Leachate Chemistry and Solids Characteristics in Mill Tailings Near Magdalena, New Mexico

By

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ABSTRACT

There is a need to measure characteristics of existing mine tailings sites and use these observations to predict the chemical evolution of the tailings. Mine tailings near Magdalena, NM were examined for solid and aqueous phase characteristics. SiO_2, FeS_2, Fe_2O_3, $CaCO_3$, and $ZnCO_3$ composed the bulk of the solids. Columns of tailings were leached under simulated rainfall. Leachate from columns of tailings contained much Zn, Mn, and SO_4. The geochemical equilibrium model, MINTEQ (Felmy et al., 1983), yielded good predictions of leachate composition. Sorption capacity of the alluvium for zinc was considerable (1800 ppm) but not enough to prevent ultimate migration of zinc to groundwater. Travel-time to the groundwater by an ideal tracer was estimated to be 40 years. Zinc travel-time to the groundwater was estimated to be long (>100,000 yrs.) since the retardation factor is high (98,000). A rapid decrease of metals underlying the tailings within 10 cm of the soil/tailings interface suggested that there was a very slow travel time for metals (Zn, Pb and Cu). Thus, zinc is not an immediate groundwater threat at the site.

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I. INTRODUCTION

There are large numbers of sites of abandoned mill tailings resulting from past mining activities throughout the United States. Most tailings sites receive no environmental monitoring until a problem, e.g., ground water contamination or erosion of tailings by water and wind, has occurred. There is a need to measure characteristics of existing tailings sites and use these observations to predict the chemical evolution of the tailings.

The site of the study was the Waldo mill-tailings impoundment, located 1.5 miles south of Magdalena, NM (Fig. 1). The New Mexico State Mining and Mineral Research Institute was interested in funding research on mineralogy and hydrogeochemistry of the site; and cores from this site were available from a previous study (Johnson, 1987). Samples from this site included mill tailings from the Waldo-Graphic lead-zinc mine. The tailings impoundment is stratigraphically placed above alluvium (Fig. 2). Most of the tailings was accumulated by ASARCO, starting in 1943 and ending in the early 1950's (Johnson, 1987).

Earlier work in the region was mainly on the geology, and especially mineralogy, of the Magdalena mining district (Loughlin and Koschmann, 1942). Geochemical examination, which found trace amounts of mercury and other heavy metals within many rock units in the region, including the Kelly Limestone, from which the tailings were generated, was done later (Missaghi, 1966). Additionally, general analyses of

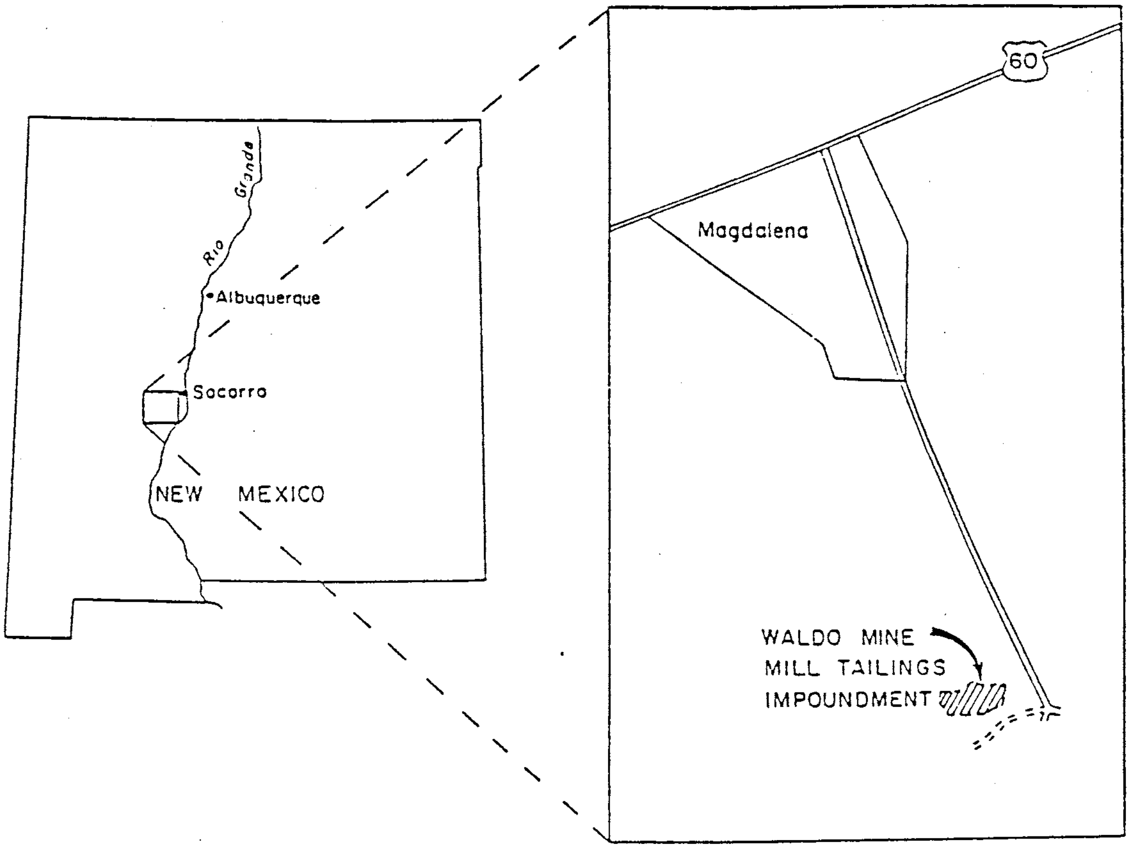

Figure 1. Location map of the Waldo Mill tailings impoundment. (Johnson, 1987)

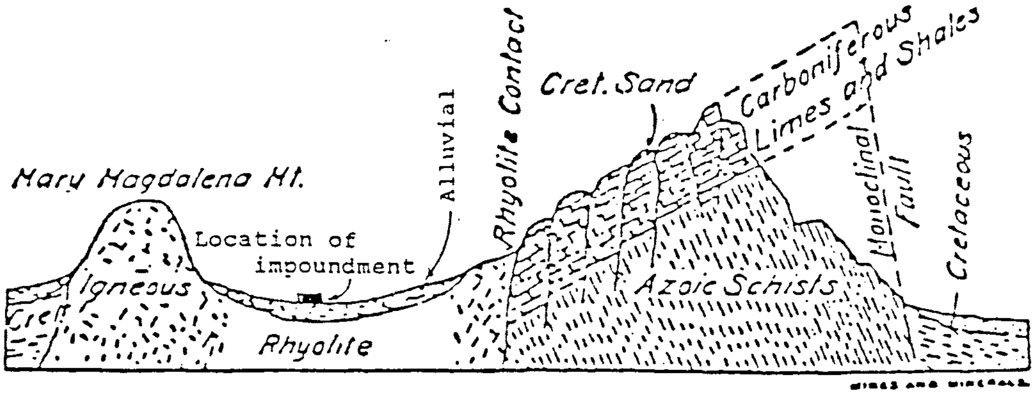

Figure 2. Geology of the field site area. Cross section of the Magdalena Range looking north. (Johnson, 1987)

groundwater in the Magdalena Mountains were completed by Summers et al. (1972).

Much past research on mill tailings has dealt with the improvement of the stability of the embankment dams. Research by Soderburg and Busch (1975) and Highter and Valle (1980) examined tailings from a soils engineering viewpoint. McWhorter and Nelson (1980) examined the prediction of seepage through tailings. More recently, Johnson (1987) examined the spatial variability of hydraulic properties in the Waldo mill-tailings impoundment.

In this study, samples from the mill tailings were examined for parameters relating to their solid-phase chemistry and potential for chemical leaching. The objectives of the study were:

<u>Objectives</u>

1. Determine the chemical characteristics of the solid phase in the mill tailings samples.
2. Determine the chemical characteristics of the liquid phase in mill tailings samples.
3. Quantify the transient nature of leachate chemistry by using a laboratory simulation of long-term leaching under saturated conditions.
4. Simulate future equilibrium leachate chemistry with a geochemical model.
5. Determine the potential for ground water pollution underlying the tailings.

The results of this research yielded estimates of the potential leachability of metals in a heterogeneous tailings deposit. This research will help in evaluating the potential adverse environmental impacts of such disposal sites, and help direct where remediation measures will be most useful and effective, e.g., in the slime versus the sand potions of a tailings pile.

II. MATERIALS AND METHODS

Description of tailings & alluvium

The principle source for the tailings was a mill processing ore from the Kelly limestone formation. Over fifty different minerals were found in the district including primary ore minerals such as smithsonite ($ZnCO_3$), cerrusite ($PbCO_3$), and galena, along with gauge minerals such as quartz, pyrite, hematite, calcite, and gypsum (Loughlin and Koschmann, 1942).

There were three major periods of layering at the site (layers 1-3). Layer 2, the largest of the three layers, is approximately 100 by 200 meters in areal extent, averaging approximately five meters in depth (Johnson, 1987) and is illustrated in Fig. 3 and 4. The work in this study, which used the core samples of Johnson (1987), was to follow up Johnson's work. Core samples of the mine tailings were taken using split-spoon sampling in six locations with depths of up to 6 m (Figs. 3 and 4). The triangles (Fig. 3) symbolize neutron probes installed by Johnson (1987). The letters starting with "V" were core samples from Johnson's study from which samples were taken for this study. Johnson originally used these cores for a geostatistical study of spatial variability in sediment texture and moisture content in the tailings pile.

The research utilized three of the six cores from the Johnson study. The sample numbering system is as follows: The number before the first dash is the core number. The

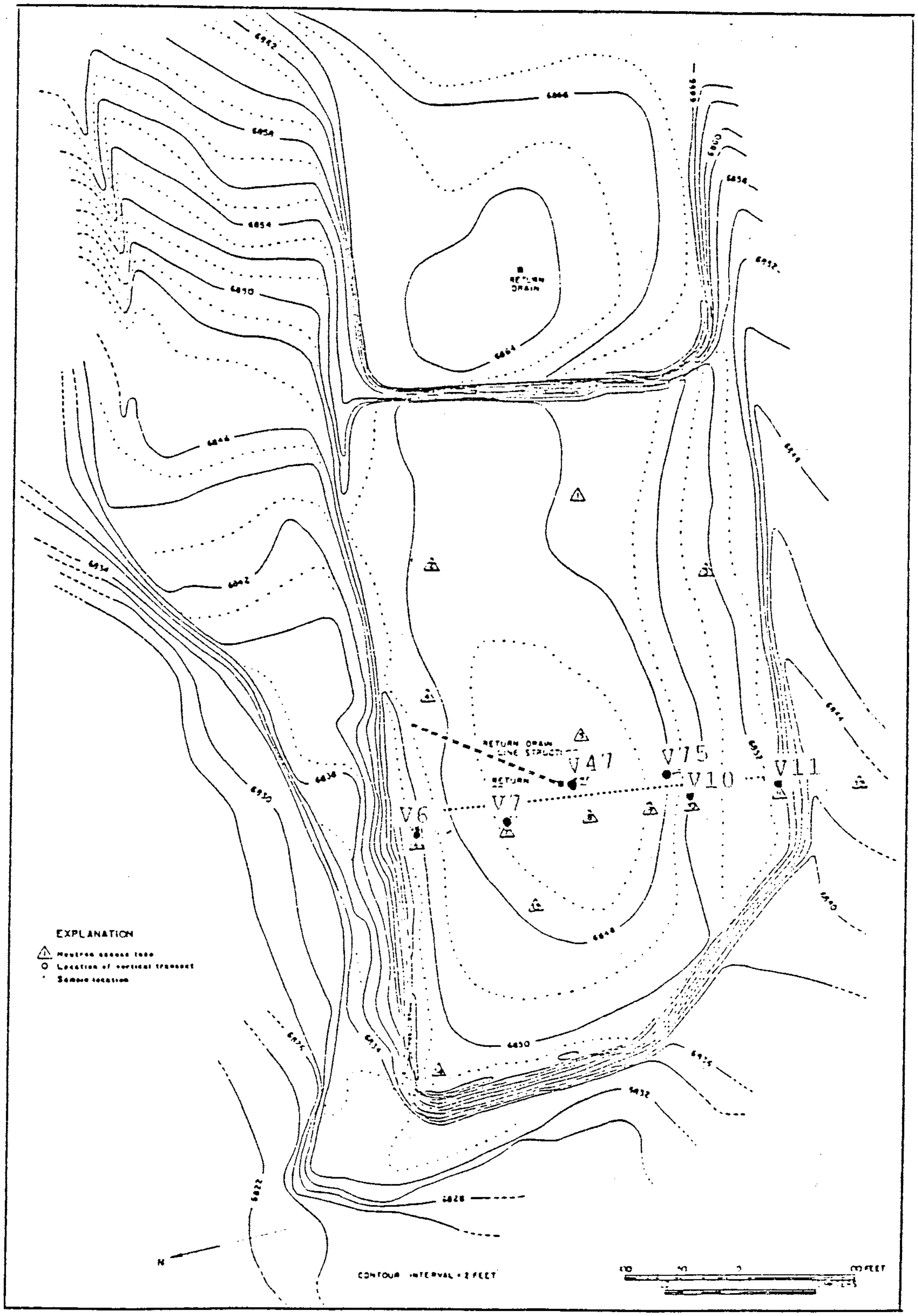

Figure 3. Locations of sampling transects and neutron-probe access tubes. (Johnson, 1987)

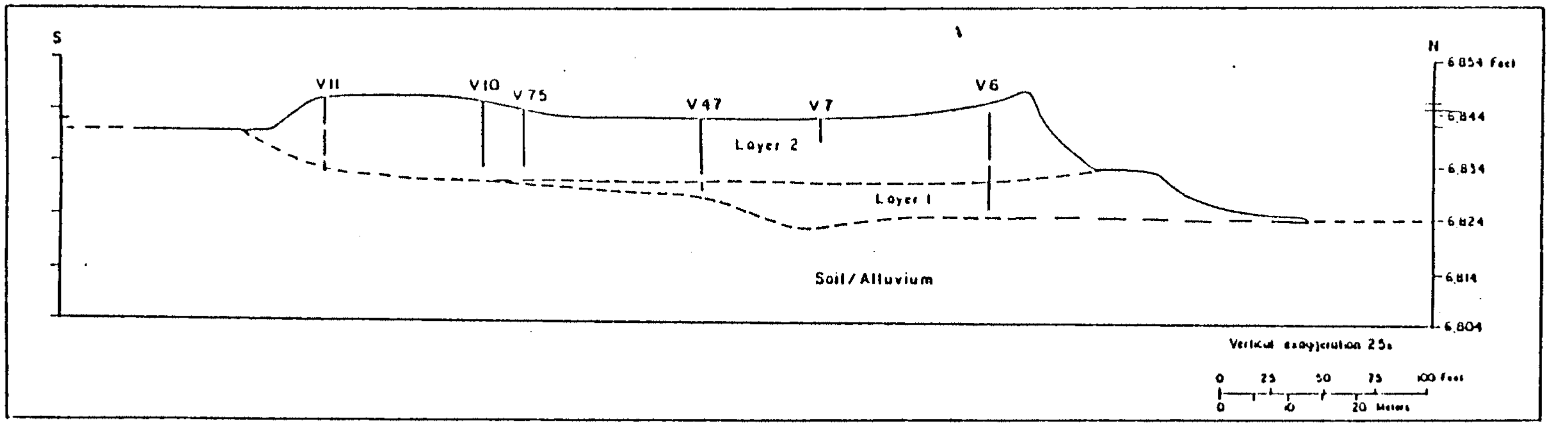

Figure 4. Cross section showing positions of core samples in the tailings. (Johnson, 1987)

number after the first dash is the depth in centimeters to the top of the sample. The number after the second dash is the depth in centimeters to the bottom of the sample. The tailings' grain sizes ranged from clay to sand size (Johnson, 1987). The grain size generally decreased toward the center of the tailings. Samples used in the X-ray diffraction and X-ray fluorescence study were examined for their color. This was to see if the visible differences in color could help identify layers that were chemically different. Color of the tailings samples used in chemical studies varied from gray to yellowish brown (Table 1). Some of samples were ultimately used in the laboratory experiments explained below.

Table 1
Color variation in the tailings
(colors from Munsell Soil color chart)

Sample #	Color	
V6-104-120	5yr V5/chr/2	(olive gray)
V6-104-158	2.5yr V6/chr/2	(lt. brownish gray)
V6-118-131	10yr V3/chr/2	(v. dk. grayish brown)
V6-262-314	10yr V6/chr/1	(light gray)
V47-103-106	10yr V6/chr/4	(lt. yellowish brown)
V47-107-152	10yr V5/chr/1	(gray)
V47-207-210	10yr V4/chr/2	(dk. grayish brown)
V75-65-78	5yr V5/chr/1	(gray)
V75-103-157	10yr V5/chr/1	(gray)
V75-251-314	10yr V6/chr/1	(light gray)

Saturated hydraulic conductivity of the tailings ranged from 10^{-2} to 10^{-7} cm/sec (Johnson, 1987). Generally, the hydraulic conductivity increased toward the edge of the tailings pile (Johnson, 1987).

Strata description and cross section were completed from visual analysis of the cores (Fig. 5). It showed that there

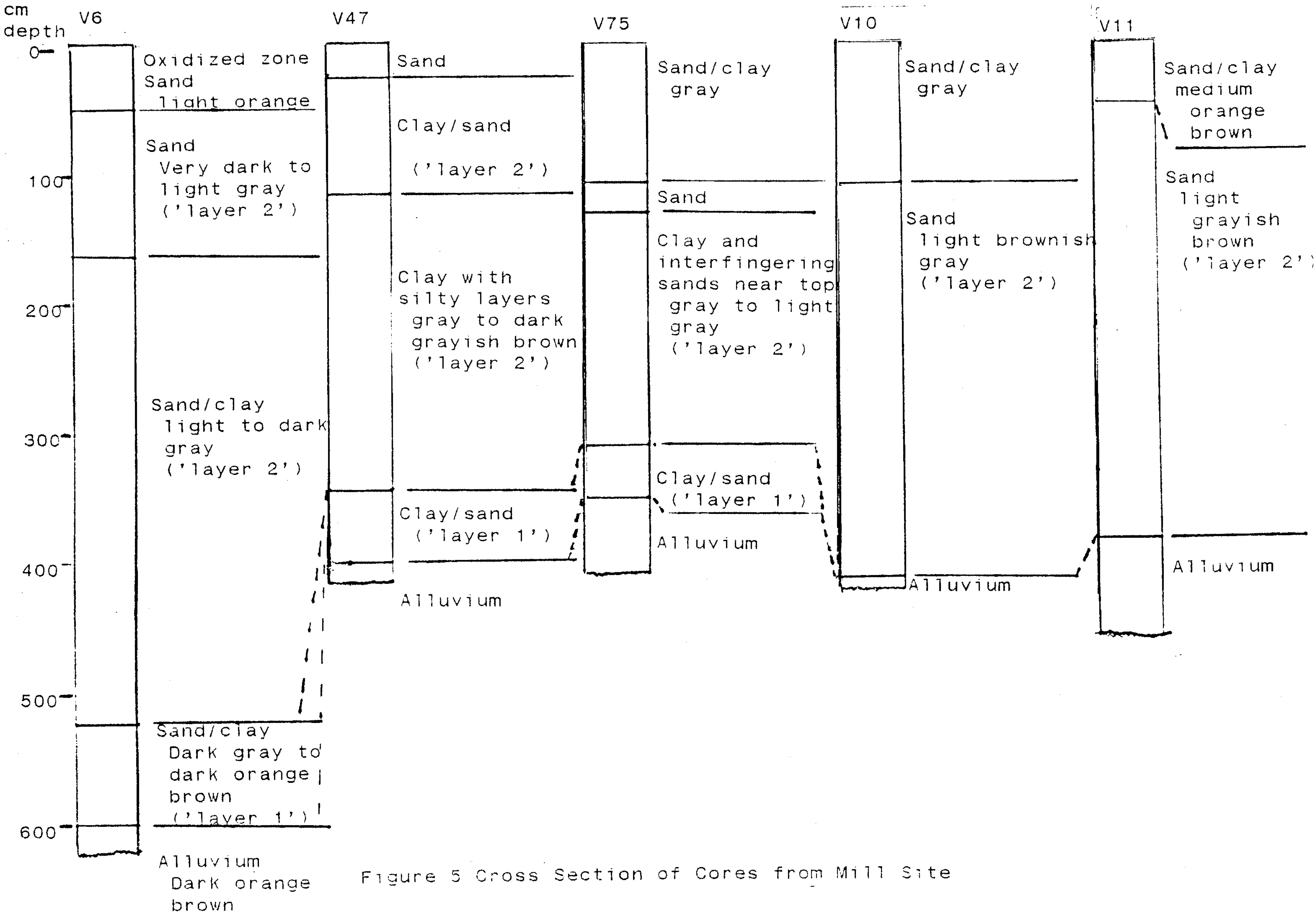

Figure 5 Cross Section of Cores from Mill Site

was a decrease of grain size towards the center of the tailings pile.

Mineralogical/Chemical Analyses

Cores from the abandoned lead-zinc mine tailings were examined for solid and aqueous chemistry. Ten samples from the cores, chosen using the criteria listed below in the section, "Leaching Experiments", were examined by X-ray fluorescence and X-ray diffraction. The samples were prepared for X-ray fluorescence and X-ray diffraction analysis using the Microjet 5 (Micro Materials corp.) high-speed grinder to provide samples with a smooth, talcum-powder-like consistency, i.e., with an average grain diameter of less than ten microns. Uniform sample weights were ground for uniform lengths of time to ensure reproducibility. Additional preparation included using a twenty-ton high pressure press to make disk-shaped briquets. Boric acid was used for the backing material for all briquets.

Further analysis was completed by atomic absorption (AA) to reveal the aqueous chemistry of the supernatant derived from core samples in equilibrium with type I water, i.e., double-distilled and deionized water. Because x-ray fluorescence analysis accounted for less than 95% of the total mass in all the samples, e.g., some analyses only accounted for 68%, AA and other chemical analyses were performed on the solid phase.

Ten samples were placed in centrifuge tubes and equilibrated with type I water for 30 days or more. The tailings/solution ratio for these ten samples was one-to-one.

During the equilibration period, the samples were shaken periodically to accelerate the equilibrium process. Aqueous extracts were then obtained by filtration. Aqueous analyses for Zn, Pb, and Cu were completed for the samples. Additional aqueous analyses for pH, Na, K, Ca, Mg, Fe, Mn, SO_4, Cl, and HCO_3 were completed for four of the ten samples. These four samples were later packed in leaching columns. The columns were set up to simulate extended periods of seepage that may occur periodically as a result of ponding during summer rains and winter snowmelts. In order for there to be sufficient solution volume to analyze, the tailings/solution ratio was approximately one-to-thirteen for these four samples.

A 12 cm core sample of the alluvium underlying the tailings was divided into 2 cm segments. The segments were then analyzed for Pb, Zn, Cu, Mn, and Fe. These analyses helped determine if there was any transport of metals beneath the tailings. It was assumed that if the total per cent weight of the metals decreased to near background levels in the measured samples, there was little vertical transport of the metals.

Sample preparations

Leaching Experiments

Samples were separated under several criteria for a leaching experiment with six columns. Four of these leaching columns were homogeneous (single-layered). The two other columns were two-layered, consisting of two single layers placed on top of each other in the same stratigraphic order as in the core samples.

Criteria for choosing layers in the leaching columns were as follows:

1. The core samples should penetrate layer 2 of the tailings pile since layer 2 is the majority of the tailings.
2. The core should have layers with different chemical compositions.
3. There should be enough material for lab analysis (i.e. 1 Kg of sample)
4. The hydraulic conductivity should be relatively high (greater than 10^{-7} cm/sec)
5. The distinct layers should be adjacent to each other

Four out of the ten samples satisfied these conditions and were packed into single-layer columns for leaching under simulated rainfall conditions.

The leaching columns (Fig. 6) were constructed from one-foot-long plexiglas tubing, 1.75 inches in diameter. A disk of plexiglas was epoxied to the bottom of each tube; and a nylon filter was placed at the bottom of each column. Additionally, a drain valve was attached to the bottom of each column.

Tailings were sieved with a 200 mesh sieve. The portion of the tailings passing the sieve was placed in a column to a depth of about 6 cm. Four different solid samples were packed in leaching columns using various combinations of single-layer and two-layer packing configurations (Table 2).

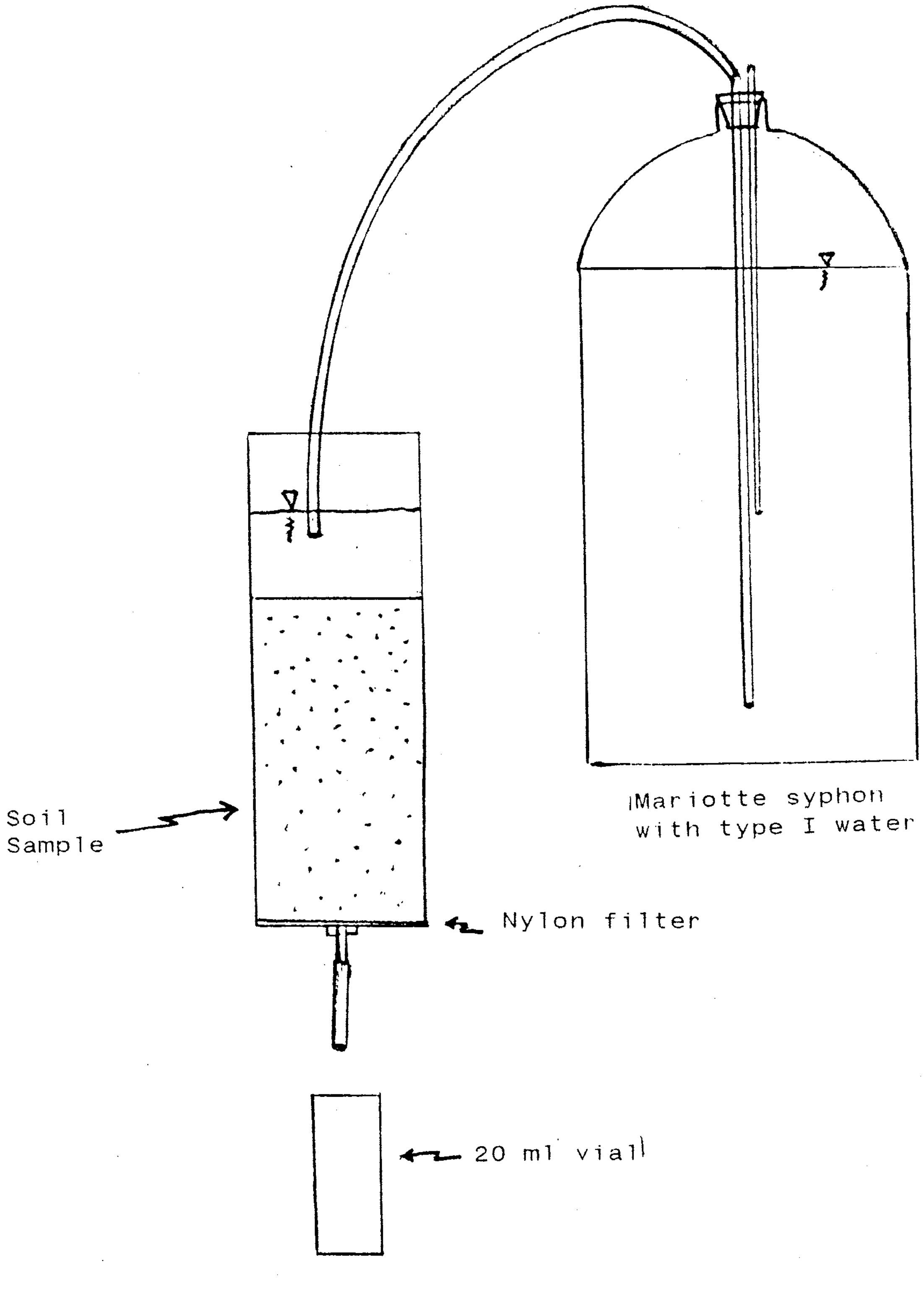

Figure 6 Leaching Column Setup

Table 2

Tailings Identity in Leaching Columns

	Sample #
Col 1	V6-262-314
Col 2	V75-103-157
Col 3	V6-104-158
Col 4	V75-157-310
Col 5	V6-104-158 over V6-262-314
Col 6	V75-103-157 over V75-157-310

A Mariotte siphon was attached to the valve to saturate the sample from the bottom to minimize entraped air. About 5 cm of water was allowed to pond above the sample. The water was allowed to equilibrate for at least three days. The tube from the Mariotte siphon was placed in the ponded water to maintain a constant head. The Mariotte reservoir was filled with type I water to simulate rain water leaching into the tailings. Ten ml of leachate was collected in 20 ml sample bottles every other day from each column for at least 40 days. Water remained static between sampling events, when it was allowed to drain freely through the sample. Leaching rates were measured by timing leachate collection and weighing sample bottles before and after leaching. The pore volume of each column was determined by weighing the columns before and after they were saturated; the difference between the two weights was the pore volume.

The chemistry of the leachate was analyzed at discrete time intervals. Emphasis was on zinc leaching, since zinc was a primary metal in the tailings and the zinc ion was easily measured in aqueous equilibrium with the tailings.

The leaching process was modelled using MINTEQ by assuming the effluent from one homogeneous layer was the input solution for the layer immediately below it. The composition of the final column effluent was compared to that predicted by the geochemical model. The fundamental assumption was that the solid phases were in equilibrium with aqueous and gas phases.

Leaching Studies

Initial mineral equilibrium

Initial mineral equilibrium's purpose was to determine what concentration of zinc and lead in solution was in chemical balance with the solid phase. Twenty grams of tailings was placed in a 50-ml polypropylene screw-cap centrifuge tube ("Oak Ridge" type). Twenty ml of type I water was added by a pipet to the centrifuge tube. The sample was shaken frequently over at least 24 hours for equilibration. The supernatant solution was separated from the soil by centrifugation and/or filtration. Supernatant from the tubes was placed in sample bottles. Samples were diluted to a linear-concentration range of the cation on the AA. The aqueous phase was analyzed for concentrations of Zn, and Pb by using absorption AA.

Pb Measurement on the AA

Special procedures were followed to compensate for sulfate interference of the absorption AA for the lead ions. Gypsum was added to lead standards so that sulfates were in equilibrium with the gypsum. Half a gram of gypsum was allowed to equilibrate for at least 24 hours in each 50 ml volume standard. Everything else in the procedure used the standard methods.

Measurement of transient concentration of Zn & pH

During the preparation for the AA analysis, the aqueous phase was separated from the solid phase by two different filter materials, paper and nylon. The initial equilibrium experiment used paper filters, but after it was determined that the zinc was sorbing to the paper filter, nylon filters were used after the first mineral equilibrium.

Second mineral equilibrium

A second batch equilibrium was started to quantify transient, pre-equilibrium concentrations of zinc in the most extreme cases. About 25 grams of samples V75-251-310, and V47-103-106 were placed in 250 ml bottles with 250 ml of type I water. Supernatant was filtered and analyzed for zinc at different times to check when equilibrium occurred. When equilibrium occurred, as indicated by stable zinc concentration, additional chemical analyses for Ca, Mg, Na, K, Fe, SO_4, and Cl were performed.

MINTEQ Method

MINTEQ (MINeral Thermodynamic EQuilibrium, version A2.0, Felmy et al., 1983) is a versatile geochemistry computer model for predicting the equilibrium speciation of a set of components in an aqueous system. For this experiment, the model was used primarily to estimate the concentration of ions and complexes in solution at equilibrium with minerals in the solid phase or, more specifically, the concentrations of ions in equilibrium with the tailings.

The first series of MINTEQ simulations were set up using the X-ray diffraction data for possible solid phases, and measured pH from the second batch equilibration. The model was run to solve for equilibrium conditions considering solid, aqueous, and gas phases.

The second series of MINTEQ simulations were set up using the X-ray diffraction data from the bottom layer in leaching experiment for possible solid phases, and the AA and wet chemistry analysis of the first layer experiment. Analyses of column leachate effluent were compared to the MINTEQ model. Each column was leached with type I water, and the composition of the leachate (pH, metal, and anions) was monitored as a function of time and volume of effluent. The composition of the effluent was compared with the composition predicted from geochemical models based upon solids analysis and batch extractions.

Single Layer Leaching Experiments

Minerals confirmed by X-ray diffraction were placed in the model. The pH and temperature measured in the leaching columns were other inputs to the model. The MINTEQ model then calculated the equilibrium speciation of the aqueous phase.

Double Layer Leaching Experiments

In the double layer case, the MINTEQ model was used to model the ultimate equilibrium conditions of type I water leaching through two different layers. The input of the model used aqueous analyses data measured from the single layer leaching column with the mineralogical analysis of the second layer.

Batch Isotherms

Zn with underlying soil

Solutions of zinc perchlorate in type 1 water, ranging in concentration from 10 to 5000 ppm, were shaken for at least 24 hours with 20 grams of soil at a soil/solution ratio of one-to-one. The soil used in this experiment was the alluvium underlying the tailings. Supernatant was filtered to separate suspended and solid particles. Next, the supernatant was analyzed by AA. The same equipment was used as with in initial batch equilibration. Differing initial concentrations of zinc were added to the soil underlying the tailings. Soil (20 g) was added to each of six centrifuge tubes in duplicate. Zinc solution (20 ml) was added to each tube in the following concentrations: 1000, 800, 600, 400, 200 mg/l Zn in type I water; type I water with soil (soil blank); and type I water without soil (soil-less blank). As before, the solution was shaken for at least 24 hours and supernatant analyzed by AA for zinc.

Column leachate with underlying soil

Leachates from five of the columns, each containing differing concentrations of Zn, were placed in contact with the soil underlying the tailings. Tubes containing soil/solution ratio of 1:10 were shaken for at least 24 hours to equilibrate with each other. As in the previous experiment, the supernatant was filtered and analyzed for zinc by AA.

III. RESULTS & DISCUSSION

Properties of the tailings and Alluvium

Bulk density was estimated from laboratory analysis of intact sections of core samples. Volume of tailings was estimated from a map and thicknesses in a longitudinal cross-section (Figs. 3 and 4). Volumetric field capacity of the tailings was estimated from an average of previous measurements (Johnson, 1987). Recharge to tailings was estimated from a previous study (Stephens, 1985).

Mineral/Chemical Analyses

Ten samples from the cores examined by X-ray fluorescence and diffraction revealed high percentages of sulfide and carbonate minerals (Tables 3 and 4). Further analysis by atomic absorption (AA) revealed that the samples' solid-phase contained up to 5% zinc and 1% lead. The chemical analyses revealed that there was more total iron and

Table 3
Minerals found by X-ray diffraction
and their relative quantity

Sample#	Qua	cal	pyr	gyp	smi	chl	hem	sid	dol	flu	kao
V47-107-152	X	M	M			M	tr?	tr?			
V47-103-106	X	X	tr		M	M			tr?	tr?	
V6- 120-131	X		M	tr	M	tr					
V6- 262-314	X	M	M								
V6- 104-120	X	M	tr	M		tr					
V6- 104-158	X	X	M	tr		M					
V75-251-310	X	X	M			M					
V75- 65-78	X	tr	X	tr		tr					
V47-207-210	X	tr	X	M							tr

X= major phase; M= minor phase; tr= trace phase
tr?= uncertain trace phase
Qua= Quartz; cal= calcite; pyr= pyrite; gyp= gypsum
smi= smithsonite; chl= chlorite; hem= hematite sid= siderite; dol= dolomite; flu= fluorite; kao= kaolinite

Table 4
Solid Phase Chemistry (% by wt)
(by X-ray fluorescence)

Sample #	V6-104-158	V6-262-314	V75-103-157	V75-251-310
LOI	8.79	12.75	7.04	8.65
S	2.19	3.57	1.74	2.43
Fe_2O_3	20.55	21.52	21.71	20.21
Na_2O	0.10	0.18	0.83	0.33
MgO	1.21	0.73	0.75	1.13
CaO	18.42	12.02	7.02	15.88
K_2O	0.54	0.38	0.27	1.26
MnO	1.53	0.95	1.08	1.37
CuO	0.013	0.070	0.18	0.062
PbO	0.20	0.24	1.51	0.50
ZnO	0.44	1.16	4.85	1.34
SiO_2	35.04	35.28	32.06	30.93
Al_2O_3	3.02	2.03	1.91	5.54
TiO_2	0.24	0.13	0.13	0.27
P_2O_5	0.03	0.01	0.02	0.03
TOTAL	92.31	91.02	81.10	89.93

Table 5
Solid Phase Chemistry (% by wt)
(by wet chemical analysis)

Sample #	V6-104-158	V6-262-314	V75-103-157	V75-251-310
CO_2	15.8	13.3	9.2	15.4
FeS_2	12.00	14.38	5.04	14.74
S as non-FeS_2	0.68	1.01	0.61	1.51
Fe_2O_3*	13.47	16.88	37.84	13.04
Na_2O	0.12	0.1	0.10	0.11
MgO	0.39	0.2	0.24	0.38
CaO	13.9	10.4	5.4	11.5
K_2O	0.55	0.38	0.26	1.34
MnO	0.06	0.04	0.04	0.06
CuO	0.023	0.061	0.14	0.73
PbO	0.22	0.194	1.18	0.49
ZnO	0.39	0.872	3.24	1.9
SiO_2	33.	37.	37.	33.
Al_2O_3	2.4	1.4	1.6	4.5
TOTAL	93.00	96.217	101.89	98.70

* all Fe as non-FeS_2 is assumed to be Fe_2O_3

sulfur than indicated by the analyses by the X-ray fluorescence method. Total mass returned on most of the later chemical analyses gave better results and were within 5% of 100% (Table 5).

Leaching Studies

Initial mineral equilibrium

The origin of high concentrations of sulfates and calcium in solution was unclear. There were three possibilities: 1) dissolution of gypsum, 2) dissolution of anhydrite or 3) Oxidation of pyrite and reaction with calcite (Drever, 1982).

$CaSO_4*2H_2O = Ca^{2+} + SO_4^{2-} + 2H_2O$

$FeS_2 + 3.75\ O_2 + 3.5\ H_2O = Fe(OH)_3 + 4\ H^+ + 2\ SO_4^{2-}$

$4\ H^+ + 2\ CaCO_3 = 2\ Ca^{2+} + 2\ H_2CO_3$

There is no way to determine which one of the three possibilities is correct unless sulfur isotope study is completed on the samples.

The origin of the zinc in solution appeared to be due to dissolution of smithsonite as in the following reaction:

$2\ ZnCO_3 + 2\ H_2O = 2\ Zn^{2+} + 2\ HCO_3^- + 2\ OH^-$

In a similar way, lead carbonate reacts with water in the following equation.

$2\ PbCO_3 + 2\ H_2O = 2\ Pb^{2+} + 2\ HCO_3^- + 2\ OH^-$

Initial batch equilibria showed there were significant amounts of Zn and Pb in solution. Aqueous solutions in equilibrium with samples contained up to 40 ppm Zn and 0.6 ppm Pb (Table 6). Both measurements are over the groundwater standards for New Mexico. The Pb levels may have been elevated due to interference from high sulfate concentrations (Lynn Brandvold, personal communication 1990).

Table 6
Aqueous Phase Chemistry (PPM)

Sample#	V6-104-158	V6-262-314	V75-103-157	V75-251-310	(S)
pH	7.6	7.6	7.2	7.0	6-9
Na	0.08	0.17	0.16	7.9	
K	1.9	1.0	1.0	11.	
Ca	406.	106.	590.	580.	
Mg	8.9	7.7	4.6	40.	
Zn	0.58	0.72	6.4	29.	10.
Pb	0.381	0.415	0.541		0.05
Cu	<0.1	<0.1	<0.1	<0.2	1.
Fe	<0.5	<0.5	<0.5	<0.2	1.
Mn	1.2	0.67	2.8	28.	0.2
SO_4	970.	275.	1,540.	1,950.	600.
Cl	<1.	<1.	<1.	1.2	250.
HCO_3	62.	73.	41.	56.	

(s) Drinking water standards, state of New Mexico (NMWQS, 1988)

The data was not corrected for potential sulfate, since the interference effect was negligible. The pH of the samples remained near neutral (Table 6).

Measurement of transient concentration of Zn & pH

Aqueous analyses of the transient chemistry of the Zn ion revealed that equilibrium occurred after more than 30 days (Fig. 7 and Appendix A). The curve indicates the dissolution of zinc from the tailings with respect to time. Note that the zinc concentration appears to reach equilibrium after thirty-five days. The two lines in Figure 7 are the boundaries of the zinc concentration according to the MINTEQ simulation at pH of 6 and 7. Measurement of the pH revealed

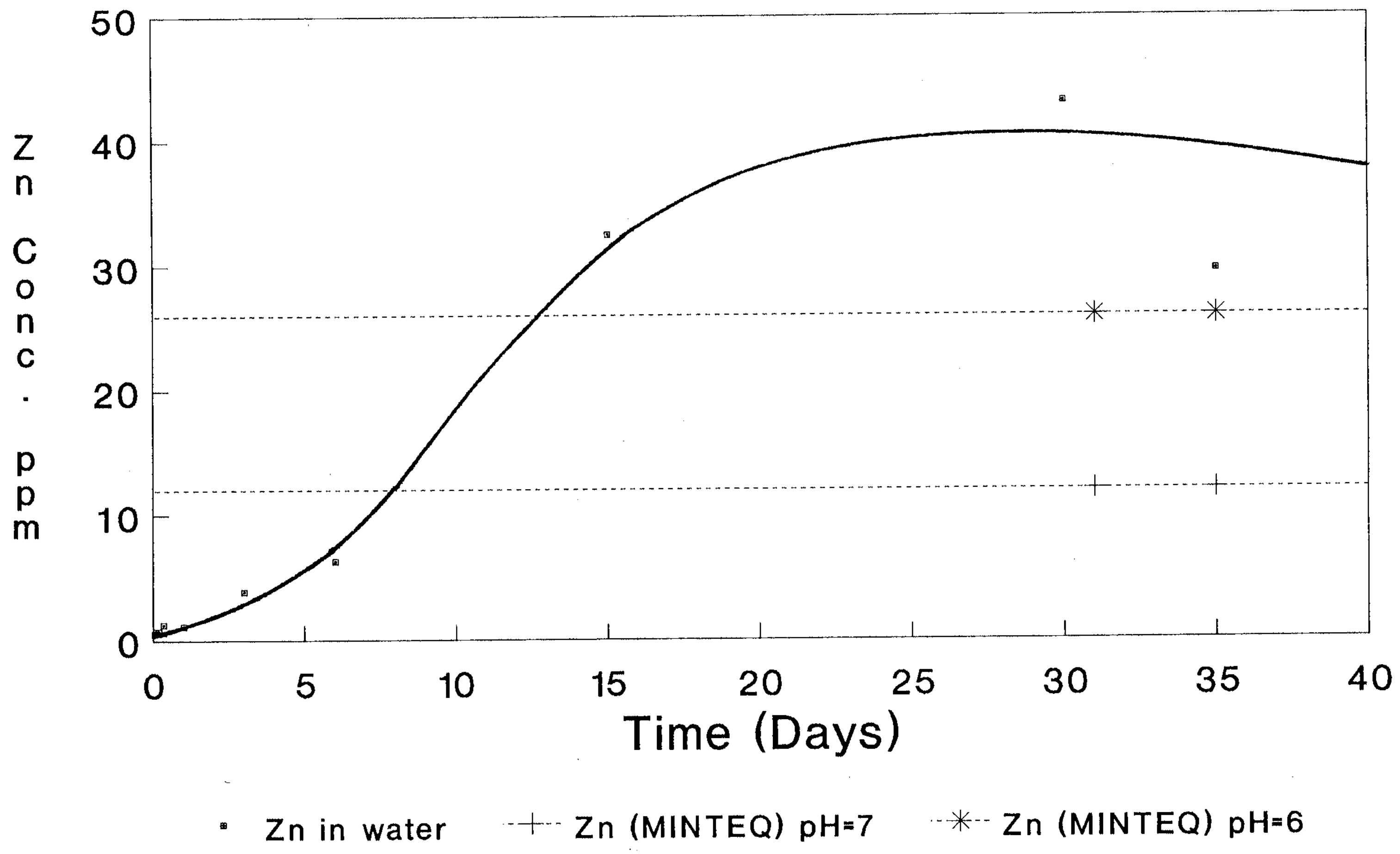

Figure 7. Kinetics of zinc minerals

that samples varied around neutral pH, i.e., from 6.8-7.5.

Nylon vs. paper filter

During the initial batch equilibria, the MINTEQ computer model was run to corroborate the results. Initially, the element concentrations based on analyses derived from the solid phase were used as input. However, when the computer-simulated equilibrium ion concentrations were compared with the concentrations obtained in the analyses from the initial batch equilibria, the metal ion concentrations simulated in MINTEQ were much higher. One possibility was that the paper filters used in filtering particulates from the leachate were adsorbing metal ions. In comparing the paper filters with nylon filters, it was found that the paper filters seemed to sorb more zinc than the nylon ones (Table 7). Thus, filters were switched to nylon filters immediately. If this factor was not taken into account, ultimate metal concentration in solution would have been off by approximately 20%. By comparison, when the filtrate was separated by the nylon filter, it gave more accurate concentrations of the zinc in solution (Table 7).

Table 7
Zinc Sorption of different filters

	filter	conc.
1 ppm Zn	paper	0.799
1 ppm Zn	nylon	0.958

Second mineral equilibrium

The geochemical model, MINTEQ (Felmy et al., 1983), confirmed that the aqueous samples were consistent with equilibrium conditions in solid-phase mineralogy (Tables 6 & 8). For example, gypsum was used in the model since this mineral appeared in the X-ray diffraction analysis. When gypsum was input into the MINTEQ model, the sulfate concentration closely matched two of the aqueous analyses.

Table 8
MINTEQ Model (single layer)

Minerals

Calcite (CaCO$_3$)
Gypsum (CaSO$_4$)*2H$_2$O
Hematite (Fe$_2$O$_3$)
Smithsonite (ZnCO$_3$)
Malachite (Cu$_2$CO$_3$(OH)$_2$)
Cerussite (PbCO$_3$)
Dolomite (MgCa(CO$_3$)$_2$)
Hausmannite (MnMn$_2$O$_4$)
Quartz (SiO$_2$)
Kaolinite (Al$_4$Si$_4$O$_{10}$(OH)$_8$)

	Concentration (PPM)		
	V47-103-106		V75-103-157
pH	7.57	-	6.89
Ca	167.	-	419.
Zn	12.	-	26.
Cu	0.13	-	0.25
Fe	<.5	-	<.5
Mn	18.	-	<0.1
SO$_4$	1,778.	-	1,472.
HCO$_3$	112.	-	271.
K	0.04	-	<0.01
Mg	82.	-	219.
Pb	0.3	-	0.4
pE	6.50	-	13.7

Other minerals important for controlling concentrations of ions in solution were calcite, smithsonite, and cerussite. Calcite contributed to calcium and bicarbonate concentration in solution. The MINTEQ simulation predicted higher bicarbonate concentration than actually measured (Table 6 and 8). Smithsonite contributed to the zinc concentration in solution. The MINTEQ simulation prediction showed a close match of zinc concentrations to at least two samples, V75-103-157 and V75-251-310 (Table 6 and 8). Zinc concentrations in the other samples may have been lower due to less smithsonite in the samples. Cerussite contributes to the total lead in solution. The MINTEQ simulation closely matched the lead concentrations in the equilibrium sample (Table 6 and 8). Also, the general conditions consistent with the aqueous geochemistry are near neutral pH and slightly reducing conditions. More detailed data from MINTEQ is in appendix C.

Column leaching experiment

Single and double layer setup

Column leaching simulated an equivalent of 2-3 years of leaching on site assuming a recharge rate of 5.8 cm/yr (Stephens, 1985). Chemical analyses of the single and double layer leaching models showed a small variation in the concentration of the ions in solution. Zinc concentrations from the leachate of the double-layer column 5 matched the zinc concentrations of the single-layer column 3 (Fig. 8 and Table 9). This was consistent with the idea that the bottom layer of the double-layer column controlled the ultimate concentration of the leachate.

Table 9
PPM in Leachate Solution (averaged over 20 days when zinc concentration was stable)

	pH	HCO_3	SO_4	Ca	Mg	Mn	K	Na	Cl	Zn
Col 1	7.3	66	1460	540	20.	9.8	5.3	1.3	0.2	3.3
Col 2	7.2	55	1480	570	1.3	13.	2.5	4.8	1.6	12.4
Col 3	7.6	76	1510	550	41.	16.	9.7	1.3	0.7	2.1
Col 4	7.4	21	1510	530	24.	16.	8.7	2.3	0.4	6.1
Col 5	7.5	58	1580	540	67.	9.3	11.	2.3	0.3	4.1
Col 6	6.4	33	1770	540	100.	21.	21.	9.3	1.1	4.9

However, zinc concentrations from leachate of the double-

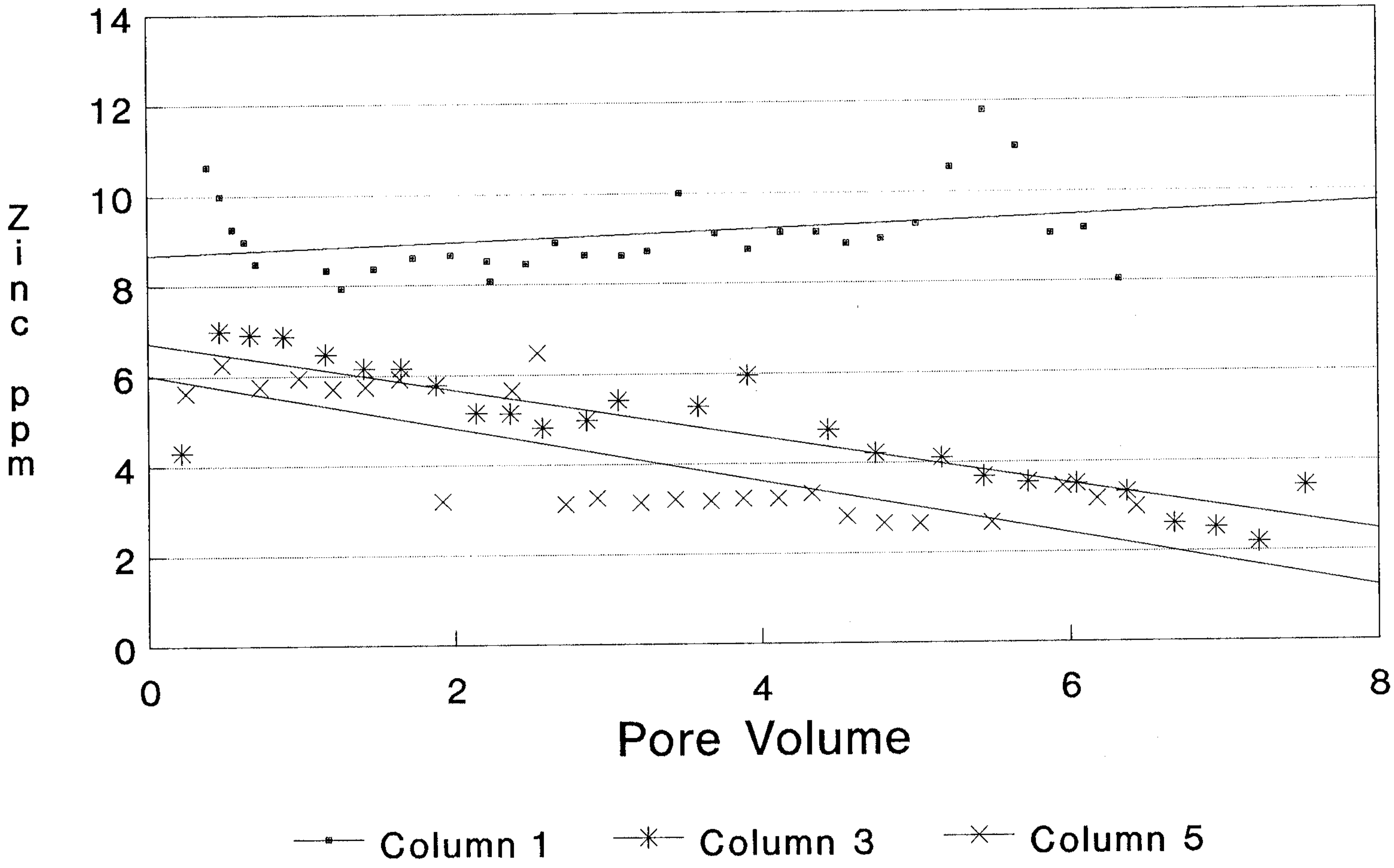

Figure 8. Column leachate

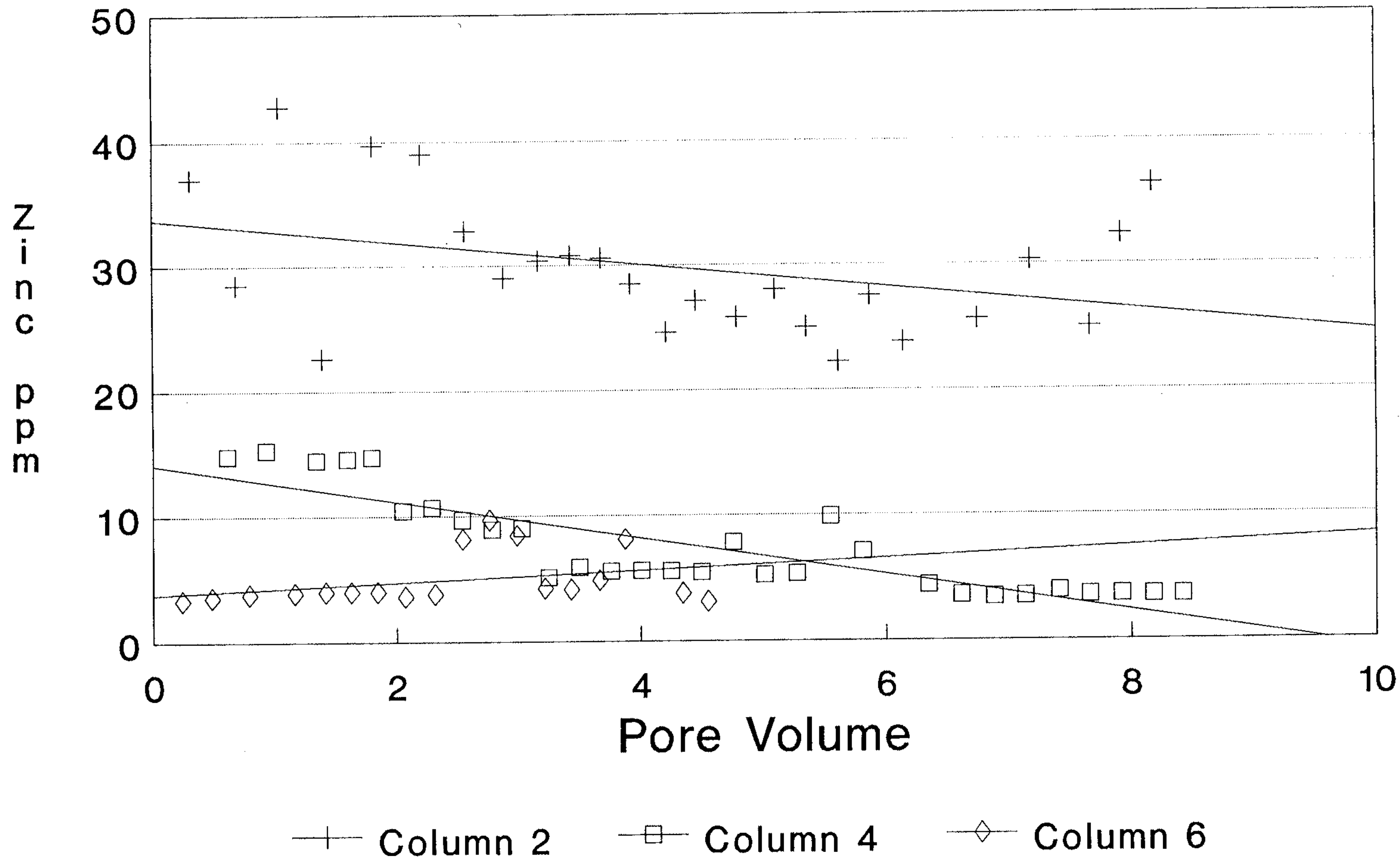

Figure 9. Column leachate

layer column 6 more closely matched leachate from single-layer column 4, which was the top layer in column 6 (Fig. 9). This discrepancy may have been caused by nonequilibrium conditions in the double-layer column. More detailed data from the leaching columns is located in appendix B.

MINTEQ Method

Single layer leaching experiments

The MINTEQ model output was compared to the chemical analysis of the single layer leaching columns. The pE was measured by an indirect method with the MINTEQ model. Estimates of pE in leaching columns were completed by concentration of Mn in solution with a mineral. The pE was altered in the model until the Mn concentration matched Mn concentrations in leaching columns. At this match point the pE was recorded.

Double layer leaching experiments

The double layer model output was close to the output of the single layer model (Table 10).

Table 10
MINTEQ Model (double layer)

Minerals	Concentration (PPM)		
		Col 5	Col 6
Calcite ($CaCO_3$)	pH	7.3	7.4
Gypsum ($CaSO_4$)*$2H_2O$	Ca	5,948.	3,261.
Hematite (Fe_2O_3)	Zn	2.1	12.4
Smithsonite ($ZnCO_3$)	Mn	16.0	13.0
Malachite ($Cu_2CO_3(OH)_2$)	Fe	< 0.5	< 0.5
Dolomite ($MgCa(CO_3)_2$)	SO_4	409.	465.
Hausmannite ($MnMn_2O_4$)	HCO_3	11.8	12.8
Quartz (SiO_2)	K	9.7	2.5
Kaolinite ($Al_4Si_4O_{10}(OH)_8$)	Mg	41.1	1.3
	pE	10.4	10.1

Batch Isotherms

The soil beneath the tailings showed it was highly sorbent to zinc. Up to 1800 ppm zinc was sorbed to the soil at an initial concentration of 5000 ppm. Overall, the data seemed to follow a logarithmic curve (Fig. 10). A sorption isotherm was constructed (Fig. 11) which compared the zinc sorption by the alluvium from a leachate matrix to the sorption of zinc by the alluvium from zinc perchlorate standards. Differences due to matrix were minimal.

Estimate of K_d

K_d is the slope of the batch isotherm line (Fig. 12). Under the laboratory experiment the data was not linear in the entire range of the zinc concentrations. However, at low concentrations the data was nearly linear, so a K_d was estimated for low concentrations of zinc (less than initial concentration of 200 ppm which will have a final equilibrium concentration less than 0.04 ppm). Since all laboratory readings (from leaching columns and mineral equilibria) of zinc concentrations were less than 100 ppm initially, this was a reasonable range to analyze.

Retardation factor (Zn)

The retardation factor is a measure of the slowing of a sorbed ion relative to an ideal tracer. Retardation factor will be examined more closely in the "Potential for Pollution" section.

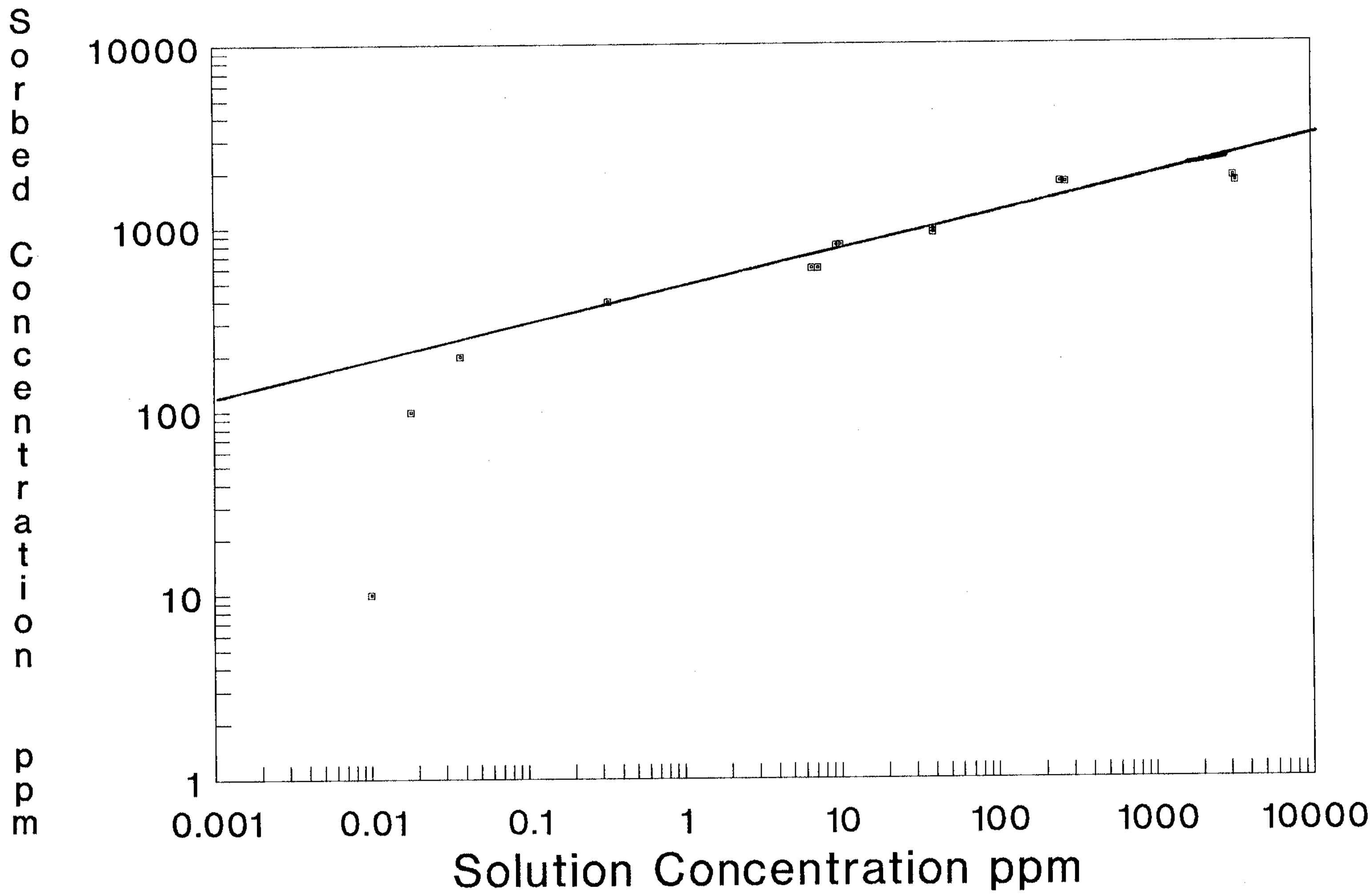

Figure 10. Zinc Soil Sorption Isotherm

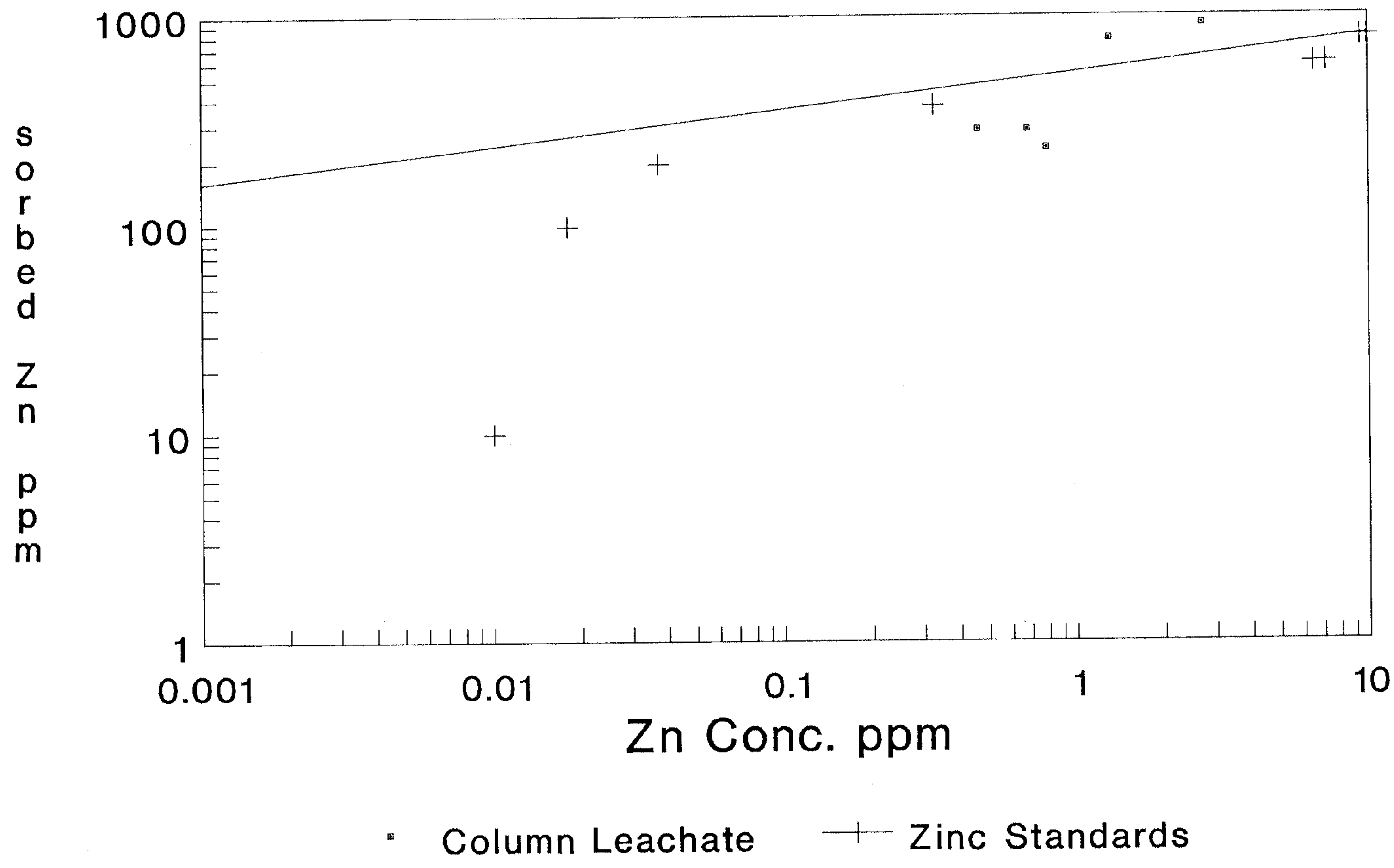

Figure 11. Sorption Isotherm w/ Alluvium

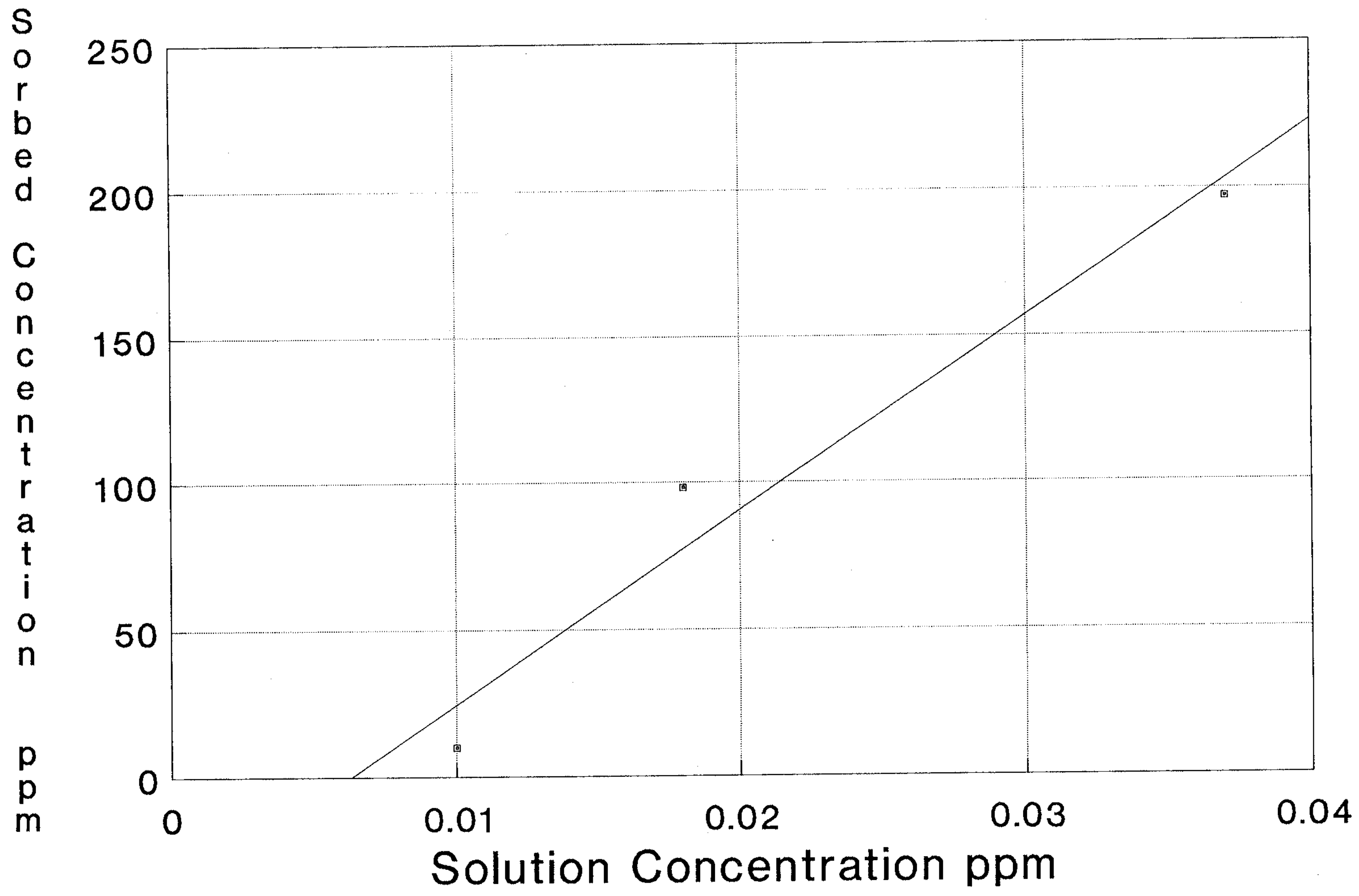

Figure 12. Zinc Soil Sorption Isotherm

Underlying alluvium sorption

The analyses of the underlying alluvium showed a clear trend of decreasing metal concentration with increasing depth (Table 11 and Fig. 13). Metal transport may have been due to movement as species dissolved or attached to particles.

Table 11
Percent Mass of Metals in Alluvium

	Pb	Zn	Cu	Mn	Fe
V75-348-350	0.238	1.3	0.067	0.11	7.2
V75-350-352	0.052	0.350	0.021	0.04	2.7
V75-352-354	0.035	0.270	0.014	0.05	2.8
V75-354-356	0.022	0.185	0.0086	0.04	2.2
V75-356-358	0.023	0.102	0.0062	0.06	2.2
V75-358-360	0.021	0.080	0.0047	0.07	2.0

A comparison of the batch isotherm with underlying soil with zinc in the leachate and zinc standards (Fig. 11) showed that the underlying soil sorbed about the same zinc from the leachate than the prepared zinc standards.

Estimates of Potential Zn Pollution from Tailings

The potential for pollution is dependent on factors such as depth to water, sorption of metal ions in the underlying alluvium, moisture content of alluvium, and recharge (Table 12). The data in table 12 was derived from many sources. The recharge of water to tailings was from previous research on recharge in New Mexico (Stephens, 1985). Total volume of tailings was estimated from the cross section and map of the tailings (Fig. 3 and 4). Average bulk density of tailings and alluvium was measured from lab analyses of the cores' physical mass and dimensions.

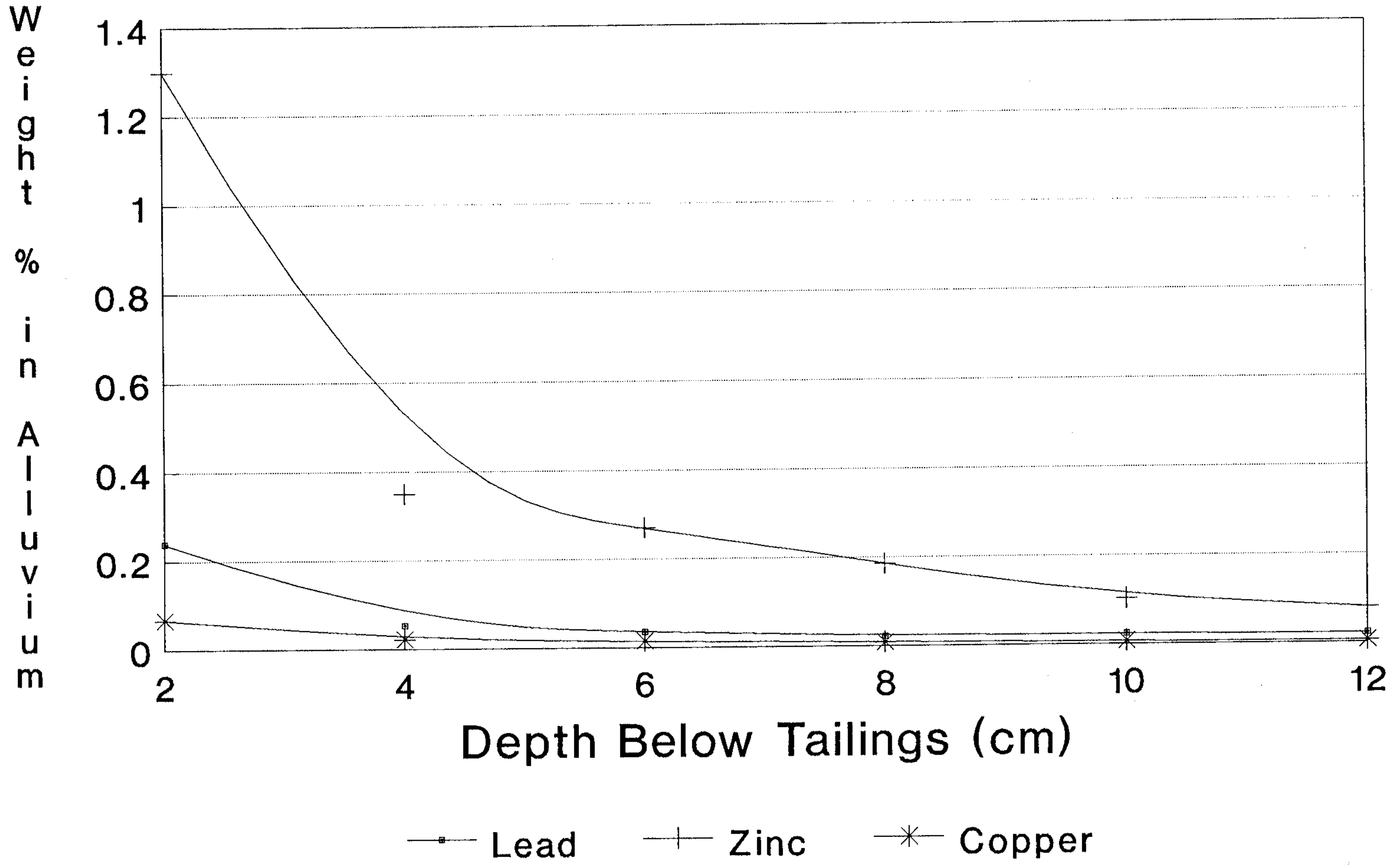

Figure 13. Weight % Metals (V75)

Table 12
Zinc data

Recharge to tailings	5.8 cm/yr [1]
Total Volume of tailings	1.57 e 11 cm^3
Avg. Bulk Density of tailings	2.15 g/cm^3
Avg. Bulk Density of Alluvium	1.9 g/cm^3
Avg. Zn by wt.	2.0%
Avg. Depth of tailings	5.5 m
Mass Zn per Area	23.5 g/cm^2
Max soil sorption	1800 ppm
Depth of alluvium needed for sorption of all Zn	69 m
Avg. clay content of Alluvium	10% [1]
Estimated field capacity	0.126
Kd from Zinc isotherm	4.8
Retardation factor (Zn)	72.

[1] Stephens (1985)

Average zinc by weight was calculated from the average of the zinc in the cores from AA analyses of the core samples (Table 13). Average depth of the tailings was estimated from the cross section (Fig. 4). Mass zinc per area was calculated from the average bulk density of tailings, average zinc by weight, and average depth of the tailings. Maximum soil (alluvium) sorption was estimated from a zinc sorption

Table 13
WEIGHT PERCENT IN SOLID PHASE (Tailings)

	Pb	Zn	Cu
V6-104-120	0.25	1.6	0.046
V6-104-158	0.20	0.31	0.018
V6-118-131	0.32	2.8	0.069
V6-262-314	0.18	0.70	0.049
V47-103-106	3.2	5.3	0.33
V47-107-152	0.40	0.87	0.034
V47-207-210	0.43	3.1	0.096
V75-65-78	0.62	1.2	0.046
V75-103-157	1.1	2.6	0.11
V75-251-310	0.45	1.5	0.058
AVERAGE	0.72	2.0	0.086
S.D.	0.866	1.41	0.086

isotherm (Fig. 10). Depth of alluvium needed for sorption of all zinc was estimated from maximum soil sorption and mass zinc per area. Average clay content of alluvium was from a plot of alluvium textural range (at 50% finer, Fig. 14, Johnson, 1987). Estimated field capacity was from a previous study (Johnson, 1987). K_d was from the linear portion of the zinc sorption isotherm (Fig. 12). The retardation factor was calculated below in the text.

Zinc occurs in the tailings in significant quantities (up to 5%), often as the highly soluble mineral, smithsonite ($ZnCO_3$). Zinc was above the drinking water standard in at least one equilibrium experiment (Table 6). Let us estimate alluvium sorption of Zn, travel time to water table and retardation factor to get a better estimate on the pollution potential.

First, let us estimate if there is enough alluvium beneath the tailings to sorb all the Zinc. Alluvium samples were tested for sorption capacity for Zn (Fig. 10). They showed that the alluvium was highly sorbent of Zinc with maximum Zinc sorption up to 1800 ppm. Considering the bulk density of both alluvium and tailing, the required depth to sorb all the zinc would be 69 m. The depth of the water table below the tailings was estimated to be about 18.2 m (Clark, 1968). This vadose zone is much shallower than the required depth of 69 m to sorb all the Zn. Thus, the Zinc will eventually seep into the groundwater. But, how long is that time for the zinc to reach the groundwater?

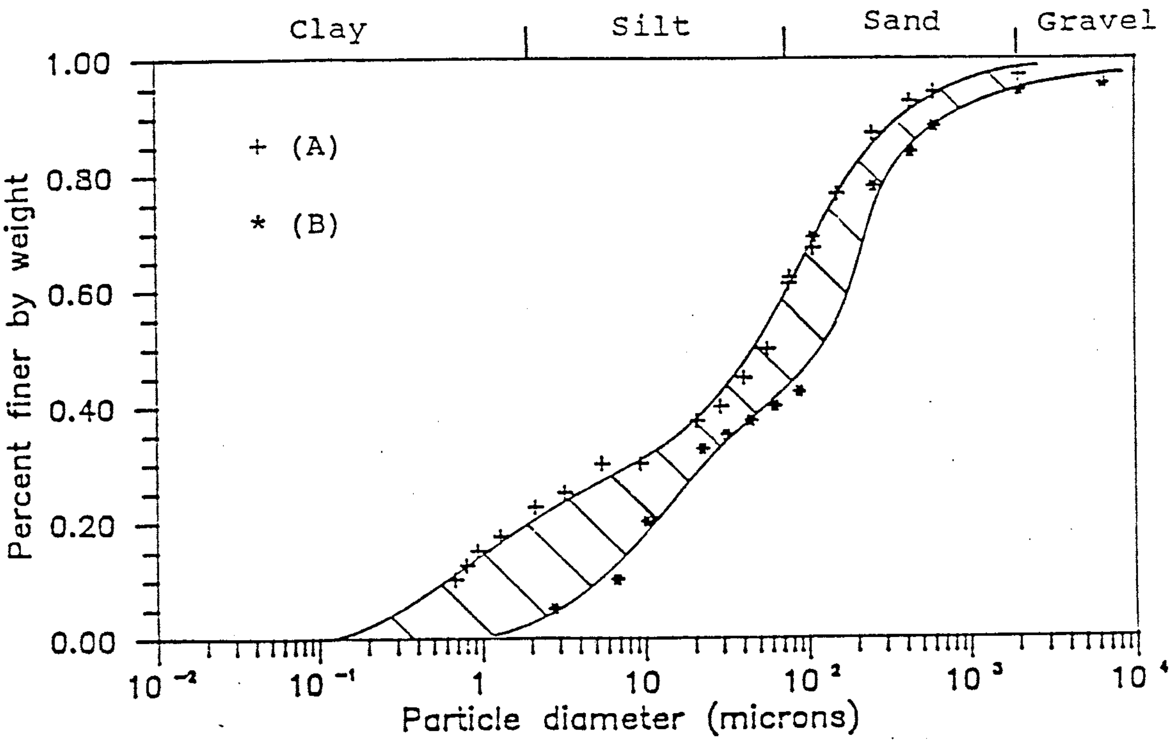

Figure 14. Range in grain size curves for the underlying soil.

Soil Textural Triangle

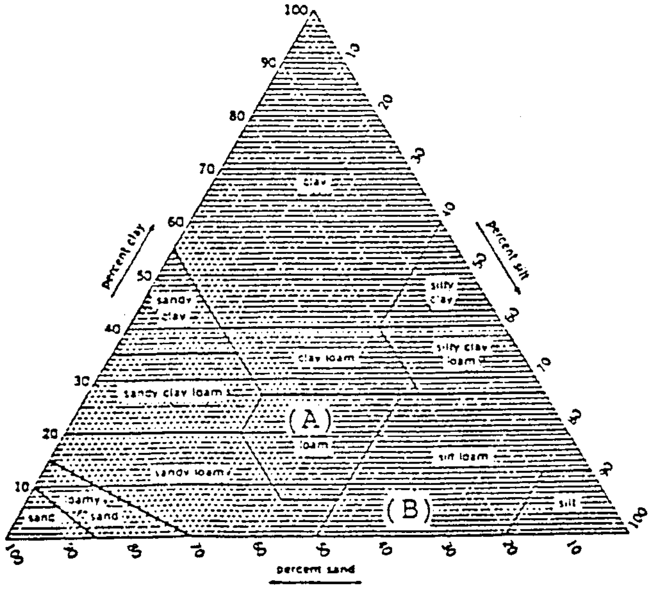

Figure 15. Grain size extremes for the underlying soil.

Second, we will estimate the ideal tracer travel time to the water table. Travel time can be estimated from the equation:

$$Tw=(L)*Thfc/q$$

Where: Tw= travel time; L= depth to water table
Thfc= field capacity moisture
q= water flux

field capacity can be estimated from the equation:

$$Thfc=0.674*(\text{Clay Content }\%)+5.88$$
(A. Mercado, personal communication, 1990).

From a previous study (Johnson, 1987), the clay content of the alluvium was estimated to average 10% (Fig. 14 & 15). If zinc behaved as an ideal tracer, the travel time of the zinc from the surface to the water table is about 40 yrs. This is a relatively small amount of time, since it has been over 40 years since the tailings were started. However, zinc is retarded in the alluvium.

Retardation can estimated from the following equation:

$$Rf= 1+((Ro)*K_d/Th)$$

where: Rf= retardation factor Ro= bulk density of alluvium
K_d = Slope of sorption isotherm
Th= volumetric moisture content

Note: K_d is only an estimate from figure 12. Although the graph is not linear at high concentrations, the K_d was estimated from Zn concentrations in column leachate.

The result of the equation yields 98,000 for Rf of the zinc. This is an extremely high retardation factor, suggesting the zinc will not be a problem for a long time (>100,000 years).

IV. SUMMARY AND CONCLUSIONS

Mine tailings near Magdalena, NM were examined for solid and aqueous phases. SiO_2, FeS_2, Fe_2O_3, $CaCO_3$, and $ZnCO_3$ compose most of the solids. Columns of tailings were leached under simulated rainfall. Leachate from columns of tailings contained much Zn, Mn, and SO_4. MINTEQ model simulations compared well to leachate from columns. Sorption capability of the alluvium was considerable (1800 ppm) but not enough to prevent ultimate migration into groundwater. Water travel-time estimate (40 yrs.) and zinc retardation factor (98,000) show that zinc transport time to groundwater is long (>100,000 yrs.). A rapid decrease of metals underlying the tailings within 10 cm implies that there is a very low migration rate for metals. Thus, zinc is not an immediate groundwater threat at the site.

Lead is another ion that may pose a potential threat to the groundwater. There was a concern that the lead may get transported to the groundwater or get transported from the tailings to residents in Magdalena by wind transport. The study did not encompass the wind transport of the tailings. However, like the zinc mentioned above lead ions appear to be highly retarded beneath the tailings and does not seem to pose an immediate threat to the groundwater.

Further Analyses of Pb are needed to check if the Pb is sorbed as much as zinc to the soil beneath the tailings.

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APPENDICES

LIST OF APPENDICES

APPENDIX A

Data from solid Chemistry analyses

Solid Phase Chemistry (% by wt)
(by X-ray fluorescence)

Sample #	V6-104-120	V47-107-151	V47-103-106	V47-207-210
LOI	8.79	8.12	13.47	8.92
S	2.76	3.09	0.32	2.31
Fe_2O_3	23.33	22.78	15.81	22.05
Na_2O	0.43	0.41	1.53	1.37
MgO	0.88	1.25	2.51	0.67
CaO	11.20	11.03	12.58	7.01
K_2O	0.42	0.49	0.89	0.14
MnO	1.20	1.57	1.52	0.84
CuO	0.06	0.04	0.41	0.13
PbO	0.27	0.43	3.45	0.46
ZnO	1.99	1.08	6.60	3.86
SiO_2	31.08	31.74	29.06	24.84
Al_2O_3	2.54	3.28	5.96	1.32
TiO_2	0.18	0.19	0.33	0.08
P_2O_5	0.02	0.02	0.03	0.01
TOTAL	85.15	85.55	94.47	74.02

Solid Phase Chemistry (% by wt)
(by X-ray fluorescence)

Sample #	V6-120-131	V75-65-78
LOI	6.24	17.11
S	1.19	6.54
Fe_2O_3	19.79	21.15
Na_2O	1.15	0.45
MgO	0.73	0.87
CaO	3.74	8.75
K_2O	0.09	0.44
MnO	0.80	0.76
CuO	0.09	0.06
PbO	0.34	0.67
ZnO	3.49	1.49
SiO_2	29.40	25.25
Al_2O_3	1.13	2.54
TiO_2	0.07	0.15
P_2O_5	0.01	0.02
TOTAL	68.27	84.25

APPENDIX B

Data from laboratory leaching columns

Column 1 (V6-262-314)

1 PORE VOLUME= 45.86 cm^3

SAMPLE #	CONC. (Zn) ppm	WATER (g)	PORE VOLUME
1	10.64	17.8	0.388
6	9.99	3.92	0.474
9	9.26	3.62	0.553
10	8.97	3.66	0.632
11	8.48	3.31	0.705
12	8.34	21.15	1.166
14	7.93	4.54	1.265
15	8.37	9.71	1.476
16	8.6	11.67	1.731
17	8.66	11.23	1.976
18	8.52	10.86	2.213
19	8.07	0.79	2.230
20	8.46	10.75	2.464
21	8.92	8.68	2.654
22	8.64	8.81	2.846
23	8.63	11.08	3.087
24	8.72	7.9	3.259
25	10.0	9.61	3.469
26	9.11	10.67	3.702
27	8.75	9.94	3.918
28	9.12	9.74	4.131
29	9.12	10.57	4.361
30	8.87	8.81	4.553
31	8.98	10.31	4.778
32	9.29	10.38	5.005
33	10.55	9.96	5.222
34	11.8	9.88	5.437
35	11.0	9.86	5.652
36	9.07	10.4	5.879
37	9.18	10.1	6.099
38	8.03	10.28	6.323

COLUMN 2 (V75-103-157)

1 PORE VOLUME= 41.12 cm^3

SAMPLE #	CONC. (Zn) ppm	WATER (g)	PORE VOLUME
1	37.0	12.77	0.311
2	28.5	15.61	0.690
3	42.8	14.48	1.042
4	22.6	14.54	1.396
5	39.7	16.98	1.809
6	39.0	16.18	2.202
7	32.8	14.69	2.560
8	29.0	13.13	2.879
9	30.4	11.7	3.163
10	30.8	10.79	3.426
11	30.6	10.53	3.682
12	28.5	9.71	3.918
13	24.6	12.19	4.214
14	27.1	10.1	4.460
15	25.8	13.52	4.789
16	28.0	12.88	5.102
17	25.0	10.5	5.357
18	22.2	10.71	5.618
19	27.5	10.52	5.874
20	23.8	11.03	6.142
21	25.6	24.96	6.749
22	30.3	17.89	7.184
23	65.3	9.38	7.412
24	25.0	10.58	7.670
25	32.4	10.45	7.924
26	36.3	10.41	8.177

COLUMN 3 (V6-104-158)

1 PORE VOLUME= 36.72 cm^3

SAMPLE #	CONC. (Zn) ppm	WATER (g)	PORE VOLUME
1	4.31	7.96	0.217
2	7.00	9.15	0.466
3	6.91	7.39	0.667
4	6.87	7.92	0.883
5	6.48	10.11	1.158
6	6.16	9.27	1.411
7	6.15	8.87	1.652
8	5.79	8.28	1.878
10	5.16	8.42	2.136
11	5.15	8.05	2.355
12	4.83	7.71	2.565
13	4.99	10.63	2.855
14	5.43	7.62	3.062
20	5.28	10.32	3.588
21	5.96	11.87	3.911
22	10.8	8.97	4.156
23	4.75	10.05	4.429
24	4.21	11.16	4.733
25	4.11	15.64	5.159
26	3.68	10.04	5.433
27	3.55	10.67	5.723
28	3.51	11.64	6.040
29	3.33	12.08	6.369
30	2.61	11.18	6.674
31	2.51	9.99	6.946
32	2.18	10.21	7.224
33	3.45	10.99	7.523
34	0.31	10.26	7.803
35	4.17	10.6	8.091
36	0.03	10.83	8.386
37	0.44	11.12	8.689
38	0.34	10.16	8.966
39	5.71	11.23	9.272
40	4.46	10.6	9.560

COLUMN 4 (V75-157-310)

1 PORE VOLUME= 40.51 cm^3

SAMPLE #	CONC. (Zn) ppm	WATER (g)	PORE VOLUME
1	14.8	24.82	0.613
2	15.3	12.87	0.930
3	14.5	16.66	1.342
4	14.6	10.2	1.593
5	14.7	8.2	1.796
6	10.45	10.28	2.050
7	10.7	9.61	2.287
8	9.7	9.88	2.531
9	8.94	9.84	2.774
10	9.00	9.94	3.019
11	5.1	8.99	3.241
12	5.91	10.21	3.493
13	5.56	10.55	3.753
14	5.59	10.03	4.001
15	5.57	10.06	4.249
16	5.48	10.09	4.498
17	7.83	10.42	4.756
18	5.22	10.44	5.013
19	5.33	10.53	5.273
20	9.87	11.18	5.549
21	7.09	10.5	5.808
22	40.7	10.65	6.071
23	4.36	10.94	6.341
24	3.58	10.98	6.612
25	3.43	10.83	6.880
26	3.46	10.3	7.134
27	3.92	11.4	7.415
28	3.56	10.01	7.663
29	3.59	10.46	7.921
30	3.57	10.42	8.178
31	3.58	9.76	8.419

COLUMN 5 (V6-104-158 over V6-262-314)

1 PORE VOLUME= 44.90 cm^3

SAMPLE #	CONC. (Zn) ppm	WATER (g)	PORE VOLUME
1	5.63	10.87	0.242
2	6.25	10.74	0.481
3	5.76	11.04	0.727
4	5.94	11.38	0.981
5	5.70	10.04	1.204
6	5.74	9.65	1.419
7	5.91	9.85	1.639
8	3.19	12.61	1.919
9	5.65	20.19	2.369
10	6.49	7.37	2.533
11	3.11	8.15	2.715
12	3.25	9.2	2.920
13	3.14	12.83	3.205
14	3.21	10.26	3.434
15	3.17	10.54	3.669
16	3.22	9.45	3.879
17	3.22	10.2	4.106
18	3.33	9.78	4.324
19	2.81	10.13	4.550
20	2.64	10.71	4.788
21	2.63	10.28	5.017
22	10.24	10.73	5.256
23	2.65	10.34	5.486
24	21.16	10.72	5.725
25	3.46	10.14	5.951
26	3.17	9.97	6.173
27	2.98	11.44	6.428

COLUMN 6 (V75-103-157 over V75-157-310)

1 PORE VOLUME= 49.32 cm^3

SAMPLE #	CONC. (Zn) ppm	WATER (g)	PORE VOLUME
1	3.32	11.81	0.239
2	3.58	11.95	0.482
3	3.79	15.35	0.793
4	3.88	18.36	1.165
5	3.97	12.46	1.418
6	3.99	10.45	1.630
7	4.01	10.67	1.846
8	3.63	11.12	2.072
9	3.81	11.85	2.312
10	8.16	11.09	2.537
11	9.70	10.74	2.754
12	8.47	11.04	2.978
13	4.23	11.4	3.209
14	4.13	10.74	3.427
15	4.86	11.57	3.662
16	8.11	10.39	3.872
17	3.79	11.83	4.112
19	3.15	10.28	4.552
20	7.42	10.14	4.757

Kinetics of Zinc dissolution from Tailings

V75-251-310

Time	Zn Conc.
1hr	0.506
2hr	0.705
4hr	0.727
8hr	1.23
1 day	1.10
3 days	3.87
6 days	6.26
15 days	32.5
21 days	57.5
30 days	43.1
35 days	29.6

APPENDIX C

Input/Output data for MINTEQ models

```
PC VERSION: MINTEQA2
DATE OF CALCULATIONS:  8-OCT-89  TIME:  6:13:22


Magdalena Mill Tailings
   For Table 11, V47-103-106
-----------------------------------------------------------
Temperature (Celsius):  25.00
Units of concentration: MOLAL
Ionic strength to be computed. If specified, total carbonate
concentration represents
     total inorganic carbon. Do not automatically terminate
if charge imbalance
     exceeds 30% Precipitation is allowed only for those
solids specified
     as ALLOWED in the input file (if any).
The maximum number of iterations is: 200 The method used to
compute activity coefficients is:
     Davies equation
Print the full species database including gram-formula
     weights and Debye-Huckel parameters.
-----------------------------------------------------------

             INPUT DATA

          140  0.000E+00  -16.00
          330  0.269E-07   -7.57
            2  0.555E+02    1.00
            1  0.316E-06   -6.50
          150  0.000E+00  -20.60
          770  0.000E+00  -20.98
          732  0.000E+00  -20.98
          950  0.000E+00  -20.82
          231  0.000E+00   -0.80
          730  0.000E+00  -20.52
          230  0.000E+00  -20.80
          600  0.000E+00  -16.00
          280  0.000E+00  -16.00
          281  0.000E+00  -16.00
           30  0.000E+00  -16.00
          410  0.000E+00  -16.00
          460  0.000E+00  -16.00
          471  0.000E+00  -16.00
          470  0.000E+00  -16.00
```

```
          S(0) HAS BEEN INSERTED FOR POLYSULFIDE CALCULATIONS
                    3   10
NAME           ID#
CO2 (g)        3301403     20.6658     -0.5300
HS-/SO4-2      7307320     33.6600    -60.1400
CU+1/CU+2      2302310      2.7200      1.6500
GYPSUM         6015001      4.8480     -0.2610
CALCITE        5015001      8.4750      2.5850
QUARTZ         2077002      4.0060     -6.2200
FE+3/FE+2      2812800     13.0320    -10.0000
MN+3/MN+2      4714700    -25.5070     25.7600
E-1                  1      6.5000      0.0000
H+1                330      7.5700      0.0000
                    4    7
MALACHITE      5023101      5.1800     15.6100    1.000E-01
SMITHSONITE    5095000     10.0000      4.3600    1.000E-01
CERRUSITE      5060000     13.1300     -4.8600    1.000E-01
KAOLINITE      8603001     -5.7260     35.2800    1.000E-01
HEMATITE       3028100      4.0080     30.8450    1.000E-01
DOLOMITE       5015002     17.0000      8.2900    1.000E-01
HAUSMANNITE    3047000    -61.5400     80.1400    1.000E-01
                    5    1
               1028003     18.4790    -11.3000

            S(0) HAS AN ACTIVITY OF 1 AND IS TYPE 3

           INPUT DATA BEFORE TYPE MODIFICATIONS

ID        NAME         ACTIVITY GUESS     LOG GUESS
140       CO3-2             1.000E-16       -16.000
330         H+1             2.692E-08        -7.570
  2        H2O              1.000E+01         1.000
  1        E-1              3.162E-07        -6.500
150        Ca+2             2.512E-21       -20.600
770      H4SiO4             1.047E-21       -20.980
732       SO4-2             1.047E-21       -20.980
950        Zn+2             1.514E-21       -20.820
231        Cu+2             1.585E-01        -0.800
730        HS-1             3.020E-21       -20.520
230        Cu+1             1.585E-21       -20.800
600        Pb+2             1.000E-16       -16.000
280        Fe+2             1.000E-16       -16.000
281        Fe+3             1.000E-16       -16.000
 30        Al+3             1.000E-16       -16.000
410         K+1             1.000E-16       -16.000
460        Mg+2             1.000E-16       -16.000
471        Mn+3             1.000E-16       -16.000
470        Mn+2             1.000E-16       -16.000
731           S             1.000E+00         0.000
```

SPECIES: TYPE III - FIXED SOLIDS

ID	NAME
731	S
2	H2O
330	H+1
1	E-1
3301403	CO2 (g)
7307320	HS-/SO4-2
2302310	CU+1/CU+2
2812800	FE+3/FE+2
4714700	MN+3/MN+2
5015001	CALCITE
6015001	GYPSUM
2077002	QUARTZ

SPECIES: TYPE IV - PRECIPITATED SOLIDS

ID	NAME
3028100	HEMATITE
5015002	DOLOMITE
3047000	HAUSMANNITE
5095000	SMITHSONITE
5060000	CERRUSITE
8603001	KAOLINITE
5023101	MALACHITE

SPECIES: TYPE V - DISSOLVED SOLIDS

ID	NAME
1028003	PYRITE

SPECIES: TYPE VI - SPECIES NOT CONSIDERED

ID	NAME
3300021	O2 (g)
3301404	CH4 (g)

```
                SPECIES:   TYPE  III - FIXED SOLIDS

ID          NAME       CALC MOL          LOG MOL  NEW LOGK
     731       S      -2.800E-29         -28.553     0.000
       2     H2O       5.553E+01           1.745     0.007
     330     H+1       2.252E-02          -1.647     7.570
       1     E-1      -2.260E-04          -3.646     6.500
3301403  CO2 (g)      -1.268E-02          -1.897    20.666
7307320  HS-/SO4-2     3.000E-29         -28.523    33.660
2302310  CU+1/CU+2     6.824E-12         -11.166     2.720
2812800  FE+3/FE+2     2.223E-18         -17.653    13.032
4714700  MN+3/MN+2     9.914E-24         -23.004   -25.507
5015001  CALCITE       1.773E-02          -1.751     8.475
6015001  GYPSUM       -1.852E-02          -1.732     4.848
2077002  QUARTZ       -9.572E-05          -4.019     4.006


SPECIES:   TYPE  IV - PRECIPITATED SOLIDS

ID          NAME        CALC MOL         LOG MOL     NEW LOGK
3028100  HEMATITE       1.000E-01        -15.347      4.008
5015002  DOLOMITE       9.663E-02         -2.473     17.000
3047000  HAUSMANNITE    9.989E-02         -3.946    -61.540
5095000  SMITHSONITE    9.982E-02         -3.751     10.000
5060000  CERRUSITE      1.000E-01         -5.805     13.130
8603001  KAOLINITE      1.000E-01         -8.766     -5.726
5023101  MALACHITE      1.000E-01         -6.002      5.180


SPECIES:   TYPE  V - DISSOLVED SOLIDS

ID          NAME        CALC MOL     LOG MOL      NEW LOGK
1028003  PYRITE         0.000E-01    -148.215     18.479


SPECIES:   TYPE  VI - SPECIES NOT CONSIDERED

ID          NAME        CALC MOL       LOG MOL     NEW LOGK
3300021  O2 (g)         1.397E-27     -26.855     -83.120
3301404  CH4 (g)        0.000E-01     -93.111      40.100
```

```
          PERCENTAGE DISTRIBUTION OF COMPONENTS AMONG
            dissolved and adsorbed species

E-1
      55.6     PERCENT BOUND IN SPECIES #4700020 MnO4  -

      44.4     PERCENT BOUND IN SPECIES #4700021 MnO4  -2

Ca+2
      27.5     PERCENT BOUND IN SPECIES #    150 Ca+2

      71.9     PERCENT BOUND IN SPECIES #1507320 CaSO4  AQ

SO4-2
      69.3     PERCENT BOUND IN SPECIES #    732 SO4-2

      12.6     PERCENT BOUND IN SPECIES #4607320 MgSO4  AQ

      16.2     PERCENT BOUND IN SPECIES #1507320 CaSO4  AQ

       1.3     PERCENT BOUND IN SPECIES #4707320 MnSO4  AQ

Mn+2
      29.7     PERCENT BOUND IN SPECIES #    470 Mn+2

      69.4     PERCENT BOUND IN SPECIES #4707320 MnSO4  AQ

Zn+2
      19.2     PERCENT BOUND IN SPECIES #    950 Zn+2

      57.9     PERCENT BOUND IN SPECIES #9507320 ZnSO4  AQ

       6.0     PERCENT BOUND IN SPECIES #9507321 Zn(SO4)2-2

       3.8     PERCENT BOUND IN SPECIES #9501400 ZnHCO3 +

      11.2     PERCENT BOUND IN SPECIES #9501401 ZnCO3  AQ

Pb+2
       1.6     PERCENT BOUND IN SPECIES #    600 Pb+2

       1.1     PERCENT BOUND IN SPECIES #6003300 PbOH +

      11.7     PERCENT BOUND IN SPECIES #6007320 PbSO4  AQ

      82.2     PERCENT BOUND IN SPECIES #6001401 PbCO3  AQ

       2.0     PERCENT BOUND IN SPECIES #6001402 PbHCO3 +
```

```
----------- EQUILIBRATED MASS DISTRIBUTION -----------

          IDX NAME         MOL/KG

          410  K+1         1.090E-16
          731  S           2.800E-29
          140  CO3-2       1.870E-03
          330  H+1         1.931E-03
            1  E-1        -9.000E-30
            2  H2O         5.388E-06
          730  HS-1        3.000E-29
          230  Cu+1        6.824E-12
          280  Fe+2        2.223E-18
          471  Mn+3        9.914E-24
          150  Ca+2        4.160E-03
          732  SO4-2       1.852E-02
          770  H4SiO4      9.572E-05
          281  Fe+3        8.965E-16
          460  Mg+2        3.369E-03
          470  Mn+2        3.394E-04
          950  Zn+2        1.775E-04
          600  Pb+2        1.568E-06
           30  Al+3        3.427E-09
          231  Cu+2        1.992E-06

CHARGE BALANCE: SPECIATED

SUM OF CATIONS =  4.647E-03 SUM OF ANIONS   2.740E-02

PERCENT DIFFERENCE =
     7.100E+01   (ANIONS - CATIONS)/(ANIONS + CATIONS)
```

```
Saturation indices of some minerals

    ID #      NAME       Sat. Index
6015000 ANHYDRITE       -0.196
5015000 ARAGONITE       -0.139
5015001 CALCITE          0.000
2077000 CHALCEDONY      -0.483
2077001 CRISTOBALITE    -0.419
2003002 DIASPORE         0.000
5015002 DOLOMITE         0.000
6015001 GYPSUM           0.000
3028100 HEMATITE         0.000
5046002 MAGNESITE       -0.496
1028003 PYRITE        -148.215
2077002 QUARTZ           0.000
2077003 SIO2(A,GL)      -0.988
3047100 BIXBYITE         0.001
3047000 HAUSMANNITE      0.000
2047100 MANGANITE       -0.071
5047000 RHODOCHROSITE    0.880
2023101 TENORITE         0.127
5095000 SMITHSONITE      0.000
5095001 ZNCO3, 1H2O      0.253
2095004 ZN(OH)2 (E)     -0.842
2095005 ZNO(ACTIVE)     -0.644
2095006 ZINCITE         -0.474
1095001 SPHALERITE     -73.610
8295000 ZNSIO3           3.730
8095000 WILLEMITE        1.996
5060000 CERRUSITE        0.000
6060003 ANGLESITE       -1.698
1060001 GALENA         -73.226
2060004 PB(OH)2 (C)     -0.622
8603001 KAOLINITE        0.000
8603002 PYROPHYLLITE    -0.681
5023101 MALACHITE        0.000
  73100 SULFUR         -65.652
8646006 Montmorillon    -0.749
```