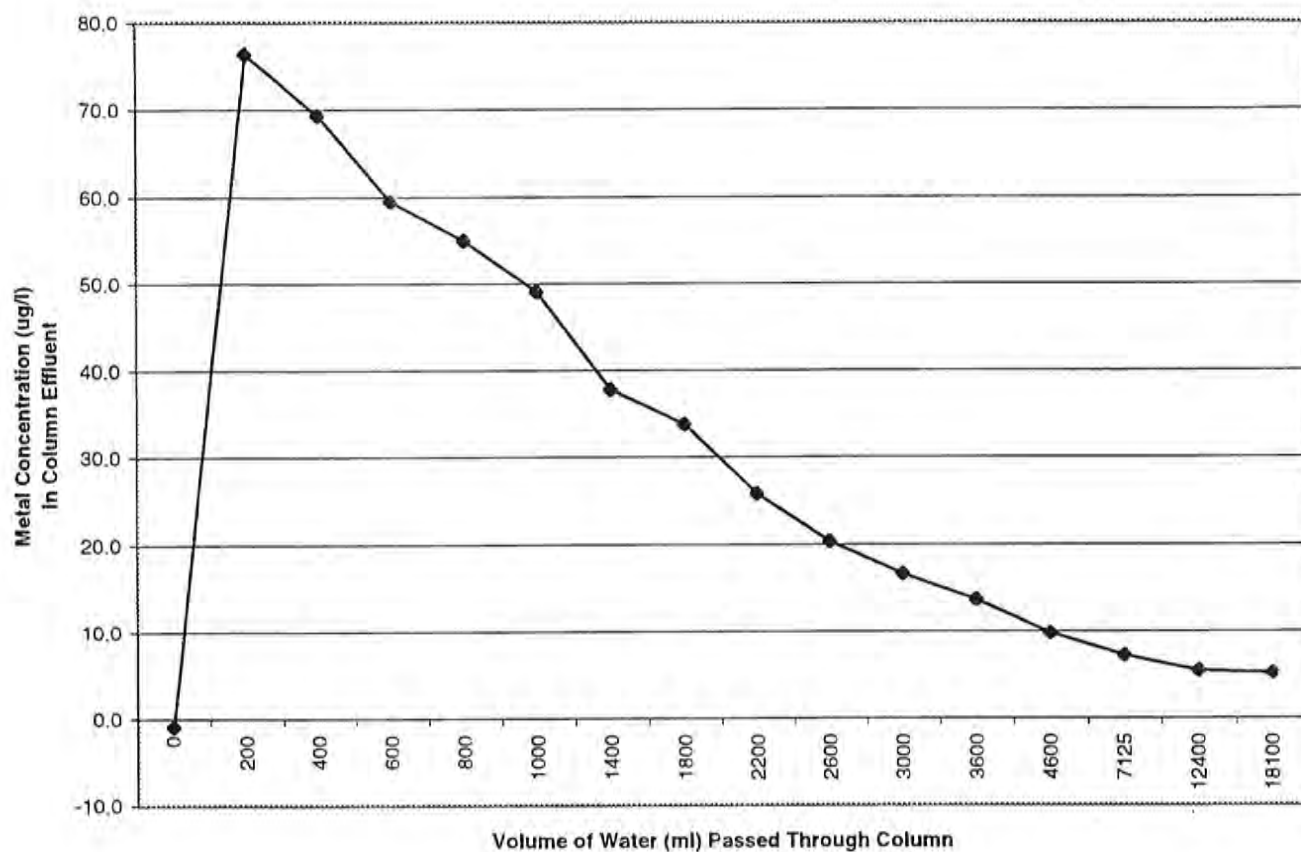


Figure 17. Gies mine arsenic concentration, Z-134, (17a) test #1, (17b) test #2.

µg/L after 20 min (200 mL), then decreasing steadily to a concentration slightly above the beginning concentration (figure 17b).

A similar trend was not observed during previous testing; however, arsenic was not routinely analyzed. The test water used previously also had substantial arsenic concentrations that may have masked a leaching or flushing of arsenic from the Z-127 or Z-134 zeolite material.

Economic Evaluation of the Grasshopper Creek Zeolite Deposit

The economic evaluation deals with Grasshopper Creek zeolite deposit located in Beaverhead County, southwestern Montana, about 3 miles west of Interstate 15, and accessible from exit 59, 10 miles south of Dillon (figure 18). The principal zeolite deposit is partially on homesteaded land on which the surface estate is privately owned and the mineral estate held by the federal government. Other zeolite deposits in the area occur on public and private land. Zeolite is a locatable mineral, which means that zeolite claims can be obtained under the 1872 Mining Law.

The purpose of this evaluation was to estimate whether or not a Montana zeolite deposit could be profitably mined under reasonable economic constraints. The scope of the study is very limited because of the preliminary nature of physical and economic data available. A base-case computerized spreadsheet model (Appendix II) was developed using best estimates of costs, prices, and production levels, and technology suitable for this particular example. Key variables were then tested to determine the physical and economic limits in which mining could take place.

Common and Potential Uses of Zeolites

Zeolites, sometimes called “molecular sieves,” are valuable minerals because of their ability to capture and exchange various ions and to act as catalysts. The CEC is the measure of this ability. The practical application of cation exchange is most commonly encountered by the public in household and industrial water softeners, although that market is met principally by synthetic zeolite. Natural zeolites are used in odor control for barnyards and pet litter because they are particularly effective in capturing ammonia. Other uses in agriculture are for soil conditioning, feed supplements, aquaculture filters, and carriers for fungicides. Some industrial applications are in heavy-metal extraction from nuclear, mine, and industrial waste waters, and as catalysts in purification of gaseous hydrocarbons and production of

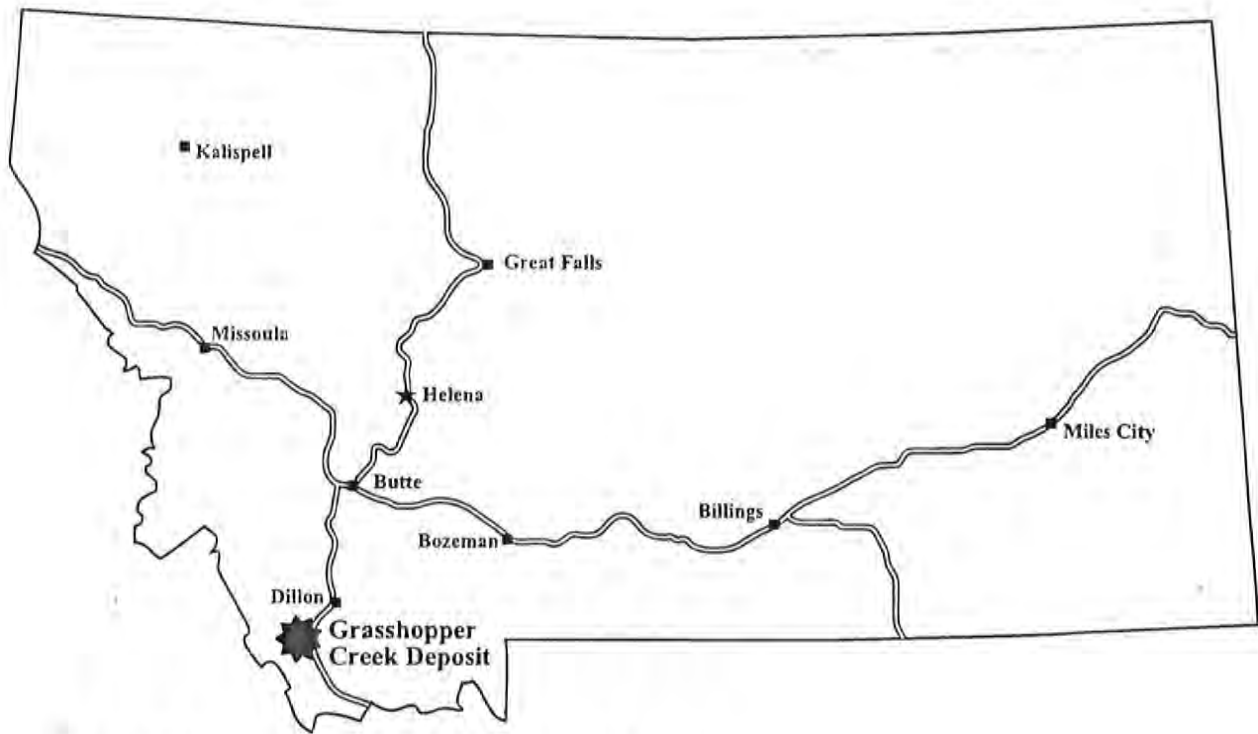


Figure 18. Location map of Grasshopper Creek deposit.

high-octane fuel such as methanol from natural gas. Other and potentially large uses include applications such as stack gas cleanup, oil spill cleanup, and paper filler as a substitute for kaolin clay (Holmes 1994).

Geology and Mineralogy

The geology and mineralogy of this deposit is described in Appendix III, a report by Cox and Brenner-Younggren 1993. They report that Cretaceous volcanic rocks outcrop discontinuously over a 7.5-mi² (200 km²) area and include a basal zeolitic tuff 100 ft to almost 350 ft (30–100 meters) thick in the area of interest. The zeolite minerals consist of clinoptilolite and mordenite in a ratio of 7:1. Ore-grade rock is considered here to be tuffs that have a combined zeolite content of greater than 50%.

Field investigations apparently show that ore-grade rock occurrences indicated by site sampling, and inferred from geologic extrapolation, contain resources more than sufficient for any level of mine production postulated in this economic analysis. Sampling of sufficient extent to calculate grade in terms of weight percent of zeolite, their cation exchange capacity, tonnage and volume of mineable reserves has not been done at this stage. But, as indicated above, it is assumed those reserves would be sufficient based on preliminary work, that is, approximately 500,000 short tons. Moreover, it is assumed that the zeolite material would perform as intended in terms of cation exchange in actual use.

Industry Structure, Production, and Markets

The natural zeolite industry is not large compared to mining of most other metals and industrial rocks and minerals. Production in 1993 was only 45,200 short tons (41,002 metric tons). There are nine potential producers (Virta 1994):

GSA Resources	AZ	
UOP	AZ	
Saint Cloud Mining, Winston	NM	12,400 kt/yr
Steelhead Specialty Minerals	ID	
AIMCOR Corp.	ID	
Teague Minerals	OR	
Zeotech	TX	24,000 kt/yr
American Resources	NV	
U.S. Zeolites	WY	

The producers whose tonnages are reported ship mostly bulk and bagged commodity to the animal litter and agricultural markets. The other producers tend to ship packaged product tailored to specific specialty applications, such as nuclear plant water cleanup. However, their annual production levels are comparatively small (Eyde and Eyde 1993).

In any case, even the two relatively large producers have daily tonnage's ranging only from about 50 to 100 tons per day, quite small by mining industry norms. These rates would correspond to several semi-trailer loads or a single rail car load per day. The transportation cost of low-value commodities is one of the most difficult problems facing such producers.

Mining and Processing Methods

In general, zeolite mining is by low-cost surface-mining methods, using common earth moving machinery. Overburden is removed and zeolite ore extracted with bulldozers with rippers and moved or piled with front-end loaders. Fractured ore is then crushed in a series of jaw, cone, and/or impact crushers, dried and screened to various product sizes. It may be shipped bulk in hopper cars or trucks, in bulk sling bags, or in super sacks. Special high-value products are shipped a few pounds at a time, packaged rather than bulk.

A processing sequence and indication of equipment requirements for the Grasshopper deposit could be as follows:

RIPPER/LOADER
JAW CRUSHER
CONE CRUSHER

COARSE SCREEN
DRYER
IMPACT CRUSHER

Once the thin overburden has been scraped aside, bulldozers with rippers break the zeolite ore, which is then loaded by front-end loaders into haul trucks and transported to the nearby crushing plant. Jaw crushers reduce large boulders to sizes small enough for the gyratory cone crusher to handle. Outflow from that is screened, with fines passing directly to the appropriate stockpile or downstream screen. Oversize is dried, impact-crushed, and screened for fine, intermediate, and coarse product, which are then sent to their appropriate stockpiles, or the intermediate/coarse material given a final fine/scalper screening. Various conveyer belts transfer material from one stage to the next, and a radial conveyor/stacker dumps the final product, perhaps three sizes, into the appropriate bins or hoppers.

The product would then be selectively taken to the loadout facility for loading onto trucks for either direct truck delivery, or in the case of the Grasshopper Creek deposit, for transfer to a siding on the Union Pacific rail line approximately nine miles away.

Additional support facilities, utilities, and maintenance equipment also are required.

Cost and Price Estimates

Mining Costs

The small size of typical zeolite operations does not lend itself to economies of scale, but the simplicity of the earthmoving and screening operations compensates for that factor.

Holmes (1994) reports that "[m]ining costs are fairly low, typically in the \$3.00 to \$6.00 range, unless very selective mining is done." Selective mining would of course increase mining costs. Indeed, one small-volume, selectively-mined deposit is thought to have mining costs of \$70/ton meanwhile sells its specialized product for several dollars per pound, effectively compensating for the high mining cost. Calculation of mining costs by use of a regression equation developed by the U.S. Bureau of Mines, based on southwestern copper mines, results in costs of \$10.55/short ton (IC9298 1992), or \$11.29 in 1994 dollars, adjusted for inflation by the Marshall and Swift index (Chemical Engineering 1994). The calculated copper mining cost serves only as a rough cross-check on those for zeolite reported above, particularly because copper mining is of a different type, and the zeolite operation is far smaller than the sizes intended for use in the equation. But, at least it shows that the order of magnitude is about right. So, for the purposes of this study, the higher reported zeolite mining cost of \$6.00/short ton was used,

thus taking into account the effect of a more severe climate in Montana than that experienced by most other zeolite mines.

It might be possible to reduce these costs considerably by (a) contracting-out the mining and hauling, thus avoiding capital expenditures, and (b) conducting the mining more intensely, over a short period of time, and then processing a large stockpile of raw ore over an extended period of time. This would permit the use of larger scale mining equipment, which results in lower cost per ton if scaled properly to mining rates.

Equipment Costs

Equipment requirements depend on mining and processing design, and on production rates. Here, rates between 50 and 100 tons per day seem appropriate, and as indicated above, the process seems straightforward, thus giving a good idea of machinery requirements. Another important aspect of the low mining rate is that it keeps the operation below 5 acres and 36,500 tons per year, thereby qualifying for the small miners exclusion for operating (SMES) permits (McCulloch 1993). It was further assumed that investors would want to purchase used equipment to reduce capital requirements, which are already significant. Therefore, equipment prices were obtained from current issues of used machinery trade publications (Mine and Quarry Trader 1994). Equipment lists and costs are shown in Appendix III, the Economic Evaluation, and total more than \$700,000, with over \$400,000 in heavy earthmoving machinery alone. As mentioned above, a cost saving alternative to purchasing earthmovers might be to have the ore contract-mined intensively for say a two-month period, and then fed from a stockpile to the crushers and screens on a year-round basis.

Pre-Production Activities and Costs

Ore Reserve Evaluation

Ten surface samples have been analyzed with x-ray diffraction methods for zeolite grade, and their locations plotted on a map of the proposed mine area (Cox and Brenner-Younggren 1993 Appendix III). This verifies the presence of zeolites and provides sufficient justification for a pre-feasibility economic analysis. However to reduce the risk of unexpectedly low grades and absence of sufficient tonnage of ore, a detailed geological map needs to be prepared. Diamond core or rotary drill samples need to be taken on spacing sufficiently close so as to permit calculation of grade and tonnage to a high degree of confidence. Inasmuch as the economic value of zeolite ore is not just a function of the weight

percent of contained zeolite but also is a function of the zeolite's CEC for quantity and kinds of cations, additional laboratory analyses of grade in terms of CEC need to be performed. CEC is commonly determined by testing with the ammonia ion, and thus commonly stated as the ammonia ion exchange capacity. In practical terms, it is a measure of the amount of cations per unit weight of the zeolite that are available for exchange with other ions; it is typically stated in milliequivalents per gram of zeolite, i.e., meq/gm (Holmes 1994). Some examples of CEC's for certain clinoptilolites are listed below ([table 9] Griffiths 1987).

Table 9 . Examples of cation exchange capacities for selected clinoptilolites.

Location	Material	CEC meq/gm
Ash Meadows, CA	Sample	1.85
Mud Hills, CA	PDZ-140	1.65
Mud Hills, CA	PDZ-150	1.55
Winston, NM	Sample	1.85 to 2.20
Naples, Italy	Sample	2.37

No implications are to be made from these data, except to observe that they are from commercial products. However, it should be noted that the CEC for ammonia does not imply that a given zeolite would be effective for some other ion, e.g., copper, zinc, or iron. As a practical matter, a given zeolite would have to be field tested to determine its effectiveness in capturing given ions.

In addition to lab and field work discussed above, an environmental assessment (EA) would no doubt need to be submitted, but probably not a full-scale environmental impact statement (EIS). Expenses for an EA include field time to collect data, assay lab fees, contract drilling, and secure permits for exploration and related activities. Costs in the range of \$40,000 are typical versus costs of \$100,000 or multiples thereof for an EIS.

Once these steps have been completed, zeolite ore needs to be prepared for mining by removing and stockpiling overlying soil that appears to be only a few inches to a few feet thick over the mine area. Commencement of this phase of work would require posting of up to a \$5,000 state reclamation bond (McCulloch 1993). Earthmoving costs depend entirely on the terrain, overburden removed, and push or haul distances. Two weeks of bulldozer work, at a rate of \$100/hr, plus mobilization charges could easily total \$10,000. As a cross check, this was found to be consistent with the cost of clearing five acres of

similar land, calculated with the methods described in Stebbins (1987), namely \$6,300. For this study, the \$10,000 cost is more likely.

Road Building

Road building is the largest single pre-production expense because some three miles of heavy-duty road capable of handling loaded semi-trailers, or hopper trucks and trailers would be needed, as well as a substantial bridge across Grasshopper Creek. A gravel road with a 40-ft roadbed is assumed. Two independent estimates were made; both were in general agreement. The methods used in Stebbins (1987) result in a cost of \$243,462, and those in Camm (1991) a cost of \$282,303, both corrected by the Marshall and Swift index to 1994 costs. The arithmetic average is about \$263,000. A heavy-duty bridge of steel beams and concrete abutments could easily cost \$25,000. So, for this study, a total road and bridge cost of \$290,000 is used.

Utilities

Three miles of 220v, 3-phase power line is estimated to cost roughly \$50,000, confirmed by conversation with Montana Power Company representatives. Three miles of telephone line at a cost of \$1.28/ft, cited by U.S. West engineers as a typical cost, would be \$20,000. Drilling and equipping of a water well, plus distribution lines and tanks is estimated to cost \$10,000. A simple settling or catchment basin lined with clay and/or plastic would be needed to prevent runoff from entering Grasshopper Creek, estimated to cost about \$5,000. Total pre-production costs are over \$400,000, recovered through amortization over a five-year period.

Other Economic Estimates and Constraints

Mine Life and Production Rates

Given the extensive occurrence of zeolitic tuff throughout the study area and the absence of any data to the contrary, ore sufficient to sustain a mine life of 20 years is assumed. A daily mining rate of 100 tons is assumed, and 250 days per year of operation, resulting in 25,000 tons/yr mined, for a total of 500,000 short tons. Not all material mined is processed and recovered, so a recovery of 80% is used, resulting in 20,000 tons/yr of zeolite being shipped. In practice, if recovery were improved, less raw ore would have to be mined to attain the same shipping rate, thus resulting in lower total operating costs,

or conversely, more zeolite could be shipped, using the same or existing mining rate for lower unit costs. Another consideration is the physical location of the crusher and load-out facility. Location at or nearer the interstate highway and Union Pacific rail line would reduce the cost of power lines, and possibly provide the opportunity for capturing lower freight rates from the railroad or truckers looking for loads so as to avoid empty back-hauls.

Prices

A conservative delivered price of \$60/short ton is used, bearing in mind that existing producers are reported to be getting delivered prices of about \$91/short ton or less (Eyde and Eyde 1994). But, an average figure such as this would include bagged product, which commands a substantially higher price than bulk. Holmes (1994) reports prices of \$30–\$70/short ton for granular products down to 40 mesh, and \$50–\$120/short ton for ground products in the range of minus 40 to minus 325 mesh. Consumer products such as pet litter and fish tank filters sell at retail from \$4.50 to \$4,000/ton. In any event, a price of \$60/short ton appears to fall into a reasonable range; moreover, a new entrant into a small market might have to offer lower prices to attract customers. Price would ultimately have to be determined as a joint function of mining costs, acceptable profits, and market strategy.

Transportation Costs

Transportation is a key element of marketing, and its cost is a major factor and uncertain at this stage. A 1,000-mile marketing radius (figure 19) is assumed, which would include all of the major cities in the West from southern California and Denver north, and east to Minneapolis. It is estimated that truck haulage for the entire distance would cost \$40/ton, and 6,000 tons per year would be shipped in that mode. Rail haulage would take the remaining 14,000 tons per year at a cost of \$14/ton. In practice, sales would not all take place at the extreme market radius, but rather throughout the market area to result in a lower weighted average cost. None the less, substantial transportation distances and costs are involved, therefore, high estimates are used.

Loadout Plant

A facility for transferring ground zeolite product from stockpiles or bins to awaiting hopper trucks is required, as are truck scales to determine the actual tonnages shipped. The facility could be

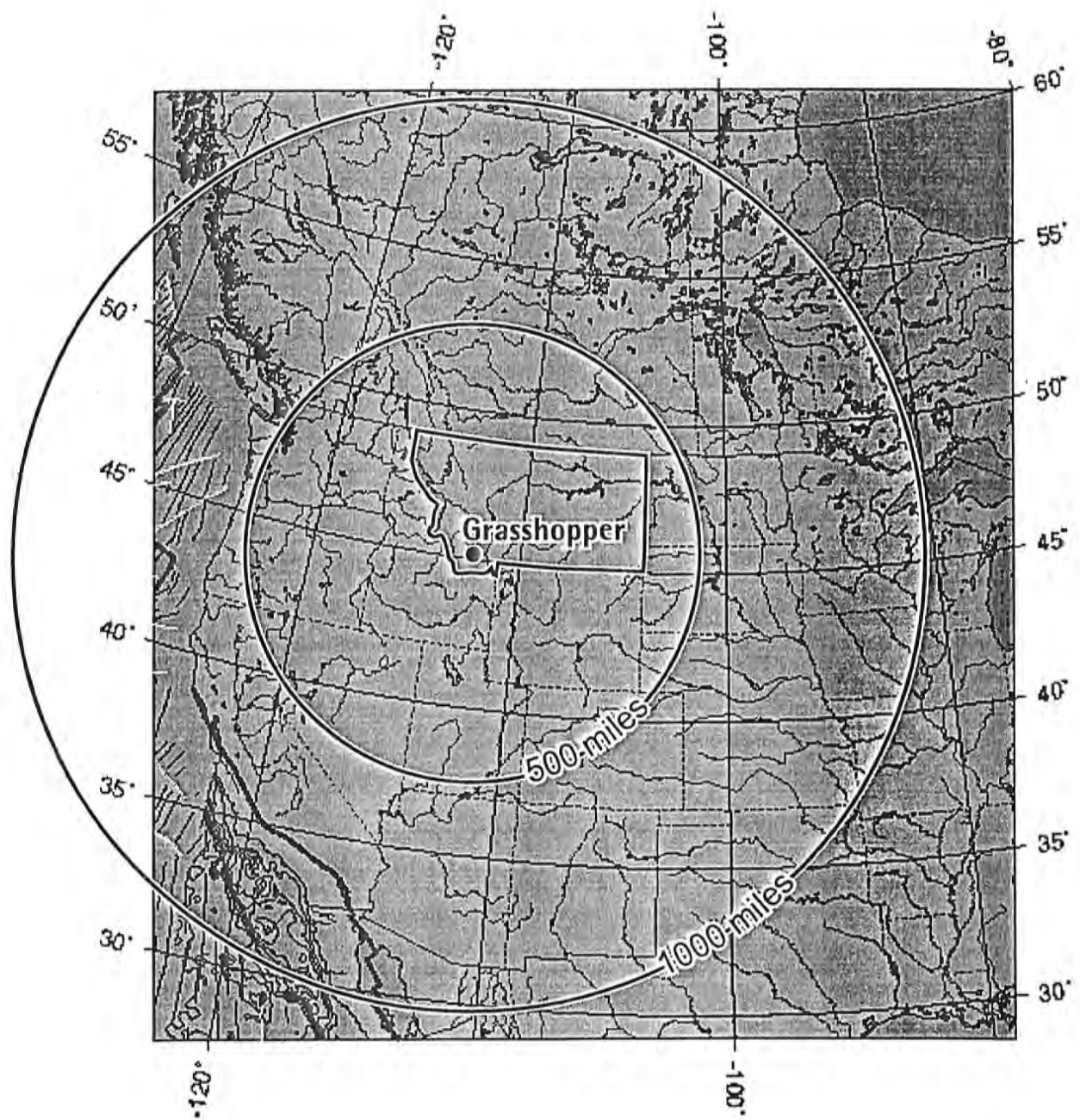


Figure 19. A 1,000-mile marketing radius.

simple bins or silos with passages underneath for trucks to drive through for loading, or could be a conveyor belt system. To simplify the estimates for operations and marketing and to reduce capital costs, no bagging equipment is included for this analysis but would be a likely addition later on, in order to sell a higher priced product. Three employees should be able to operate the loadout facility. Their labor plus overhead, and electric utilities are included in the analysis to total \$108,500/yr.

Taxes and Royalties

Royalties

Miners of locatable (patentable) minerals are not now required to pay production taxes or royalties to the federal government, but it is likely that some level of royalty will be required in the future. Therefore, a royalty of 4% is included to at least partially model the effect of its payment on net income and rate of return on investment (DCF/ROR). Examination of typical state royalties and mineral taxes (Bourne 1994) also seems consistent with this approximate level of governmental taxation. Alternatively, even if no royalty were to be paid, the surface owner would require compensation for disturbance, loss of grazing, etc., and the 4% royalty would allow for that detail.

State and County Taxes

All miners pay a Resource Indemnity and Groundwater Assessment Tax (RIGWAT) of 0.5% of the gross value in excess of \$5,000 of the resource produced. In this case, the tax is about \$6,500/yr. A net proceeds tax is payable to Beaverhead County, based on sales revenues minus allowable cost deductions. In the absence of actual accounting records, this tax is difficult to determine, so for the purposes of this study the tax is assumed to be about 10% of gross revenues, similar to the levels being paid by nearby talc producers and amounting to \$35,000–\$40,000/yr for the assumed levels of zeolite sales. Beaverhead County also levies county property taxes on land, buildings, and equipment. These taxes are estimated by use of standard tax assessment property class categories, average county mill levies, and book values taken after depreciation. State income tax is calculated after expenses, amortization, depreciation, and depletion (Montana Dept. of Revenue 1992).

Federal Taxes

A federal income tax of 34% is deducted after state taxes, to arrive at net income. Depletion allowance is calculated as a straight percentage depletion of 14% of gross revenues after royalties.

Economic Evaluation Synopsis

The key variables for the base case analysis are as follows:

- 20-year mine life
- mining rate of 25,000 short tons per year
- sales of 20,000 short tons
- mining cost of \$6.00/short ton
- sale price of \$60/short ton, delivered.

Taxes and other costs are proportional to revenue and production levels. With the base case assumptions, gross revenues are \$1,300,000 per year to yield a 43% discounted cash flow rate of return (DCF/ROR). If mining actually commenced, it would be most unlikely that *precisely* this DCF/ROR would be realized. It should be emphasized that while the assumptions used in this analysis have been made as realistic as possible, the information base is preliminary, and therefore, conclusions as to profitability are only indicative. The analysis does suggest, however, that given the particular mix of variables used, or more favorable ones, the deposit is mineable at rates of return required for investment in new, high-risk mining ventures, namely the 40% range.

Sensitivity Tests

It is informative to exam the effect on the discounted cash flow/rate of return (DCF/ROR) of having prices, production rates, and mining costs different from those of the base case listed above. The impact prices varying between \$50/short ton and \$75/short ton, production between 70 tons/day and 120 tons/day, and mining costs between \$5/tons and \$10/tons are listed below. Only one variable is tested at a time, with the other two being held at their base case levels.

<u>Price/short tons</u>	<u>DCF/ROR</u>
\$50	16%
\$55	29%
\$60	43% (base case)
\$65	56%
\$70	69%
\$75	82%

<u>Daily Production</u>	<u>DCF/ROR</u>
<u>Tons per day</u>	
65	11%

70	19%
80	27%
90	35%
100	43% base case
110	51%
120	58%

<u>Mining Cost/short tons</u>	<u>DCF/ROR</u>
\$ 5	46%
\$ 6	43% base case
\$ 7	39%
\$ 8	35%
\$ 9	32%
\$10	28%

From this limited examination, it is clear that the price is the most critical variable. Changes in the DCF/ROR are much less sensitive to production rates and mining costs.

A thorough sensitivity analysis can be performed using the Monte Carlo technique in which all values of variables over given ranges of occurrence, e.g., \$5 to \$10/ton mining costs, are assigned a probability distribution with probabilities ranging between zero and one. Then, typically one hundred or more computer "runs" are made, each one using a different mix of values of variables. The values for any given run are determined by random sampling of the distribution for that particular variable. The results of the "runs" are reviewed to identify the most likely and least likely occurrences of various DCF/RORs. As indicated earlier, the data here are too preliminary to warrant such advanced analysis. However, it is beneficial to examine "optimistic" and "pessimistic" cases, and compare the results to the base case, or "best guess" scenario:

	Price	Daily Production	Mining cost	DCF/ROR
Pessimistic:	\$55/short tons	70 short tons/d	\$7/short tons	7%
Base Case:	\$60/short tons	100 short tons/d	\$6/short tons	43%
Optimistic:	\$70/short tons	110 short tons/d	\$5/short tons	84%

Economic Evaluation Results

There is a range or mix of costs, prices, and production, typical of other zeolite mines in which the Grasshopper Creek deposit also might be mined at a profit, and conversely, sets of possible values

in which the operation would be a financial failure. The most important assumption of all is that a market would exist for the product.

Phase III - Greenhouse and Field Test Plots

Late spring snow storms and heavy summer rains prevented field testing of zeolites on abandoned mine(s) discharge during 1995 and 1996. These storms also prevented the establishment of soil test plots at selected abandoned mine sites in the Deerlodge National Forest. Therefore, a greater emphasis was placed on soil amendment tests undertaken in a greenhouse environment and test plots established on various metal contaminated soils throughout Butte.

Greenhouse Experiments

The Buckeye-Enterprise mine, an abandoned mine, located near Basin, Montana, in the Deerlodge National Forest, contains soils covered with tailings from a former mill and soils impacted by heavy metals from waste dumps and or runoff from tailings resulting in barren soils. Soils from this site appear to be washed into Basin Creek during precipitation and runoff events. Site soils were collected and used during greenhouse tests, utilizing zeolites as a soil amendment, to aid in the establishment of various grasses.

Soils were collected from a 6-acre area, to approximately 8 in. below ground surface and placed into burlap bags for transport. Approximately 100 lbs of soil were collected from 8 areas within the area. Samples were allowed to air dry, then homogenized using a cement mixer to ensure soils from each sample area were thoroughly mixed. Table 10 contains trace-metal results from lab analyses of soils from each locations.

Z-134 zeolite material, 10–18 mesh (standard sieve size) was mixed with the soils at 1%, 5%, and 10% rates for each of the eight locations and placed in planters. An additional planter was prepared for each sample location without the addition of any zeolites. Four planters were prepared using potting soils, with the same amendment rates as above. Duplicate planters were prepared for each of the above described locations.

A seed mixture designed, similar to that used by the U.S. Forest Service for use on mine tailings was used. This mixture consisted of 25% red fescue, 25% crested wheat, 20% white clover, 15% red top, and 15% creeping bentgrass. Three grams of this mixture were added to each planter.

Plant growth was established in each planter within weeks of planting. However, in several planters the grass quickly died out. Planters with no zeolite amendment and with only 1% amendment quickly developed a hard pan layer on the surface. This hard pan appeared to act as a barrier to water infiltration because water ponding was obvious during watering. A noticeable density distribution of growth was observed, with a greater density of plants occurring in planters as the percent amendment increased. That is, the best growth of grasses occurred in the planters with a 10% zeolite amendment. Figures 20 and 21 show the difference in plant growth for the various planters over a one-month period. Figure 22 shows growth variation for planters with various rates of amendments and potting soil with a 5% zeolite amendment.

Table 10. Soil sampling results of buckeye-enterprise mine site (concentrations are mg/kg).

Sample Location/ Site ID	As	Cd	Cu	Pb	Zn
A-1	8,180	5.7	84.	16,000	801.
A-2	13,000	4.9	150.	22,000	629.
A-3	12,000	4.3	122.	11,000	513.
A-4	11,000	<4.	160.	10,000	398.
A-5	7,342	<4.	184.	11,000	254.
A-6	14,000	4.4	180.	11,000	394.
VS*	3,904	<4.	169.	2,258	340.
NVS**	5,819	<4.	158.	4,201	247.

* Soil Sample from vegetated portion of site

** Soil Sample from non-vegetated portion of site

Table 11. Vegetation analysis of selected greenhouse plots (concentrations are mg/kg).

Sample Location/ Site ID	Percent Zeolite	As	Cd	Cu	Pb	Zn
PS*	1%	7.38	<2.	41.6	8.78	170.
A-1	5%	129.	<4.	377.	2,817.	411.
A-2	1%	2,558.	<2.	241.	1,963.	177.
A-3	10%	4,418.	6.27	289.	2,056.	391.
A-4	1%	1,661.	8.96	697.	1,959.	1448.

* Potting Soil

Studies have been undertaken to not only use zeolites as a soil amendment preventing the migration (leaching) of heavy metals into the soil profile, but to also inhibit the uptake of metals in edible plants.

Ellis (1986) and Robinson (1988) describe the uptake of radioactive cesium in food grown on Bikini Atoll, an island in an area where aboveground nuclear testing took place. They reported that the addition of clinoptilolite to soils significantly reduced cesium levels in sweet potatoes grown in contaminated soils.

Leppert (1990) reported on the efforts to use zeolites to immobilize lead and reduce plant uptake levels below toxic concentrations for plant growth, at the Bunker Hill, Idaho, EPA Superfund site. While the initial field tests failed because of the extremely high lead levels, he reported that others investigators had been successful using zeolites as a soil amendment to establish plant growth.

Table 11 contains results of vegetation samples, from selected planters. Lead and arsenic concentrations (uptake) in these tissue samples vary from less than 2% to almost 40% of the soil concentrations. It appears that the addition of zeolites to contaminated soils may have reduced the uptake of certain trace metals by the grasses selected for this study, although, the degree of reduction was not great. No plant growth was established and maintained in any of the unamended soils from the Buckeye-Enterprise mine site.

Field Test Plots

Field test plots were established at three different areas near Butte. The areas were selected to represent different soil conditions. The areas selected for plots were as follows:

MT Tech—an area of soil wash from the BA&P railroad tracks, southwest of MT Tech. There appeared to be waste rock and tailings material washing over soil adjacent to railroad. No apparent vegetation growth in areas where test plots were established.

MPC—an area of land adjacent to Silver Bow Creek, near its confluence with Blacktail Creek. It appears that mine waste, including tailings, have washed over soils near the stream. Vegetation is sparse throughout the area, while salt precipitates are present on the surface. No vegetation was present in the areas used for test plots.

MR—an area west of concentrator and south of crusher, in an area where Montana Resources (MR) has conducted revegetation studies previously. The vegetation in this area is in revegetation test plots.

Four test plots were established at each location with each test plot being approximately 6 ft by 6 ft. Of the four test plots one was unamended, and the other three plots received zeolite (Z-134) amendment rates of 3%, 6%, and 13%, respectively. The size of the zeolite material used was 3/4 in. minus, with a fair amount of fine material. Each plot was initially tilled, the zeolites were then applied, and the plot was re-tilled. The grass seed was then sown onto each plot at a rate of approximately 630 lbs/acre. The seeds were raked into the soil and hand tamped with a rake. Bulk soil samples were collected and composited from all four plots at each site and submitted for lab analysis. Soil sample results are contained in table 12.

Lodgepole pine and quaking aspen trees were planted on the edges of the MR test plots. Twenty trees of each species were planted. One-half of the trees were planted with no amendment, while the other half had approximately 20 lbs of zeolite added to the hole. Trees also were ordered for the other two sites; however, they did not arrive in time for planting.

The establishment of grass in the various test plots was very mixed. A good growth of grass was established in all four of the MT Tech plots, while grass germinated at the three amended plots at MR but then appeared to die out. There was no germination of grass in the unamended plot. It appears the grass died off as a result of non-watering and extreme summer heat. The plots were established during late June and early July, when temperatures were reaching their highest levels and precipitation was sparse. The MPC test plots also were established during the same time period. No growth was observed in any of the four test plots until collecting soil samples the end of September. A small patch of grass was evident in plot #4, which received the highest amended rate.

Soil samples were collected and analyzed from each test plot at the end of September 1996. Samples were collected from barren portions of the test plot (i.e., MT 1-1) and also from areas with plant growth (i.e., MT1-2). Results of this sampling are contained in table 12.

Two things are apparent from table 12. The first being that arsenic (As), copper (Cu), lead (Pb), and zinc (Zn) concentrations are highly variable at each site, with concentrations of samples collected in the fall higher than those from spring/summer background samples. Secondly, pH values for the MPC site were higher after being amended, while pH values from the MT Tech site with vegetation were higher than those in the non-vegetated areas of the plot. This was true at the one MPC plot with grass establishment. It appears that in the acidic soils, the applied zeolite amendment acted to help neutralize the soil.

Table 12. Zeolite field test plots soil analysis.

Zeolite Test Plots									
Plots Amended with Z-134									
Sample Site *	Percent Amendment	pH	As mg/kg	Cu mg/kg	Pb mg/kg	Zn mg/kg	Comments		
MPC		3.38	78	152	249		141 Background, composite sample		
MPC1-1	None	4.20	260	1862	327		1288		
MPC2-1	3%	3.78	219	974	316		981		
MPC3-1	6%	4.64	103	1204	327		1166		
MPC4-1	13%	3.75	66	141	231		189		
MPC4-2	13%	4.24	72	177	218		254 Small area of grass growth in NW corner		
MT Resources		7.23	25	1926	86		388 Background, composite sample		
MR1-1	None	6.95	9.9	2610	127		560		
MR2-1	3%	7.25	14	1442	58		337		
MR3-1	6%	7.19	9.1	1760	121		421		
MR4-1	13%	6.43	21	124	65		162		
MT Tech		6.74	15	114	61		161 Background, composite sample		
MT1-1	None	5.94	18	135	59		184		
MT1-2	None	6.81	22	146	57		186		
MT2-1	3%	6.60	22	209	54		443		
MT2-2	3%	7.25	20	117	88		602		
MT3-1	6%	5.20	32	182	88		378		
MT3-2	6%	5.55	31	132	93		623		
MT4-1	13%	6.90	13	2276	68		613		
MT4-2	13%	6.92	38	156	155		549		

* Suffix -1 Barren Soil

* Suffix -2 Vegetated Soil

SUMMARY AND CONCLUSIONS

This study was broken into three phases: 1) literature search, 2) laboratory attenuation tests and economic evaluation, and 3) greenhouse and field test plots. In addition, the MBMG conducted a companion field investigation locating and identifying zeolite occurrences throughout Montana. Positive findings were necessary at the completion of each of the first two phases for the project to continue on to the following phase.

Phase I—The literature search revealed numerous references in the literature relating to zeolites and heavy metals; zeolites have been used for the removal of ammonia from waste waters and in the cleanup of radioactive wastes at nuclear facilities; and the study proposed was unique and would not be a repeat of previous studies, but would complement ongoing U.S. Bureau of Mines research.

MBMG geologists examined 39 localities and verified the presence of zeolites, of one type or another. One hundred ninety samples were collected and analyzed by x-ray diffraction. Clinoptilolite was the dominant zeolite identified in all occurrences.

Phase II—Laboratory attenuation tests determined that selected Montana zeolites removed concentrations of copper, cadmium, and zinc in solution when minor amounts of zeolite was added to the solution and left in contact for various times ranging from 10 to 1,000 minutes.

Further attenuation tests using test columns filled with zeolites also removed (lowered) numerous trace-metal concentrations from sample waters that were passed through the columns. Waters used for testing were from a highly contaminated ground water and from a discharge at an active mine. Tests were run using four different Montana zeolites and two commercially available, non-Montana zeolites. Once again, tests results showed the Montana zeolites were capable of lowering trace-metal concentrations in the test waters; however, each zeolite performed differently, that is, while they all removed trace metals from solution, the level of removal was variable. The two commercial zeolites and Montana Z-466 were the top performers.

Cation exchange capacity (CEC) was determined on 81 of the 190 samples collected during field activities. CECs varied considerably from a low 0.08 meq/g to a high of 1.90 meq/g. The average CEC for the Montana zeolites was 0.97 meq/g.

An economic evaluation for the development of a Montana zeolite deposit was completed, using the Grasshopper Creek deposit for cost estimates. This deposit was the largest one investigated during the MBMG companion study. While this evaluation included a considerable number of assumptions, as

most economic evaluations do, it did determine that the deposit could be mined at a profit, although, there are several options under which the development would be a financial failure. The evaluation considered a market area (radius) of 500 and 1,000 miles.

The final phase of the project consisted of greenhouse and field test plot studies. Water treatability tests at abandoned-inactive mine sites were originally part of the study, but the late winter and early spring snow storms during 1995 and 1996 prevented this from occurring. Therefore, activities focused on soil treatability tests; however, they were affected by the same weather conditions.

Greenhouse studies were begun using highly contaminated soils from an abandoned mine site. These soils were amended with zeolite additions of 0%, 1%, 5%, and 10%. Control plots also were established using potting soil. The level of zeolite addition affected the level of plant growth, with the greatest density of plants occurring in the higher amended soils. Plant growth was not established in the untreated soils.

The field test plots had mixed results, possibly as a result of highly variable soil conditions, planting time and weather conditions, especially the lack of rain for long periods of time, followed by short-duration, high-intensity storms.

This study produced initial data for comparing the effectiveness of Montana zeolites in the attenuation of toxic, heavy metals against commercially available zeolites. While not all phases of the project produced the results or data originally hoped for, it established that a Montana zeolite deposit could economically be developed and that Montana zeolites compare favorably to existing commercial deposits in the attenuation of selected heavy metals.

The MBMG is using information from this study to design zeolite test columns to be used for removal of iron, turbidity, and trace metals (i.e., copper and lead) from small municipal water supplies.

MBMG personnel also will continue to monitor the progress of the field test plots to determine if additional vegetation will be established or if existing vegetation dies out.

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APPENDIX I
BIBLIOGRAPHIC DATABASE LISTING

1978 Combined effluent streams treatment combats cost, energy consumption 21-23

1989 Groundwater quality and waste management research 8 A Listing of Electric Power Research Institute Publications

1989 Zeolites: Facts, Figures, Future New York, New York Elsevier Science Publishing Company Inc. 49 1466

1989 Heavy metal removal from gold mining and tailings effluents using indigenous aquatic macrophytes P. Lane and Associates Limited June, 1989 Gold mining in Nova Scotia. Ways to reduce ecological consequences of reclaiming gold from tailings in Nova Scotia. Mercury and Arsenic

1990 Bio-recovery systems removal and recovery of metal ions from groundwater US Government Printing Office 45 EPA su

R. Aiello, A. Nastro and C. Colella 1978 Chemical aspects of one iron removal process 18 611,613,615,617 This paper represents the first part of a larger research still in progress and presents the results of an experimental investigation into the possibility of using chabazite tuff, suitably treated, as manganese zeolite in the process of iron removal from water.

By comparing the breakthrough curves of various manganese ion exchangers, the larger capacity of chabazite tuff for iron removal is demonstrated in comparison with the more usually employed greensand and clinoptilolite tuff. The aptness of chabazite tuff to act as manganese zeolite even after several regenerations is finally emphasized.

Z. Alikhani, G. S. V. Raghavan and E. Block 1990 Effect of particulate medium drying on nutritive quality of corn 79-83

P. I. Andreev and N. M. Anichenko Natural Zeolites as regulators of flotation of polymetallic ores 99-101

R. D. Andrews, D. Bucknam and D. Holm 1991 Using Clinoptilolite for the Removal of Toxic Heavy Metals from Contaminated Mine Drainage 1-6

M. Arnould, C. Clement, D. Gouvenot and R. Struillou 1991 New sorbing grouts for radioactive and toxic heavy metals 30 127-139

O. Y. Ataman and H. B. J. Mark 1977 Determination of ammonia in aqueous solutions by infrared spectrometry following preconcentration of zeolite 49 1331-1335 A new method for the determination of ammonia in aqueous solutions has been developed. In this method, NH_4^+ species is preconcentrated on zeolite AAA matrix in a batch process, and then a portion of the zeolite is sampled using a KBr pelleting technique. The infrared spectrum of the pellet is taken and the intensity of the NH_4^+ bending vibration band at 1402 per cm is used to calculate the $\text{NH}_3\text{-N}$ concentration in the sample solution. The results of analyses had recoveries better than 95.0% and the precision of the method was varying from 5 to 12 % mean deviation for the $\text{NH}_3\text{-N}$ concentrations between 14.0 to 0.50 ppm. this infrared method using preconcentration is useful for field studies as it has the advantages of simplifying the transportation and eliminating the necessity of preservation of the samples.

B. E. Blom 1974 Sorption of Cadmium by Soils 1-32 A brief review of the literature on cadmium in the environment, with emphasis on its role in soils and water, is presented. Experimentally, the interaction of cadmium with two soils and one naturally occurring zeolite was examined using calcium-saturated and potassium-saturated samples. The soils preferentially bound cadmium in the presence of either calcium or potassium with decreasing calcium sensitivity as the fractional cadmium surface coverage increased. Cadmium sorption was relatively higher for the potassium soils as compared with the cadmium soils. For the loamy fine sand this increase was accounted for by electroselectivity principles, while such reasoning was inadequate to explain the increases observed with the Charleston loam sample. The preference for cadmium over calcium, as measured by the selectivity coefficient, was higher for the sandy soil. The zeolite was found to be calcium-selective. A method for monitoring the flow of cadmium through soil columns was examined. The use of spatial filtering, involving Fourier Transforms, was found

to be a suitable technique for monitoring the changes in cadmium concentration as it flows through soils. The experimental technique involves the use of gamma-emitting metal isotopes in conjunction with an external scintillation counter; thus the soil column remains undisturbed and may be used for several experiments.

D. W. Breck 1974 Zeolite Molecular Sieves New York John Wiley & Sons 771

D. W. Breck 1984 Zeolite Molecular Sieves Malabar, Florida Robert E. Krieger Publishing Company 771
Introduction to zeolite molecular sieves. Details on structure, properties, characterization, synthesis, chemistry and commercial materials

G. H. Bryan, R. W. Goles, C. A. Knox and D. H. Siemens 1984 Summary of Radioactive Operations for Zeolite Vittrification Demonstration Program 1-31 The Zeolite Vittrification Demonstration Program (ZVDP) has successfully vittrified the zeolite used in the Submerged Demineralizer System (SDS) at Three Mile Island (TMI) Unit 2 to a borosilicate glass product. Under the ZVDP, the U.S. Department of Energy authorized the Pacific Northwest Laboratory (PNL) to demonstrate the vittrification process on a full scale by use of the in-can melter process.

This program was accomplished in two phases. The first phase developed a glass formulation and demonstrated the vittrification process with nonradioactive materials. The second phase recieved three radioactive liners from the SDS and vittrified the zeolite contained in each.

The first of the three radioactive liners contained a total of ~13,000 Ci (137Cs, 90Sr, and associated daughter products), and was recieved from TMI during May of 1982. The second and third SDS liners were recieved in January of 1983 and contained a total of ~113,000 Ci each.

The radioactive zeolite from each of the three liners was vittrified in four canisters. Each canister was filled to a height of 2 m with vittrified product and weighed about 170 kg. The process effluents were also characterized to provide basic off-gas engineering data around which an effective off-gas processing system could be designed.

These studies concluded that emission of melter-generated aerosols is responsible for most radioactive, process-related losses to off-gas system. Tritium, in the form of water vapor, is the only significant gaseous radioactive effluent generated by the vittrification of TMI zeolite waste.

L. Burris 1985 Nuclear Technology Programs Quarterly Progress Report 1-46 Studies of the ability of backfill to inhibit groundwater flow in a nuclear waste repository are reviewed. They involve permeability measurements, which are fundamental in determining whether the waste may be considered to remain isolated in the repository. Additional data on zeolite compositions have been obtained using new instrumentation and techniques for mineral separation. Tests using natural humic and fulvic acids taken from surface waters and added to groundwaters from wells in the Columbia River basalt show a strong correlation of americium complexation with acid concentrations in the groundwaters, but a weak correlation in the case of neptunium. A new effort to study the use of a TRUEX solvent extraction process for the Plutonium Finishing Plant waste stream is under way. The process is to remove plutonium and americium and then separate them. Destructive analyses of irradiated fuel rods continues. Work on several of the anticipated 16 or 17 rods has been completed.

R. M. Carland and F. F. Aplan 1988 Stability and ion-exchange capacity of natural sedimentary zeolites in acidic solutions 292-305

M. J. T. Carrondo, J. N. Lester and R. Perry 1981 Type A zeolite in the activated sludge process-II: heavy metal removal 53 344-351

M. J. Carrondo, J. N. Lester and R. Perry 1983 Sedimentation of zeolite type A in water and wastewater 23 271-280

P. C. Chan, J. W. Liskowitz, M.-S. Sheih and R. Trattner 1983 Polishing industrial waste stream effluents using fly ash - natural clay sorbent combination 1-48

N. Y. Chen and T. F. Degnan 1988 Industrial catalytic applications of zeolites 84 32-41

E. D. Collins, J. M. Begovich, C. H. Brown, D. O. Campbell, L. C. Lasber, M. I. Morris, S. M. Robinson and C. B. Scott 1988 An Improved ion exchange method for treatment of slightly contaminated wastewaters 1-15
An improved method is being developed for the treatment of wastewaters that contain predominantly calcium, sodium, and magnesium bicarbonates and are slightly contaminated with ^{90}Sr and ^{137}Cs . The process decontaminates the water sufficiently for release to the environment while concentrating the radioactive materials into a nonhazardous waste form that can be safely stored with minimum surveillance. The water is passed through a series of columns containing a natural chabazite type zeolite. The loaded zeolite in discharged columns is dewatered and transferred to a disposal container. Excellent results have been obtained in both partial and full-scale tests. The process is simple, reliable, and economical.

T. H. Eyde 1978 Bowie Zeolite an Arizona industrial mineral 8 1-5

T. H. Eyde 1982 Zeolite deposits in the Gila and San Simon valleys of Arizona and New Mexico 65-71 Several deposits of zeolite minerals occur in Cenozoic rocks in the Gila and San Simon Valleys both in New Mexico and Arizona. Zeolite deposits occur not only in the lacustrine beds within the valleys but also in vitroclastic tuff beds intercalated with the volcanic rocks that form many of the mountain ranges bounding the valleys. Though the geological processes that formed these two types of deposits are diverse, the actual geochemical reactions involved in zeolitic alteration are nearly identical. Zeolite minerals in both types are alteration products resulting from the reaction between volcanic glass and saline-alkaline waters. The saline-alkaline lake deposits that are the subject of this paper are the most important of the two types. These deposits consist of one or more stratiform beds of high-purity zeolite minerals interbedded in lacustrine beds. The deposits are the alteration product of volcanic ash initially ejected into the atmosphere by distant volcanism during the Pliocene-Pleistocene time. The vitric phase of the airborne volcanic ash was carried large distances by the prevailing winds and eventually deposited in shallow lakes in the Gila and San Simon Valleys. Following deposition, the ash reacted with the saline-alkaline lake waters to form zeolite minerals. Sedimentary processes in the shallow, saline-alkaline lakes were active before, during and following the deposition of the vitric ash. Consequently, the degree of zeolitic alteration as well as the thickness and areal extent of the zeolite beds are directly related to the depositional history of the basins. Two zeolite deposits in the San Simon and Gila Valleys are in production. The zeolite deposit near Bowie, Arizona has produced chabazite used to purify sour natural gases and also to remove cesium 137 and strontium 90 from liquid nuclear reactor wastes. The zeolite deposit near Buckhorn, New Mexico, produces clinoptilolite used to denitrify sewage effluent and to produce organic fertilizer from poultry manure. The chabazite deposit in the Dripping Springs Valley has been explored by drilling. Several unexplored chabazite deposits occur in the vicinity of Bear Springs, near Pima, Arizona.

S. Forberg, T. Westermarck, R. Arnek, I. Grenthe, L. Färlth and S. Andersson Fixation of medium-level wastes in titanates and zeolites: Progress towards a system for transfer of nuclear reactor activities from spent organic to inorganic ion exchanges 867-874

C. A. Fyfe, Y. Yeng, H. Grodnev, G. T. Kokotailo and H. Gies 1991 One- and two-dimensional high-resolution solid-state NMR studies of zeolite lattice structures 91 1525-1543

M. Gaspard, A. Neveu and G. Martin 1983 Clinoptilolite in drinking water treatment for NH_4^+ removal 17 279-288 The objective of this study is to develop a technique to remove ammonium ion from water intended for potable purposes. An ion exchange method is used with a selective ion exchanger, a natural cation zeolite, clinoptilolite. Glass columns are used for laboratory experiments. These experiments show that the NH_4^+ exchange capacity is very small compared to its total capacity 2.17 meq g⁻¹; its value depends essentially on the NH_4^+ initial concentration and less on the Ca^{2+} concentration in the influent water. We were particularly interested in waters weak in ammonium concentration ($\text{NH}_4^+ = 1-3 \text{ mg/l}$). In this case and for ~ 1 and 2 mg/l NH_4^+ concentration in water, the practical capacity is only 0.06 and 0.108 meq/g respectively. The leakage is smaller than the ECC limit (European Community Council) for drinking waters ($\text{NH}_4^+ < 0.5 \text{ mg/l}$) and the treated volume of water to breakthrough, defined at 0.5 mg/l of NH_4^+ is $> 720 \text{ BV}$ (BV = bed volume) in both cases.

T. Goto and T. Hakuta 1977 Pollution problems in a distillation process 23 245-253 In considering pollution of coastal seawater, one must expect some degrade of product water in a distillation process. Also, diffusion of waste brine from a desalination plant into the sea should be estimated on account of seawater intake design and of environmental protection. This paper is concerned with the pollution problems to be studied for a distillation process.

Chemical analysis of sulfide ion at concentrations lower than 1 ppm was developed, and the procedure was applied to a field survey of pollution at Tokyo Bay. Distributions of volatile pollutants in a distillation process were studied with experiments of both laboratory and field tests. The results revealed that ammonia had a tendency to concentrate in fresh water. Consequently, some processes were studied to prevent from ammonia contamination. Concerning diffusion of waste brine, fundamental experiments were combined with measurements of actual brine discharge from the test module of the National Project. It was found that a submerged type of device was effective to reduce influential extent of waste brine.⁴

J. Griffiths 1987 Zeolites cleaning up. From the laundry to Three Mile Island 19-33 Natural zeolites, despite their tremendous versatility and huge market potential, have yet to receive customer acceptance in most market area. Their synthetic counterparts, on the other hand, have already successfully established and developed a number of specific markets and, within these, producers continue to refine and add to their product range. The reason for this discrepancy appears largely to be due to the lack of facilities of the natural producers. In the last five years ownership of some deposits has changed hands several times. However, companies involved still tend to be relatively small (with some exceptions) and without the technical and financial back-up facilities to support the intensive research and development work necessary to put zeolites on the map. Instead producers must, for the most part, rely on potential customers, by contrast, tend to be large corporate entities with significant facilities and a continual eye to development. In many cases these manufacturers are producing zeolites as a complementary range to their existing product lines.

Natural zeolites have to date found their greatest acceptance as dimension stone and in markets such as water treatment, animal feed and odor control whereas synthetic zeolites have made a major impact in areas of considerably higher value-in catalysis, adsorbents/desiccants, and detergents (albeit prompted by environmental legislation and concern).

For the most part there is little overlap in the fields of application for these two zeolite groups with the exception of radioactive waste treatment where, for example, Union Carbide has been able to utilise both its natural and synthetic products. Increasingly we may witness a change in this trend and some synthetic producers have already indicated a desire to diversify further into fields "traditionally" served by natural zeolites. Similarly, if natural producers put more resources into adding value to their product, or selling zeolite together with a process, as ATEC Inc. is doing, they too may be able to infiltrate hitherto inaccessible markets. In Japan, for example, zeolites are used in paper manufacture but elsewhere their hardness and lack of brightness preclude them from this use. However, work is being conducted to look at a possible means of bleaching the natural mineral which may provide another market opening in areas lacking traditional filler minerals.

C. Gruesbeck and R. E. Collins 1982 Entrainment and deposition of fine particles in porous media 22 847-856 Entrainment and redeposition of naturally occurring fine particles in porous media has been suggested as a mechanism leading to abnormal decline in productivity of producing wells. This paper describes the results of studies conducted to determine factors affecting this phenomenon. Experimental work done as part of this study provides the basis for a proposed phenomenological theory of entrainment and deposition. the central concept of this theory is representation of both particle and pore size distributions by partitioning the porous medium at any cross section into parallel plugging and nonplugging pathways. this simple model appears to be completely adequate for describing a broad class of filtration and entrainment phenomena. We have shown that fines entrainment and redeposition are mechanisms that can cause abnormal productivity decline and are phenomena restricted to the near-wellbore region.

D. B. Hawkins 1976 Mordenite deposits and zeolite zonation in the Horn Mountains area, south-central Alaska College, Alaska Division of Geological & Geophysical Surveys 9 Horn Mountains of Alaska

D. A. Henry—1988 Minerals from the Clunes Goldfield 3 43-52 Large crystals of barium-pharmacosiderite and attractive specimens of rhodochrosite were collected from the Port Phillip Company Mine during gold mining operations at Clunes during the late 1800s. From the southern region of the goldfield and interesting suite of zeolites, including chabazite, levyne, mesolite and thomsonite, was obtained from shafts sunk through the basalts overlying deep leads.

K. J. Hofstetter, C. Hitz, K. L. Harner, P. S. Stoner, G. Chevalier, H. E. Collins, P. Grahn and W. F. Pitka 1982 Chemistry support for Submerged Demineralizer System Operation at Three Mile Island 301-312 Facilities have been designed to provide chemical analysis support for the operation of the Submerged Demineralizer System (SDS) at Three Mile Island (TMI). The SDS is designed to process 2.5 megaliters (MI) of highly contaminated water in the Unit-2 reactor containment building (RCB) and 340 Kiloliters (kl) of reactor coolant system (RCS) water. Processing is accomplished by passing the contaminated water through vessels loaded with inorganic zeolite sorbents which remove the majority of the radiocesium and radiostrontium activities. Further polishing of the water is performed using organic ion exchange resins. Special analysis methods, equipment, and techniques of handling highly radioactive samples are required. Analysis results are used to insure adequate process control and to determine radionuclide sorbent loadings. The SDS has been used to process approximately 580 kl of low-activity water stored in the reactor coolant bleed tanks (RCBT). Processing data show that the SDS can concentrate the radionuclides on a small volume of sorbents while achieving high effluent water quality.

M. H. Hulbert 1987 Sodium, calcium, and ammonium exchange on clinoptilolite from the Fort Laclede deposit, Sweetwater County, Wyoming 35 458-462 Clinoptilolite from the Fort LaCledé deposit in Sweetwater County, Wyoming, shows a moderate selectivity for NH_4^+ over Na^+ in aqueous solution. At 30 degrees C, the standard free energy of this replacement reaction is -0.7 kcal/mole at an ionic strength of 0.05 M and -0.8 kcal/mole at 0.5 M. The $\text{Na}^+ - \text{NH}_4^+$ exchange is complete within 3 days in agitated solution and proceeds to the same extent from the clinoptilolite saturated with either cation.

The $\text{Ca}^{2+} - \text{Na}^+$ exchange is also complete within 3 days in agitated aqueous solution and proceeds to the same extent from either the calcium or the sodium form of the zeolite. Using test methods which take into account the slower equilibration of Ca^{2+} -loaded clinoptilolite, the cation-exchange capacity is substantially the same over the full range of loading by Ca^{2+} and Na^+ . Ca^{2+} replaces Na^+ with the decreasing selectivity as Ca^{2+} loading increases to about 80% at 30 degrees C (95% at 63 degrees C), above which the selectivity reverses. The standard free energy replacement of two Na^+ ions by one Ca^{2+} ion in 0.05 M solution is -1.2 $\pm$ 0.2 kcal/mole at 63 degrees C and -0.3 to -0.8 kcal/mole at 30 degrees C.

H. S. Hundal, R. B. Trattner and P. N. Cheremisinoff 1979 From Screening to Filtration Treating the Water Supply 48-51

P. J. Jarvis 1983 Heavy metal pollution Geo Abstracts Ltd 420

J. F. Kerrisk 1983 Reaction-Path Calculations of Groundwater Chemistry and Mineral Formation at Rainier Mesa, Nevada 1-41 Reaction-path calculations of groundwater chemistry and mineral formation at Rainier Mesa, Nevada, have been done using a model of volcanic-glass dissolution by water that is initially saturated with CO_2 . In the reaction-path calculation, rate processes control the availability of species through dissolution of volcanic-glass, and equilibrium processes distribute the species between the aqueous phase and mineral phases in equilibrium at each step in the reaction path. The EQ36 chemical equilibrium programs were used for the calculation. Formation constants were estimated for three zeolites (clinoptilolite, mordenite, and heulandite), so they could be considered as possible mineral precipitates. The first stage of mineral evolution, from volcanic glass to a cristobalite, smectite clay, and zeolite mixture, was modeled quite well. Predicted aqueous-phase compositions and precipitates agree with observations at Rainier Mesa and other Nevada Test Site areas. Further mineral evolution, to quartz, clay, analcime, and albite mixtures, was also modeled. Decreasing aqueous silica activity from the first stage, where cristobalite precipitates, to later stages, where quartz is present, was the controlling variable in the mineral evolution.

F. M. Kishk, T. M. Abu-Sharar, N. M. Bakry and M. B. Abou-Donia 1979 Sorption-desorption characteristics of methyl parathion by clays 8 637-645 Methyl parathion (O, O-dimethyl O-(4-nitrophenyl) phosphorothioate) adsorption was studied on montmorillonite, kaolinite, halloysite, natural zeolite, ion exchange resins and calcium carbonate. Methyl parathion was highly adsorbed by montmorillonite, followed by zeolite, and very little adsorption was obtained on kaolinite and halloysite. Calcium carbonate did not exhibit any adsorption. The values of the partial molar energy " ΔG " were calculated for all systems. For the montmorillonite-methyl parathion system, the calculated partial molar heat of adsorption " ΔH ", and the conformity of the data to Freundlich equation indicated a possible physical mechanism of adsorption. Increasing acetone concentration decreases methyl parathion adsorption and dehydration increased adsorption in the nonaqueous system. Moreover, the increased adsorption on the swollen clay indicated that methyl parathion was adsorbed on the interlamellar surfaces of the clay. This was also in agreement with the results of the desorption studies, since the insecticide was not desorbed using the same aqueous acetone solution. This indicated that methyl parathion was adsorbed as a water-insoluble organic compound.

J. R. Klieve and M. J. Semmens 1980 An evaluation of pretreated natural zeolites for ammonium removal 14 161-168 Clinoptilolite has been widely studied for ammonium removal in the past 2 years. However, many investigators have reported variations in the measured capacities of samples of clinoptilolite. These studies and the factors believed to influence measured zeolite capacity are reviewed. In addition no studies to evaluate other natural zeolites for ammonium removal have been reported.

In this study samples of clinoptilolite, erionite, mordenite, and phillipsite provided by the Anaconda Company were evaluated for ammonium removal from wastewaters. In addition, samples of clinoptilolite were pretreated in various ways to determine whether an improvement in ammonium removal performance could be realized. Total exchange capacities, capacities for ammonium removal from synthetic waste, packed bed densities and crushing strengths were measured.

Phillipsite was found to have almost twice the weight capacity for ammonium removal from synthetic waste compared to that of clinoptilolite. The volumetric capacity was 26% better than that of clinoptilolite. However, the phillipsite sample was extremely friable and it could not be used for water treatment unless it was strengthened with a binder.

Pretreatment of clinoptilolite with NaOH, HNO₃ and steam did little to improve the zeolite's performance. However, heat pretreatment (600 C for 1h) improved the zeolite's selectivity for ammonium significantly. Ammonium removal capacities were increased by approximately 17% for heat treated zeolite samples although the total exchange capacity of the zeolite was reduced somewhat.

J. Klinowski and P. J. Barrie 1989 Recent Advances in Zeolite Science Cambridge Elsevier 52 List of volumes in the series and what is in them

J. H. Koon and W. J. Kaufman 1975 Ammonia removal from municipal wastewaters by ion exchange 47 448-465

D. Leppert 1990 Heavy metal sorption with clinoptilolite zeolite: Alternatives for treating contaminated soil and water. 42 604-608 Large deposits of natural zeolites may provide cost-effective alternatives for treatment of soil and water contaminated with heavy metals and radionuclides. Research on the Bikini atoll demonstrated that addition of clinoptilolite to the soil significantly reduces cesium uptake by plants. Research on the potential use of zeolites in soils at Bunker Hill. ID indicated only minor benefits at very high contamination levels vs. US Bureau of Mines (USBM) work on the use of zeolites for treatment of mine waste waters emphasized problems with natural waters that previous studies have not addressed. High levels of competing calcium in natural waters significantly decrease the effectiveness of zeolites for heavy metal sorption and may limit the usefulness in these applications.

L. Liberti, G. Boari, D. Petruzzelli and R. Passino 1981 Nutrient removal and recovery from wastewater by ion exchange 15 337-342 After about 500 cycles have been continuously performed on a laboratory pilot plant, ion exchange resins have proved to be an effective means to treat municipal secondary effluents to prevent eutrophication in the receiving water bodies. Clinoptilolite, a natural zeolite, and Kastel, A510, a strong base anion resin with adsorptive properties act selectively to remove ammonium and phosphate ions, at the same time affording filtration and adsorption of the wastewater. NaCl at sea-water concentration is used as resin regenerant. After the

recovery of products of fertilizing value, as MgNH_4PO_4 and NH_4NO_3 . From the eluates, the latter can be recycled.

S. R. Linne and M. J. Semmens 1977 Studies on the ammonium removal and filtration performance and regeneration of clinoptilolite 757-770 The need for ammonia removal from municipal and industrial wastewater has been realized for many years. There are several processes that have been studied and used for ammonium removal, one of which is ion exchange by clinoptilolite. Clinoptilolite is a natural zeolite which has a favorable selectivity and capacity for ammonium. The mineral, which is found in vast quantities in several parts of the world including the southwest United States, is easily and inexpensively mined. Ammonium removal by clinoptilolite has been used in full scale operations but, due to the costs associated with the process, its process has been limited. The high cost of the process can be attributed to two areas: regeneration and influent water pretreatment.

To improve the cost effectiveness of the process, three areas needed to be studied: the water pretreatment requirement, the regeneration conditions, and the use of clinoptilolites other than Hector clinoptilolite (the most widely studied and used clinoptilolite).

M. Loizidou and R. P. Townsend 1987 Exchange of cadmium into the sodium and ammonium forms of the natural zeolites clinoptilolite, mordenite, and ferrierite 1911-1916 The selectivity of three different natural zeolites for cadmium has been investigated using either chloride or nitrate as the co-anion in solution. The three zeolites examined (clinoptilolite, mordenite, and ferrierite) were prepared in both the sodium and ammonium forms before exchanges with cadmium were attempted, and the selectivities of these materials for cadmium were measured in terms of experimental ion-exchange isotherms at 298K. With one exception [$\text{Cd}/\text{NH}_4(\text{Cl}/\text{NO}_3)$ -clinoptilolite] all systems were shown to be reversible. Differences in selectivity when either chloride or nitrate is the co-anion are discussed, and thermodynamic data are derived for those systems shown to be reversible. In contrast to similar studies on clays, no overexchange of cadmium was observed on any of the zeolites. Of the systems studied, it is concluded that sodium clinoptilolite is the most suitable exchanger for the removal of cadmium from the solution.

A. W. Maki and K. J. Macek 1978 Aquatic environmental safety assessment for a nonphosphate detergent builder 573-580

H. Matsuzuru and A. Ito 1977 Immobilization of Cesium-137 in Cement-Waste Composites by Addition of Mineral Zeolites 643-648 The reduction of cesium leachability by addition of mineral zeolites to enhance the safety of solidification of wastes with cement has been examined. Leaching tests were carried out by the method recommended by IAEA. The naturally occurring mineral zeolites containing mordenite and clinoptilolite (Zeolite I), which have high atom ratios of silicon and aluminum, possess extremely high effectiveness for immobilizing ^{137}Cs in a cement matrix. By addition of zeolite I, the leachability is reduced by a factor of about 100. However, since increasing the amount of zeolites decreases the leachability and workability concurrently, the content of zeolites should be less than 0.25 for good workability. On the basis of the results obtained, estimates were made on the amount of ^{137}Cs leached from a cement composite (200 l. drum size, with or without Zeolite I, that is exposed to a water environment for extended periods.

M. E. McBratney 1989 Natural Zeolite in a continuous particulate medium corn dryer Macdonald College of McGill University Masters Chabazite, a naturally occurring molecular sieve zeolite, was used in a particulate medium grain dryer. The crushed mineral was heated by a propane burner and then mixed with wet corn in a continuous process. An initial medium temperature of 170 degrees C and a medium-to-grain mass ratio of 3:1 lowered the moisture content of yellow corn from an initial value of about 26% (w.b.) to a final of about 16% (w.b.) after approximately ten minutes of mixing.

A $2 \times 2 \times 2$ factorial experiment in a randomized complete block design was carried out in order to analyze statistically the effects of initial corn moisture content, initial medium temperature, medium-to-grain mass ratio and mixing time on the drying results achieved. An analysis of variance and a multiple linear regression were carried out. The regression equation was used in a simulation program.

The drying process did not result in any visible deterioration or contamination of the corn. However, the results of the simulation indicate that a single dryer able to accommodate practical quantities of corn would be rather large.

D. R. McNair, R. C. Sims, D. L. Sorensen and M. Hulbert 1987 Schmutzdecke characterization of clinoptilolite-amended slow sand filtration 74-81 Studies were conducted to characterize the growth and composition of the schmutzdecke and the associated particle removal efficiency for a field-scale experimental slow sand filtration (SSF) system for the biological treatment of Logan River water. A naturally occurring ammonium-selective zeolite, clinoptilolite, was added as a surface amendment to the sand bed of the SSF system as a reservoir of nitrogen for algae comprising the schmutzdecke. A predominance of filamentous algae at the surface of the filter was observed throughout the entire experimental period. Single-cell algae were observed at depths in the filter from 0.5 to 1 in. (15 to 30 mm). Particle removal was superior in clinoptilolite-amended SSF, even at filtration rates of two to four times greater than conventional SSF rates. The effect of schmutzdecke maturation on the removal of *Giardia lamblia* cyst-sized particles was also investigated. The growth of algae following the initiation of a filtration cycle, i.e., the maturation period of the schmutzdecke, was associated with an increase in the ability of the amended filter to remove *Giardia lamblia* cyst-size particles. The zeolite-amended SSF system treated drinking water for longer periods of time at higher filtration rates than achievable with conventional SSF without the zeolite surface amendment.

E. F. Miller 1977 Demineralization of brackish municipal water supplies - comparative costs 348-351

D. J. Morell 1985 Analysis of groundwater impacts from selected waste management practices at base metal and precious metal waste disposal facilities University of Idaho Degree of Doctor of Philosophy with a Major in Geology Monitoring groundwater at waste management practices from metal mining and beneficiation facilities.

S. D. Morton and E. W. Sawyer 1976 Clay Minerals Remove Organics, Viruses and Heavy Metals from Water 116-118,120

F. A. Mumpton Utilization of Natural Zeolites 177-204 Historically, zeolitic tuffs have been used by man for more than 2000 years as lightweight dimension stone and in pozzolanic cements and concretes; however, it has been only within the last 25 years that the zeolite content of many of these materials has been recognized. The hundreds of discoveries of high-grade zeolite deposits in sedimentary rocks of volcanic origin since 1950 has led to the development of a host of applications which take advantage of the low mining costs of the near-surface deposits and of the attractive physical and chemical properties of the zeolite structures. Compared with the several hundred million pounds of synthetic molecular sieves sold each year throughout the world, the current use of natural zeolites in commercial applications other than those in the construction industry is relatively small; however, natural zeolites are in use today in small tonnages in the United States, Japan, and several other countries. Applications and potential applications range from the use as fillers in high-brightness papers, to the upgrading of low-BTU natural gas streams, to the removal of ¹³⁷Cs from nuclear wastewaters, to dietary supplements for poultry and swine to produce larger animals at less cost.

The remainder of this chapter summarizes the current and potential uses that have been and are being developed for natural zeolites and has been taken largely from the author's article in "Natural Zeolites: Occurrence, Properties, Use," the conference volume of Zeolite '76. The author is grateful to Pergamon Press, Inc for their kind permission to use this material with but minor changes or revisions.

F. A. Mumpton 1983 Zeo-Tip '83 Lawrence, Kansas Allen Press 72

F. A. Mumpton 1984 The role of natural zeolites in agriculture and aquaculture 3-27

F. A. Mumpton 1987 Zeo-Trip '87 Lawrence, Kansas Allen Press 54

R. Olson Zeolites 1391-1431

D. Olson and A. Bisio 1984 Proceedings of the Sixth International Zeolite Conference Trowbridge, Wiltshire Butterworth & Co 1007

D. Packet, W. Debertogh and R. A. Schoonheydt 1985 Spectroscopy of Cu(II) coordinated to lattice oxygens in zeolites 351-358

M. Pansini and C. Colella 1990 Dynamic data on lead uptake from water by chabazite 78 287-295

M. Pansini, C. Colella and M. De' Gennaro 1991 Chromium removal from water by ion exchange using zeolite 83 145-157

R. Perry 1981 Detergent builders and water quality - a changing scene 21 446-449 Significant reduction in the level of sodium tripolyphosphate in detergents inevitably involves the use of substitute materials. Although this material has been used as an effective detergent builder for over thirty years and has also been used safely and extensively in foodstuffs it has been associated with eutrophication problems in surface waters. Utilization of alternative materials could involve vast tonnages of the products concerned and the viable alternatives, namely zeolites and nitrilotriacetic acids are reviewed in relation to both their performance in the washing cycle and their effect with respect to water quality. The problems remaining in relation to the potential use of nitrilotriacetic acid with respect to wastewater treatment and human safety are examined in connection with current scientific knowledge.

M. J. Plodinec 1980 Improved Glass Compositions for Immobilization of SRP waste 2 223-229

J. J. Pluth, J. V. Smith and W. J. Mortier 1977 Positions of cations and molecules in zeolites with the chabazite framework 12 1001-1007 Chabazite from Bozen, Tyrol was ion-exchanged with KCl and further exchanged with CuCl₂ solution to Cu_{1.8}K_{0.2}Si_{8.1}O₂₄·nH₂O. Both the hydrated and the dehydrated structures were determined at room temperature. Cell dimensions in R3m are: hydrated a 9.411(2) Å a 95.31(1)°; vacuum-dehydrated at 250°C a 9.310(2) Å a 92.01(2)°. All Cu²⁺ ions of d-Cu-Chabazite were located near the center of the 6-ring, 1.97 Å from three O(4) and 2.83 Å from three O(3). Displacement of Cu²⁺ by 0.15 Å into the large cage from a position for triangular coordination to three O(4) may result from either an attempt to reach a Jahn-Teller distorted tetrahedral coordination, or electrostatic repulsion from another Cu²⁺ across the ditrigonal prism, or both. The T-O distances increase as the T-O-T angles decrease. Interpretation of the electron density of h-Cu-chabazite is uncertain, but all Cu²⁺ ions and water molecules are in the large cage, perhaps as hydration complexes with Jahn-Teller distortion.

J. Rabo A. 1976 Zeolite chemistry and catalysis Washington D.C. American Chemical Society 796

G. A. Reimann 1986 Silver recovery from silver zeolite University of Idaho Master of Science with a major in Metallurgical Engineering Extracting silver from silver zeolite

H. Robson 1978 Synthesizing zeolites 176-191

D. M. Ruthven 1988 Zeolites as selective adsorbents 84 42-50

A. C. Savitsky, B. H. Wiers and R. H. Wendt 1981 Adsorption of Organic Compounds from Dilute Aqueous Solutions onto the External Surface of Type A Zeolite 15 1191-1196 Type A zeolite, an insoluble crystalline sodium aluminosilicate, has been developed as a water-hardness controlling agent for laundry detergent products. In order to assess the environmental safety of this material, we have examined the adsorption of organic compounds of varying polarity onto the external surfaces of calcium-exchanged type A zeolite in aqueous medium at pH 8. The compounds included p-chlorophenol, dieldrin, dodecylhexakis (oxyethylene) alcohol (C12E6), and tetradecyltrimethylammonium chloride. In addition, adsorption onto the sodium form of the zeolite was studied with methylene blue (to characterize the zeolite) and with linear alkylbenzenesulfonate (LAS). Type A zeolite provides a relatively weak adsorptive surface for organics of all polarities studied when compared to adsorption of these compounds onto natural clay minerals and sewage sludge. The introduction of Type A zeolite into environmental waters through its use in laundry detergents should therefore not alter the normal fate of organic molecules in the environment.

K. M. Sayell and R. R. Davis 1975 Removal of iron and manganese from raw water supplies using manganese greensand zeolite 12 20-23

R. A. Schoonheydt 1989 Combined ESR-DRS spectroscopies of transition metal ions and metal ion clusters in zeolites 50 523-539

P. K. Sharma and P. K. Seshan 1991 Copper-Exchanged Zeolite L Traps Oxygen 39

R. A. Sheppard, A. J. 3. Gude and G. M. Edson Bowie zeolite deposit, Cochise and Graham Counties, Arizona 319-328

R. A. Sheppard 1963 Zeolitic Diagenesis of Tuffs in the Miocene Chalk Hills Formation, Western Snake River Plain, Idaho. U.S. Geological Survey Zeolites are common diagenetic alteration products of silicic, vitric tuffs in Cenozoic lacustrine deposits of the western United States, especially those that were deposited in highly saline and alkaline water. Such deposits have received much attention in the last 25 years because they contain economic or potentially economic phillipsite, chabazite, erionite, and clinoptilolite. In contrast, study of zeolites in relatively freshwater lacustrine deposits has been neglected. The Miocene Chalk Hills Formation of southwestern Idaho consists of about 100m of mainly mudstone, siltstone, and interbedded vitric tuffs that were deposited in a chiefly freshwater lake. Throughout most of the outcrop belt, the tuffs are unaltered, but, locally, the tuffs are completely altered to clinoptilolite with or without smectite and opal-CT. This study was undertaken to delineate the pattern of alteration, to characterize the authigenic minerals and their paragenetic relationships, and to suggest a possible origin.

About 300 samples of fresh and diagenetically altered tuffs and tuffaceous sediments were collected throughout the formation and from an area of about 500 km². (square kilometers). A marker tuff, 1-13 m thick, is the thickest and most continuous tuff in the area, and this tuff was most extensively sampled and studied. The relative abundance of zeolites and other authigenic minerals in all samples was determined by X-ray powder diffraction. Selected samples were also studied by scanning electron microscopy and thin-section optical microscopy to ascertain the process of genesis and the paragenetic relationships of the minerals, and by X-ray fluorescence analysis to chemically characterize the zeolites and to provide data on chemical changes during alteration.

The zeolite zone in the Chalk Hills Formation is south of Oreana, Idaho, and extends parallel to the southern margin of the Snake River Plain, northwestward from Birch Creek to Hart Creek, about 21 km. Fresh, rhyolitic, vitric tuffs that are about 1 cm to 13 m thick grade laterally into zeolitic tuffs. Original textures and sedimentary structures are generally preserved in the tuffs of the zeolite zone. Fresh (unaltered) tuffs are light gray and soft, but altered tuffs are white, light yellow, or light brown and relatively hard, commonly forming ledges. Zeolitic tuff generally consists of clinoptilolite, smectite, and opal-CT. Although some tuffs are locally monomineralic clinoptilolite, most contain 40-90 percent clinoptilolite. Trace to minor amounts of erionite are associated with the clinoptilolite at a few localities. Trace amounts of fibrous to filiform mordenite are commonly associated with the clinoptilolite, but the mordenite can be recognized only by scanning electron microscopy. Phillipsite was recognized at only one locality where it makes up about 70 percent of the basal centimeter of the clinoptilolite-rich marker tuff. Other authigenic minerals locally recognized in the zeolitic tuffs are quartz, calcite, and gypsum. The common paragenetic sequence (listed early to late) is glass-smectite-clinoptilolite-mordenite. Opal-CT crystallized after smectite and either before or after clinoptilolite. Erionite, quartz, and calcite generally crystallized later than the clinoptilolite, and quartz and calcite locally replaced all of the earlier authigenic silicate minerals.

The zeolites and associated silicate minerals undoubtedly formed during diagenesis by hydrolysis and dissolution of rhyolite glass by pore water that was trapped in the tuffs during lacustrine sedimentation. Where tuffs are still unaltered, the original lake water probably was fresh. The zeolite zone probably coincides with a part of the lake that had a low to moderate salinity and a pH of 7-9.

B. B. Singh 1979 Catalytic Conversion of Methanol to Low Molecular Weight Hydrocarbons 198

J. R. Smyth 1981 Zeolite stability constraints on radioactive waste isolation in zeolite-bearing volcanic rocks 90 195-201 Silicic tuffs of the southern Great Basin and basalts of the Columbia River Plateau are under investigation as potential host rocks for high- and intermediate-level radioactive wastes. Non-welded and partially welded tuffs may contain major amounts (> 50%) of the zeolite minerals: clinoptilolite, mordenite, and analcime. Densely welded tuffs and some basalt flows may contain clinoptilolite as fracture filling which limits permeability of these rocks. The cation exchange properties of these zeolite minerals allow them to pose a natural barrier to the migration of cationic species of various radionuclides in aqueous solutions. However, these minerals are unstable at elevated

temperatures and at low water vapor pressures, and they may break down either by reversible dehydration or by irreversible mineralogical reactions. All of the breakdown reactions occurring with increased temperature involve a net volume reduction and evolution of fluids. Thus, they may provide both a pathway (shrinking fractures) and a driving force (fluid pressure) for release of radionuclides to the biosphere. These reactions may be avoided by keeping zeolite-bearing horizons saturated with water and below about 85 degrees C. This may restrict allowable gross thermal loadings in radioactive waste repositories in zeolite-bearing volcanic rocks.

J. E. Soden and J. C. Johnson 1978 Burial and Other High-Potential Response Techniques for Spills of Hazardous Chemicals that Sink 202-207

S. Stoveland, R. Perry and J. N. Lester 1979 Influence of detergent builders on metal solubility in activated sludge 19 513-519 Removal of metals during biological sewage treatment is closely related to their chemical forms. One critical factor controlling the forms of the metals in sewage is the chemical matrix of the sewage; as a consequence of their chelating capacity detergent builders are important in modifying the sewage matrix

Activated sludge from laboratory scale simulations and from a full scale treatment works has been incubated in a shaking water bath with nitrilotriacetic acid, sodium tripolyphosphate and zeolite type A. Nitrotrilotriacetic acid enhanced the solubility of cadmium, lead and zinc in both samples, and also that of copper in the sample from the full scale treatment plant. Sodium tripolyphosphate and zeolite type A had only slight effects on metal solubility.

M. Suzuki and K.-S. Ha Ammonia removal by Korean natural zeolite 265-270

K. A. Thrush and S. M. Kuznicki 1991 Characterization of chabazite and chabazite-like zeolites of unusual composition 87 1031-1035

G. P. L. Walker 1959 The amygdale minerals in the Tertiary lavas of Ireland; II, The distribution of gmelinite 32 202-217

J. R. Westendorf and A. C. Middleton 1979 Chemical aspects of the relationship between drinking water quality and long-term health effects: An overview 417-421

C. Woods, R. Svetich and R. Prettyman 1979 Ammonia removal at Tahoe-Truckee advanced wastewater treatment plant first year in review 1-8 The Tahoe-Truckee Sanitation Agency advance wastewater reclamation plant is now in its second year of operation. There are many unique and interesting aspects regarding the plant's design and operation, and the demanding environmental and political setting. This paper highlights the unique nitrogen removal process designed to meet a strict 2 mg/l total nitrogen effluent standard and produce a useful byproduct as well.

M. J. Zamzow, B. R. Eichbaum, K. R. Sandgren and D. E. Shanks 1990 Removal of heavy metals and other cations from wastewater using zeolites 25 1555-1569

M. J. Zamzow and J. E. Murphy 1991 Removal of metal and other cations from water using zeolites

1-10 Zeolites from abundant natural deposits were investigated by the Bureau of Mines for efficiently cleaning up mining industry wastewaters. Twenty-four zeolite samples were analyzed by X-ray diffraction and inductively coupled plasma. These included clinoptilolite, mordenite, chabazite, erionite, and phillipsite. Bulk densities of a sized fraction (minus 40, plus 65 mesh) varied from 0.48 to 0.93 g/mL. Attrition losses ranged from 1 to 18 pct during an hour-long shake test. The 24 zeolites and an ion exchange resin were tested for the uptake of Cd, Cu, and Zn. Of the natural zeolites, phillipsite proved to be the most efficient, while the mordenites had the lowest uptakes. Sodium was the most exchangeable ion for exchange of heavy metals. Wastewater from an abandoned copper mine in Nevada was used to test the effectiveness of clinoptilolite for treating multi-ion wastewater. The metal ions, Fe³⁺, Cu²⁺, and Zn²⁺ in the copper mine wastewater was reduced to below drinking water standards, but Mn²⁺ and Ni²⁺ were nt. Calcium and NH₄⁺ interfered with the uptake of heavy metals. Absorbed heavy metals were eluted from zeolites with 3-pct NaCl solution. Heavy metals were concentrated in the eluates up to 30-fold relative to the waste solution. Anions were not absorbed by the zeolites.11

APPENDIX II
EQUIPMENT LIST AND COSTS
ECONOMIC EVALUATION

	ZEOLITE MINE EVALUATION		Sep-94
PRE-PRODUCTION COSTS:			
Ore reserve delineation	\$ 40,000		
Clearing/overburden removal, 5 A	\$ 10,000		
3-mi access/haul road w/bridge	\$ 290,000		
Power line	\$ 50,000		
Telephone line	\$ 3,000		
Water well, lines, tanks	\$ 10,000		
Settling basin	\$ 5,000		
Reclamation bond	\$ 5,000		
Total	\$ 413,000		
EQUIPMENT COSTS (USED) :			
Wheel loader Cat 980	\$250,000		
Dozer w/ ripper Cat D9-H	\$100,000		
Grader Cat 12-F	\$20,000		
Ore trucks -2 @20 tons	\$50,000	subtotal	\$420,000
Jaw Crusher	\$30,000		
Gyratory cone crusher	\$60,000		
Impact crusher	\$20,000		
Coarse 2-deck screen	\$15,000		
Intermediate 3-deck screen	\$12,000		
Finish (scalping) screen	\$15,000		
Drier	\$20,000		
Conveyors (3)	\$ 9,000		
Radial stacker/conveyor	\$ 20,000		
Bins and hoppers	\$ 20,000		
Truck scales	\$10,000		
Maintenance equipment	\$30,000	subtotal	\$261,000
		10% installation	\$ 26,100
Total Equipment Cost			\$707,100
BUILDINGS : Office/shop, loadout			
	\$105,000		
CAPITAL COST RECAP			
Pre-production	\$ 413,000		
Land	\$ 20,000		
Buildings	\$ 105,000		
Equipment	\$ 707,100		
Working capital	\$ 51,700		
Subtotal	\$ 883,800		
Contingency @ 25%	\$ 220,950		
CAPITAL COST	\$ 1,104,750		

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20
S U M M A R Y																				
Gross revenue	\$1,220,000	\$1,220,000	\$1,220,000	\$1,220,000	\$1,220,000	\$1,220,000	\$1,220,000	\$1,220,000	\$1,220,000	\$1,220,000	\$1,220,000	\$1,220,000	\$1,220,000	\$1,220,000	\$1,220,000	\$1,220,000	\$1,220,000	\$1,220,000	\$1,220,000	\$1,220,000
Federal royalty @ 0.04	\$ 48,800	\$ 48,800	\$ 48,800	\$ 48,800	\$ 48,800	\$ 48,800	\$ 48,800	\$ 48,800	\$ 48,800	\$ 48,800	\$ 48,800	\$ 48,800	\$ 48,800	\$ 48,800	\$ 48,800	\$ 48,800	\$ 48,800	\$ 48,800	\$ 48,800	\$ 48,800
Gross After Royalty	\$1,171,200	\$1,171,200	\$1,171,200	\$1,171,200	\$1,171,200	\$1,171,200	\$1,171,200	\$1,171,200	\$1,171,200	\$1,171,200	\$1,171,200	\$1,171,200	\$1,171,200	\$1,171,200	\$1,171,200	\$1,171,200	\$1,171,200	\$1,171,200	\$1,171,200	\$1,171,200
Mining costs	\$150,000	\$150,000	\$150,000	\$150,000	\$150,000	\$150,000	\$150,000	\$150,000	\$150,000	\$150,000	\$150,000	\$150,000	\$150,000	\$150,000	\$150,000	\$150,000	\$150,000	\$150,000	\$150,000	\$150,000
Leakout costs	\$108,500	\$108,500	\$108,500	\$108,500	\$108,500	\$108,500	\$108,500	\$108,500	\$108,500	\$108,500	\$108,500	\$108,500	\$108,500	\$108,500	\$108,500	\$108,500	\$108,500	\$108,500	\$108,500	\$108,500
Transportation costs	\$408,000	\$408,000	\$408,000	\$408,000	\$408,000	\$408,000	\$408,000	\$408,000	\$408,000	\$408,000	\$408,000	\$408,000	\$408,000	\$408,000	\$408,000	\$408,000	\$408,000	\$408,000	\$408,000	\$408,000
Mineral production taxes																				
ROG/WAT tax @ 5%	0.0025	\$ 6,075	\$ 6,075	\$ 6,075	\$ 6,075	\$ 6,075	\$ 6,075	\$ 6,075	\$ 6,075	\$ 6,075	\$ 6,075	\$ 6,075	\$ 6,075	\$ 6,075	\$ 6,075	\$ 6,075	\$ 6,075	\$ 6,075	\$ 6,075	\$ 6,075
Benevolent mill levy =	0.30627																			
Net Proceeds tax base 10% pr rev	0.1	\$ 35,753	\$ 35,753	\$ 35,753	\$ 35,753	\$ 35,753	\$ 35,753	\$ 35,753	\$ 35,753	\$ 35,753	\$ 35,753	\$ 35,753	\$ 35,753	\$ 35,753	\$ 35,753	\$ 35,753	\$ 35,753	\$ 35,753	\$ 35,753	\$ 35,753
Property tax, bldgs, land, eqpt		\$ 20,658	\$ 16,933	\$ 10,877	\$ 6,906	\$ 4,630	\$ 2,353	\$ 1,195	\$ 12,895	\$ 8,943	\$ 5,940	\$ 3,971	\$ 3,267	\$ 920	\$ 8,727	\$ 6,473	\$ 5,104	\$ 3,735	\$ 3,031	\$ 2,761
Interest expense - credit line	estimate	\$ 5,000	\$ 5,000	\$ 5,000	\$ 5,000	\$ 5,000	\$ 5,000	\$ 5,000	\$ 5,000	\$ 5,000	\$ 5,000	\$ 5,000	\$ 5,000	\$ 5,000	\$ 5,000	\$ 5,000	\$ 5,000	\$ 5,000	\$ 5,000	\$ 5,000
Amortization of pre-production	\$ 413,000	\$ 82,800	\$ 82,800	\$ 82,800	\$ 82,800	\$ 82,800	\$ 82,800	\$ 82,800	\$ 82,800	\$ 82,800	\$ 82,800	\$ 82,800	\$ 82,800	\$ 82,800	\$ 82,800	\$ 82,800	\$ 82,800	\$ 82,800	\$ 82,800	\$ 82,800
Depreciation allowance		\$ 145,011	\$ 228,608	\$ 138,097	\$ 84,792	\$ 44,063	\$ 87,334	\$ 137,734	\$ 83,973	\$ 51,718	\$ 51,717	\$ 27,526	\$ 87,333	\$ 137,734	\$ 83,973	\$ 51,718	\$ 51,717	\$ 27,526	\$ 3,333	\$ 3,334
Net before depletion (operating profit)		\$ 208,403	\$ 128,733	\$ 225,498	\$ 283,572	\$ 285,850	\$ 411,458	\$ 389,343	\$ 307,443	\$ 389,448	\$ 420,815	\$ 428,375	\$ 387,272	\$ 319,218	\$ 365,172	\$ 389,681	\$ 401,051	\$ 428,811	\$ 451,508	\$ 451,777
Percentage Depletion @ 14%	0.14	\$ 163,968	\$ 163,968	\$ 163,968	\$ 163,968	\$ 163,968	\$ 163,968	\$ 163,968	\$ 163,968	\$ 163,968	\$ 163,968	\$ 163,968	\$ 163,968	\$ 163,968	\$ 163,968	\$ 163,968	\$ 163,968	\$ 163,968	\$ 163,968	\$ 163,968
tax loss carryforward		\$ 45,435	\$ (35,235)	\$ 36,844	\$ 119,804	\$ 121,882	\$ 247,488	\$ 205,375	\$ 143,475	\$ 200,868	\$ 238,847	\$ 262,407	\$ 203,304	\$ 155,250	\$ 201,204	\$ 235,713	\$ 237,083	\$ 262,843	\$ 287,540	\$ 287,809
State income tax @ 8.75%		\$ 3,067	\$ (2,376)	\$ 2,689	\$ 8,073	\$ 8,227	\$ 16,705	\$ 13,863	\$ 9,685	\$ 13,565	\$ 15,987	\$ 17,712	\$ 13,723	\$ 10,479	\$ 13,581	\$ 15,911	\$ 16,033	\$ 17,728	\$ 19,409	\$ 19,427
Federal taxable income		\$ 42,368	\$ (32,857)	\$ 37,155	\$ 111,531	\$ 113,655	\$ 220,782	\$ 181,512	\$ 133,791	\$ 187,403	\$ 219,593	\$ 228,890	\$ 186,581	\$ 144,771	\$ 187,022	\$ 219,803	\$ 221,080	\$ 244,814	\$ 268,131	\$ 268,352
Federal income tax @ 34%		\$ 14,405	\$ (11,171)	\$ 12,633	\$ 37,921	\$ 38,843	\$ 76,486	\$ 65,114	\$ 45,489	\$ 63,717	\$ 74,658	\$ 75,092	\$ 63,198	\$ 48,222	\$ 63,792	\$ 74,733	\$ 75,187	\$ 83,271	\$ 91,184	\$ 91,250
NET INCOME		\$ 27,963	\$ (21,685)	\$ 24,522	\$ 73,610	\$ 75,012	\$ 152,318	\$ 126,398	\$ 88,302	\$ 123,686	\$ 144,935	\$ 153,798	\$ 125,123	\$ 95,549	\$ 123,831	\$ 145,070	\$ 145,913	\$ 161,643	\$ 176,988	\$ 177,132
Plus depreciation		\$ 208,403	\$ 128,733	\$ 225,498	\$ 283,572	\$ 285,850	\$ 411,458	\$ 389,343	\$ 307,443	\$ 389,448	\$ 420,815	\$ 428,375	\$ 387,272	\$ 319,218	\$ 365,172	\$ 389,681	\$ 401,051	\$ 428,811	\$ 451,508	\$ 451,777
Plus depletion		\$ 163,968	\$ 163,968	\$ 163,968	\$ 163,968	\$ 163,968	\$ 163,968	\$ 163,968	\$ 163,968	\$ 163,968	\$ 163,968	\$ 163,968	\$ 163,968	\$ 163,968	\$ 163,968	\$ 163,968	\$ 163,968	\$ 163,968	\$ 163,968	\$ 163,968
Plus amortization		\$ 82,800	\$ 82,800	\$ 82,800	\$ 82,800	\$ 82,800	\$ 82,800	\$ 82,800	\$ 82,800	\$ 82,800	\$ 82,800	\$ 82,800	\$ 82,800	\$ 82,800	\$ 82,800	\$ 82,800	\$ 82,800	\$ 82,800	\$ 82,800	\$ 82,800
Plus working capital recovery																				
Minus equipment replacement																				
Equals net cash flow	\$ (1,104,750)	\$ 483,824	\$ 353,816	\$ 498,588	\$ 603,751	\$ 524,830	\$ 727,740	\$ 658,708	\$ 558,713	\$ 710,551	\$ 751,841	\$ 653,383	\$ 578,735	\$ 652,971	\$ 708,718	\$ 710,832	\$ 752,222	\$ 782,442	\$ 782,678	\$ 782,678
DCF/RIOR	45%																			

[illegible]

[illegible]

APPENDIX III
EXPLORATION OF A LATE CRETACEOUS ZEOLITE TUFF
BEAVERHEAD COUNTY, MONTANA

B. E. COX AND E. BRENNER-YOUNGGREN
1973

EXPLORATION OF A LATE CRETACEOUS ZEOLITIC TUFF,
BEAVERHEAD COUNTY, MONTANA*

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INTRODUCTION

The occurrence of clinoptilolite and mordenite in Cretaceous tuffs of Grasshopper Creek (Ktz), Beaverhead County, Montana, was first reported by Pearson in 1989. The occurrence has since been the subject of detailed geologic field work by the authors and supporting analytical work to quantify the zeolite resource. The principal exploration objectives were to determine the extent of zeolitization and to develop field methods for rapid identification of potential ore-grade zeolitic rock.

GEOLOGY OF THE TUFF OF GRASSHOPPER CREEK

Cretaceous volcanic rocks crop out discontinuously over a 200 km² area, 10-25 km southwest of Dillon. The Ktz tuff is a basal, zeolitic sequence which is 30-100 m thick in the vicinity of the subject deposit. Ktz tuff consists of graded pyroclastic flows and ash fall materials. In outcrop, Ktz is light-colored and grades between flaggy and massive. The texture ranges from uniformly fine-grained pumiceous tuff to conglomeratic tuff with 0.5-3.0 cm diameter lithic clasts.

Local stratigraphic successions of dominantly smectitic tuff to dominantly zeolitic tuff to opaline tuff suggest a vertical zoning of authigenic minerals. A 5-15 meter thick sequence of vitric tuff with a gradational lower contact and sharp upper contact is a stratigraphic datum which may have exerted a permeability control to zeolitization (Figure 1). Zeolitization is locally pervasive through the matrix and the pumiceous clasts. Clinoptilolite and mordenite are the only known zeolite species in the deposit and the ratio of clinoptilolite to mordenite is approximately 7:1.

FIELD METHODS

Initial exploration indicated that clinoptilolite and mordenite occur in a variety of tuffaceous lithologies but not in discrete zeolitic "beds". This observation and the suspected complexity of post-Cretaceous faulting prompted the search for a method for rapid identification and mapping of ore-grade zeolitic rock (i.e. >50% clinoptilolite + mordenite). Features considered potentially useful as zeolite indicators were the standard characteristics for rock type identification, outcrop weathering/soils/vegetation and outcrop location with respect to the geometry of the depositional basin and intrusives.

Empirical review of field descriptions and analyses indicates that the following rock features have moderate to strong correlation with a zeolite content >50% (clinoptilolite + mordenite):

- (1) HCl effervescence; disseminated fine grains or clots of amber-colored crystals (calcite +/- zeolites),
- (2) manganese oxides as disseminations, dendrites and fracture fillings,
- (3) pumiceous lithic fragments altered to clays, especially waxy smectitic materials,
- (4) conchoidal "breaking" which is gradational between friable (unaltered) texture and opaline texture (silicified or feldspathized) with conchoidal "fracture",
- (5) presence of open vugs as net-like textures and as spherules commonly with 1-3 mm alteration rims of manganese oxides +/- clay.

DISCUSSION

The features listed above are interpreted to be the macroscopic expression of the zeolitic alteration of tuff protolith. Features 1-3 represent the mineralogical change from a nearly monomineralic tuffaceous material to an authigenic mineralogy. Features 4 and 5 represent the textural changes of greater crystallinity and increased volume, respectively. Table 1 shows a comparison of these features for two sample groups (zeolitic and non-zeolitic) representative of the Ktz tuffs. There was no observable feature to distinguish mordenite-bearing from clinoptilolite-bearing tuff.

The analytical sample population is not currently large enough to perform a statistical analysis of the diagnostic features. However, methodical examination of hand sample features and comparison with analytical results have proven valuable for recognition of the most favorable zeolitic terrain within the tuff of Grasshopper Creek. Such empirical methods may have application for investigations of other zeolite deposits, especially where the original deposit was disrupted or obscured by post-mineral faulting and further alteration.

REFERENCES

- Cox, B. E., E.B. Younggren and C.A. Van der Poel, (1992) Geology, exploration and marketing aspects of a zeolitic tuff, Beaverhead County, Montana: presentation given to Montana Mining Assn. Annual Conv., Butte, Montana, May, 1992.
- Pearson, R. C. (1989) Zeolite-bearing Cretaceous tuff in Beaverhead County, southwestern Montana: U.S. Geol. Surv. Open-File Rept. 89-0297, 10 pp.
- * Abstract presented to the 4th International Conference on the Occurrence, Properties and Utilization of Natural Zeolites; Boise, Idaho - June 1993.

Figure 1. Generalized Stratigraphy of Zeolitic Tuffs of Grasshopper Creek

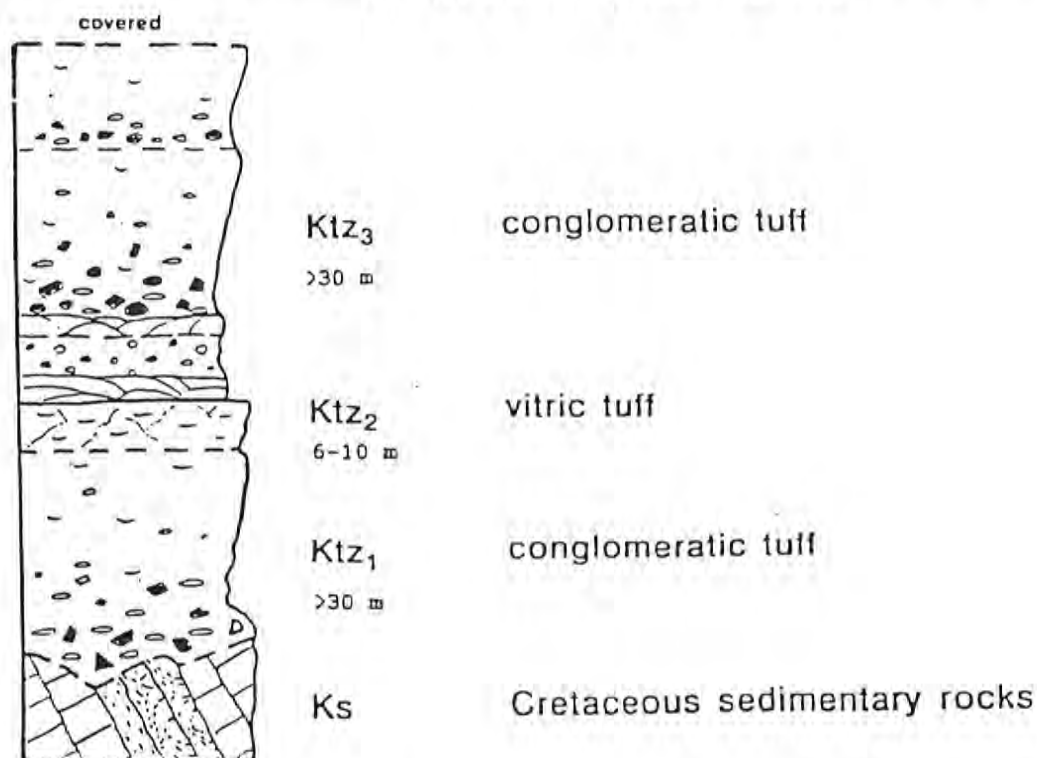


Table 1. Macroscopic characteristics of zeolitic and non-zeolitic tuff of Grasshopper Creek.

Sample	Zeolite Content	HCl Effervescence	Mn Oxide Content	Clast Alteration	Conchoidal Breaking	Vugs
ZC9205	>90% clno	none	none	n/a	strong	none
ZP8909	>90% clno	none	1-2%	strong	strong	2-3%
ZC9203	>90% clno	1-2% in vugs	2-3%	tr - 1%	mod-to-strong	3-5%
ZC9204	~70% clno ~15% mrdn	trace	1-2%	mod-to-strong	moderate	locally 1-2%
ZP8906	~55% clno ~20% mrdn	2% in vugs	tr	strong	strong	2-3%
ZC8907	~25% clno	none	trace	weak	weak-to-moderate	none
ZP8910	~15% clno	none	trace	weak	none	none
ZC8906	~10% clno	tr-1% in vugs	none	weak	weak	trace
ZY8904	0%	none	none	none	none	none
ZC8908	0%	none	none	moderate	none	none

- Samples listed represent a variety of tuff lithologies which occur within a 4 square kilometer area. Zeolite content was determined by X-ray diffraction: clno = clinoptilolite, mrdn = mordenite. HCl effervescence is a rough indication of calcite content but may also be indicative of coarsely crystalline zeolites.

EXPLANATION OF UNITS

Grasshopper Mine Area

Qal	Quaternary alluvial deposits--Unconsolidated silt, sand and gravel in valley bottoms
Qt	Quaternary talus--Unconsolidated angular debris of local origin
Qf	Quaternary fan deposits--Unconsolidated sand, gravel and silt with fan morphology
Qls	Quaternary landslide--Blocky rubble with subdued mass movement morphology
Q-Tg	Quaternary-Tertiary gravels--Unconsolidated, rounded to subrounded material. In the E1/2, SE1/4 Sec. 27, this unit mantles a gently sloping surface and resembles "pediment gravels" elsewhere in southwest Montana. This material was mapped as Beaverhead Formation by Lowell (1965) and Quaternary deposits by Pearson
Tb	Eocene basalt--Dark brown and black dense to vesicular and locally porphyritic. Unconformably overlies Cretaceous rocks.
Ktz3	Cretaceous tuff, zeolitic--Conglomeratic tuff
Ktz2	Cretaceous tuff--Vitric tuff, 6-10 meters thick
Ktz1	Cretaceous tuff, zeolitic--Conglomeratic tuff. The Ktz units were mapped as Tuffs of Grasshopper Creek by Pearson (1989). Probably part of the Beaverhead Group.
Kb	Late Cretaceous Beaverhead Formation (Group)--Rounded to subrounded pebble to boulder conglomerate, quartz sand matrix, weakly cemented by calcite, generally pink to red in color.
Kvb	Late Cretaceous basaltic volcanic rocks--Porphyritic flows and dikes, generally dark brown and crumbly on weathered surfaces.
Kva	Late Cretaceous andesitic volcanic rocks--Porphyritic flows and dikes, generally grayish green and brown and crumbly on weathered surfaces.
Kval	Late Cretaceous andesitic lahar--Angular to subrounded clasts, pebble to cobble size andesitic and basaltic volcanic rocks in a silt-sand matrix of intermediate composition. Generally light to dark green.
Ks	Cretaceous sedimentary rocks--Salt and pepper sandstone, dark gray limestone, red to green shales and siltstones,
M-Ps	Mesozoic-Paleozoic sedimentary rocks

C8905

C8906



C8907



ZEALOT SAMPLE LOCATIONS + ANALYSES

G:

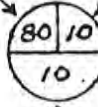
EXPLANATION

Sample w/ XRD Analysis

~%

clinoptilolite

mordenite



accessory mins.; quartz, amorphous
silica, smectite, dolomite,
etc.

X5758

