# Investigation of Acid Production, Leaching, and Transport of Dissolved Metals at an Abandoned Sulfide Tailings Impoundment: Monitoring and Physical Properties 




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# Investigation of Acid Production, Leaching, and Transport of Dissolved Metals at an Abandoned Sulfide Tailings Impoundment: Monitoring and Physical Properties 

By B. M. Stewart, B. C. Williams, and R. H. Lambeth

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## UNIT OF MEASURE ABBREVIATIONS USED IN THIS REPORT

| cm | centimeter | $\mathrm{mL} / \mathrm{min}$ | milliliter per minute |
| :--- | :--- | :--- | :--- |
| $\mathrm{cm} / \mathrm{s}$ | centimeter per second | mm | millimeter |
| $\mathrm{g} / \mathrm{cm}^{3}$ | gram per cubic centimeter | mV | millivolt |
| h | hour | pct | percent |
| ha | hectare | ppb | part per billion |
| kg | kilogram | ppm | part per million |
| m | meter | s | second |
| $\mathrm{m}{ }^{3}$ | cubic meter | vol pct | volume percent |
| $\mathrm{m} / \mathrm{d}$ | meter per day | $\mu \mathrm{L}$ | microliter |
| $\mathrm{mg} / \mathrm{L}$ | milligram per liter | $\mu \mathrm{m}$ | micrometer |
| $\mathrm{m} / \mathrm{m}$ | meter per meter | $\mu \mathrm{S} / \mathrm{cm}$ | microsiemens per centimeter |
| min | minute | ${ }^{\circ} \mathrm{C}$ | degree Celsius |
| mL | milliliter |  |  |

# INVESTIGATION OF ACID PRODUCTION, LEACHING, AND TRANSPORT OF DISSOLVED METALS AT AN ABANDONED SULFIDE TAILINGS IMPOUNDMENT: MONITORING AND PHYSICAL PROPERTIES 

By B. M. Stewart, ${ }^{1}$ B. C. Williams, ${ }^{\mathbf{2}}$ and R. H. Lambeth ${ }^{1}$


#### Abstract

Researchers at the U.S. Bureau of Mines conducted a long-term groundwater monitoring and site characterization program at an abandoned $10-\mathrm{ha}$, acid-producing, copper-gold tailings impoundment in north-central Washington State. The purpose was to investigate contaminant release and transport, and attenuation mechanisms in the tailings, sediments below the tailings, and gravels downgradient of the impoundment. This report summarizes the monitoring results and physical properties of the tailings, the sediments below the tailings, and the groundwater system associated with the tailings.

Water samples from the vadose and saturated zones of the impoundment were analyzed for 15 constituents. Concentrations of the same constituents were determined in water samples up to 3 m beneath the impoundment and in the shallow colluvium and deep bedrock at 76,335 , and 550 m downgradient and 168 m upgradient.

Constituent concentrations within the tailings are quite variable and are influenced by pH , depth of oxidation, grain-size differential (surface area), hydraulic gradient, groundwater mixing, and the presence of hardpan layers, carbonaceous material, and organic matter. Most of the metal constituents decreased to background or near-background concentrations in the farthest downgradient well.


[^1]
## INTRODUCTION

Cleanup of inactive mining-related sites and protection of the environment during current mining is a significant issue in the United States. The control of water pollution from mining and milling wastes is addressed under the Clean Water Act, which regulates the discharge of pollutants into surface waters; the Resource Conservation and Recovery Act (RCRA), which classifies the hazard potential of wastes; and the Comprehensive Environmental Response Compensation and Liabilities Act (CERCLA), which was written to guarantee the cleanup of sites not covered by other laws.

It has now been recognized that many inactive or abandoned mine sites are sources of contaminated water. Some of these mines have been placed on the National Priorities List under CERCLA and the Superfund Amendment and Reauthorization Act.

In 1988, the U.S. Environmental Protection Agency (EPA) significantly revised guidance documents and activities and prepared a National Contingency Plan that encourages and supports the use of innovative treatment technologies at Superfund sites. One provision of the plan includes selecting permanent, long-term remedies, with the highest priority for treatment to be given to "liquids, other highly mobile materials, and highly concentrated toxic compounds" (EPA, 1988).

There are currently very few, if any, cost-effective technologies to clean up surface and/or ground waters that have been contaminated by mining and milling wastes at inactive sites. Because of the complexity of the chemical and physical factors that contribute to water contamination from mining wastes, researchers at the U.S. Bureau of Mines (USBM) are conducting long-term studies on the generation, mobilization, and fate of heavy metals and other contaminants in these wastes. The results will be used to aid in the development of remediation strategies and to identify additional data needed for remediation.

The generation of acid and subsequent metal dissolution in tailings impoundments is a complex biogeochemical process involving the oxidation of pyrite and other sulfides and includes several inorganic reactions that depend upon
such factors as pH , oxidation-reduction potential (Eh), oxygen availability, and the availability of other oxidants, such as ferric iron $\left(\mathrm{Fe}^{3+}\right)$. Although oxygen initiates sulfide oxidation, at low pH levels, the important ratedetermining step(s) may involve other oxidants, such as ferric iron instead of oxygen (Nordstrom, 1982). Sulfide oxidation may also be directly or indirectly catalyzed by the presence of bacteria of the Thiobacillus genus and by other species of sulfur- and/or iron-oxidizing bacteria. Sulfides that are oxidized by oxygen and other oxidants are the source of sulfates and $\mathrm{H}^{+}$(acid) in solution. The acid dissolves and is neutralized by carbonates, aluminosilicates, and existing oxides, and by secondary aluminum hydroxides (Dubrovsky and others, 1985). Sulfates and hydroxide minerals form as precipitates when they reach geochemical saturation, depending upon the reaction kinetics. These reactions may occur near the sulfide source as well as downgradient from the point of sulfide oxidation. The degree of moisture saturation can influence the primary oxidation mechanism. A study by Taylor and others (1984) indicates that oxidation of sulfides in anaerobic, water-saturated environments occurs primarily by chemical oxidation pathways, whereas oxidation of sulfides in wellaerated vadose zone environments occurs mainly by microbially mediated pathways.

This Report of Investigations (RI) describes a research conducted at a specific mine waste site. It includes site characterization and results of analyses of water quality data collected in the vadose zone, the saturated zone, the sediments below the waste, the shallow unconsolidated aquifer, and deep zones of weathered bedrock at various distances downgradient from the waste. The primary objectives of this investigation were (1) to determine the physical property characteristics of the tailings and associated formations that affect acid production, leaching, and transport of dissolved metals from the waste and (2) to report existing water quality and other site-specific geological, physical, and hydrologic data that may be used for future site remediation work.

## SITE DESCRIPTION AND SELECTION

## SITE CRITERIA

The research objectives led to selection criteria for a tailings impoundment. Ease of access to the impoundment and adjacent watersheds were primary considerations. The following were also important:

1. A phreatic surface within the tailings profile, preferably in hydraulic connection with a shallow aquifer. This
criterion permits the vadose zone to be compared with the saturated zone. If the tailings were not separated from the underlying material with a liner, the direct contact would permit analysis of free drainage, as well as upwelling, depending upon hydraulic conditions.
2. A vadose zone no less than 2 m thick to ensure that there was an adequate thickness to identify changes in characteristics such as oxygen content.
3. A significant amount of sulfides and few carbonates, to ensure that the tailings were acid producing. Such a condition is representative of most sulfide mine wastes.
4. Tailings and water slurry yielding acidic pH values, which would also support the belief that the tailings were acid producing.
5. An impoundment where there had been relatively little disturbance since the original deposition of the tailings. Postdepositional reworking of tailings might destroy or confound earlier distributions of certain physical or chemical properties with respect to depth. Because the kinetics of some oxidation reactions are slow, physical and chemical characterizations should most closely approximate "equilibrium" (given age, location, and climate) if the tailings were undisturbed.

## SITE DESCRIPTION

After visits to many different sites, the site chosen for this research was an abandoned gold and copper tailings impoundment on the eastern slope of the Cascade Mountains in Washington State. The site receives an average of 370 mm of precipitation per year. Temperatures range from -36 to $41^{\circ} \mathrm{C}$, and the annual average is $7^{\circ} \mathrm{C}$. Figure 1 is a low-angle photograph of the research site looking down the valley to the southeast. The impoundment measures approximately 200 by 46 m , with an average depth of 6.1 m and a surface elevation of about 567 m above sea level. It contains about $33,100 \mathrm{~m}^{3}$ of material. The phreatic surface, which varies spatially and temporally, is approximately 3 to 5 m below the ground surface. A cross section of the impoundment is shown in figure 2.

The valley in which the impoundment is located is a surface expression of a northwest-trending, near-vertical, tension-gash fault in midacidic metavolcanic bedrock. The valley floor is covered with a veneer of remnant gravel, and numerous calcareous and carbonaceous lake beds, some now dry, dot the floor. The tailings were deposited on top of one of these lake beds and next to a small pond. The upper meter of the silty lake sediments below the tailings is particularly rich in organic material, but the lateral extent of these sediments is not known. The geology of the valley in which the tailings impoundment was constructed is discussed in more detail by Lambeth (1992).

Mill records indicate that copper and zinc minerals were recovered by a conventional dual-circuit flotation system maintained at pH 10 or higher by the addition of lime. The mill was operating and depositing tailings into the impoundment between 1939 and 1953. The mined ore
body, which is several miles away, is a chalcopyritesphalerite deposit containing gold and may be volcanogenic or (contact) metamorphic in origin. Mineralogical optical analysis of tailings from the chosen site indicated that tailings composition is 95 pct gangue minerals (primarily quartz and plagioclase) and 5 pct sulfide minerals (e.g., pyrite, chalcopyrite, sphalerite, and trace amounts of galena). No carbonates from the tailings were observed. Slurries composed of surface tailings mixed with deionized water yielded pH values in the range of 4 to 5 . With the exception of one $2-\mathrm{m}$-deep pit (presumably dug in recent years to determine whether it would be economical to remill the tailings), these tailings have remained undisturbed since they were deposited.

The gravel aquifer under the tailings is recharged from bedrock sources and local precipitation. The flow direction is from the topographic high at the northwest end of the site toward the topographic low at the southeast end. On the basis of upward vertical gradients between the fractured bedrock and gravel aquifer at the locations of wells BKG, M2, and M5 (figure 3), the base flow in the gravel appears to be locally augmented at certain times of the year by upward groundwater discharge from the fractured bedrock. This groundwater probably discharges into the gravel and flows under, around, and possibly into the tailings and the underlying silt. However, at well M4 and in the fall at well M2, the vertical gradient is downward, indicating possible leakage from gravel to bedrock. Precipitation infiltrates the tailings impoundment and may possibly flow through the underlying deposits of calcareous and carbonaceous silt and enters the gravel aquifer. As contaminated tailings pore water leaves the tailings, a series of processes occur that influence contaminant concentrations downgradient. These include hydrogeochemical changes, dilution, dispersion, and advection.

There may be some tendency for infiltrating water to move horizontally when it encounters abrupt zones of relatively lower hydraulic conductivity. This horizontal flow may occur along layered heterogeneities in the tailings, such as hardpan, and also at the contact between the tailings and underlying organic matter and silts. If substantial horizontal flow does occur at the base of the tailings, pore water may eventually enter the colluvium at the edges of the impoundment, where the lake sediments stop. These sediments may actually have been removed in the vicinity of the downgradient end of the impoundment when the dam was constructed; if so, downward drainage into the colluvium would be enhanced just upgradient of the dam. Evapotranspiration may account for some portion of the water lost from the tailings impoundment.

## MONITORING WELL DRILLING AND INSTALLATION

Forty-five polyvinyl chloride (PVC) and BAT Envitech, Inc., groundwater samplers for monitoring wells were installed at the field test site and are described in table 1. A plan view of the research site and the monitoring well locations is shown in figure 3. The well completion reports are given in appendix $A$.

Table 1.-Description of welle

| No. of wells | Type | Description | Location |
| :---: | :---: | :---: | :---: |
| $11 \ldots$ | PVC | P wells | Saturated zone of tailings, colluvium, and sediments below tailings. |
| 14 | BAT | B wells | Vadose and saturated zone of tailings. |
| 3 | PVC | BKG wells: multiple completions in one hole. | Upgradient colluvium and bedrock. |
| 17 | PVC | M wells: multiple completions in five holes. | Downgradient colluvium and bedrock. |

## P WELLS IN AND BELOW TAILINGS

The $\mathbf{P}$ wells in and below the tailings were installed using the hollow-stem auger method. With this method, holes are drilled to the desired depth with augers having an outside diameter of 20.3 cm and an inside diameter of 8.573 cm . The PVC casing is lowered down the inside hollow portion of the augers and the augers are retrieved, leaving the casing in place.

The $\mathbf{P}$ wells themselves consist of schedule 40 PVC pipe with an inside diameter of 3.18 cm and $61-\mathrm{cm}$-long bottom sections perforated with $0.05-\mathrm{cm}$ slots. As much as possible, all wells installed after 1987 in the saturated zone of the tailings or below the tailings were installed according to the Minimum Standards for Construction and Maintenance of Wells established by the Washington State Department of Ecology (WSDOE, 1988). Because of the granular nature of the tailings, filter packs were not used, and the saturated tailings were allowed to cave around and above the perforated section (natural completion). A bentonite plug was installed from the caved-in portion to about 130 cm below the surface. A 122 -cm-long protective cover with a locking cap was placed over the PVC pipe and grouted in place. Once in place, the wells were allowed to stabilize for 1 week and then developed. Development consisted of surging and pumping until the water was relatively clear. After development, dedicated $0.95-\mathrm{cm}$ tubing was installed in each well for sampling.

To determine contaminant concentrations below the tailings, wells P3A, P3B, and P3C (figure 3) were drilled to 6.4 m (about 30 cm below the tailings), 5.8 m (base of the tailings), and 7 m (about 90 cm below the tailings), respectively. The $61-\mathrm{cm}$ perforated section of well P3A was placed at the interface between the tailings and the organic-rich layer at the top of the lake sediment, with the upper half of the perforated section in the tailings and the lower half in the organic-rich layer. The perforated section of well P3B was completed in the tailings base, and the perforated section of well P3C was completed in the silt below the organic-rich layer. Well P3 was completed at 9.1 m , approximately 3 m in the silt below the tailings and below the organic-rich layer and just above the underlying gravel.

The depths of the $\mathbf{P}$ wells are shown in table 2 and are measured from ground level to the bottom of the $61-\mathrm{cm}-$ long perforated section. Also shown in table 2 are the completion media and the sampling method for each well. Well P7 (figure 3) never contained water and therefore is not considered in this RI.

## B WELLS IN TAILINGS

Also shown in table 2 are the depths, completion media, and sampling method for the $\mathbf{B}$ wells. Installation of the BAT samplers was done according to Petsonk (1985). The BAT sampler was chosen as the water and pressure sampling apparatus for the vadose zone and some locations in the saturated zone. This instrument operates in a manner similar to a suction lysimeter or tensiometer. It consists of a tip with a cylindrical porous filter. The porous filter chamber is topped by a septum, and the unit is installed downhole at the end of an access tube. Water sampling vials or a pressure transducer are fitted with a hypodermic needle connection. When the sample housing or transducer is lowered downhole, a spring-loaded apparatus pierces the septum to establish hydraulic connection with the tailings material. A cross section of the BAT sampler is shown in figure 4.

The BAT sampler was used in this study because it prevents exposure to air during the lengthy sampling process. At one sampling location in the vadose zone, it took at least 12 h to yield a $40-\mathrm{mL}$ sample. Exposure to air for 12 h would have risked the possibility that great changes could take place in iron chemistry.

To sample liquids in the vadose zone, BAT samplers with ceramic tips having a pore size of 1 to $2 \mu \mathrm{~m}$ were installed. The small pore size of the ceramic permits liquid samples to be withdrawn from the vadose zone according to the principles of capillarity because the pore
size is comparable to that of the fine-grained tailings. Prior to installation, the ceramic tips were boiled in deionized water to force all gas from the pore spaces. They were then transported to the site in a bucket of water so they would remain saturated. The ceramic tips were pushed (with a mobile drill rig) to the desired depth immediately after being removed from the bucket in order to establish good hydraulic contact with the fine-grained tailings. Subsequent water samples have not shown any large particles, which indicates that the installations were successful, that is, that none of the ceramic filters have cracked. After 1 week, considered sufficient time for hydraulic contact to develop between tip and tailings, multiple-tip volumes were drawn through the tips to flush out deionized water with tailings pore water. One disadvantage of the BAT samplers was that at 61 cm , the tips became desaturated a few months after installation, and water samples could not be obtained. Consequently, wells B1-2c and B2-2c were not used. Gas samples, however, were obtained from wells B1-2p and B2-2p.

Table 2.-Monitoring wells in and below tailings ${ }^{1}$

| Well 10 ${ }^{2}$ | Depth, m | Completion media |
| :---: | :---: | :---: |
| P1 | 4.9 | Organic/gravel (BT). ${ }^{3}$ |
| P2 | 5.7 | Gravel (BT). |
| P2A | 4.9 | Saturated tailings. |
| P3 | 8.9 | Saturated volcanic ash (BT). |
| P3A | 6.5 | Organic layer (BT). |
| P3B | 5.9 | Saturated tailings base. |
| P3C | 7.1 | Saturated ash/organic (BT). |
| P4 | 4.6 | Saturated tailings. |
| P5 | 4.4 | Fluctuation zone. ${ }^{4}$ |
| P6 | 5.0 | Saturated tailings. |
| B1-2 | 0.6 | Vadose taillngs. |
| B1-4 | 1.2 | Vadose tailings. |
| B1-7 | 2.1 | Capillary zone. |
| B1-16 | 4.9 | Saturated tailings. |
| B2-2 | 0.6 | Vadose tailings. |
| B2-4 | 1.2 | Vadose tailings. |
| B2-8 | 2.4 | Vadose tailings. |
| B2-16 | 4.9 | Saturated tailings. |

[^2]Thermoplastic tips with larger pore sizes were installed to collect water samples from the saturated zone. A small pore size is not required if water is being sampled at positive pressure. The thermoplastic tips did not require
saturation prior to installation because they were installed below the water table, and their large pore size permitted water to displace air freely when suction was applied.

## BKG AND M WELLS UPGRADIENT AND DOWNGRADIENT OF TAILINGS

Monitoring wells were installed upgradient of the tailings to determine water quality before the water had been influenced by the tailings and downgradient of the tailings to determine water quality after the water had been influenced by the tailings. The five downgradient wells ( $M$ wells) were drilled on pads leveled by a bulldozer. The pads were constructed perpendicular to and across the downgradient surface drainage. All the M wells were multiple completions with PVC casing at two or three different depths in each well. The shallow M wells (M1 through M4) were drilled using the downhole airhammer method, and the deep $M$ well (M5) and upgradient well (BKG) were drilled using the air rotary method. In both methods, temporary casing was installed through the gravels. Forced air was used to remove the cuttings.

After reaching the desired depth, the holes were flushed with air until the discharged water became relatively clear. Once this initial development was completed, the first monitoring well (schedule 40 PVC pipe with a $61-\mathrm{cm}$ perforated section) was set, and a filter pack of $20 / 30$ silica sand was placed around and above the perforated section. Next, a bentonite plug was placed above the filter pack by slowing pouring bentonite chips in the annulus between the casing and the PVC pipe. This procedure was repeated for the second and third wells in the multiple completion. The temporary casing was pulled after the monitoring wells were set in place. After the drill was moved off the hole, a $1.2-\mathrm{m}$-long protective cover with a locking cap was placed over the wells and grouted in place with a gravel-cement mix. At the surface, the mix was sloped away from the protective cover.

Wells M1 and M2 were placed on one pad 15 m apart and 76 m downgradient of the tailings impoundment. Wells M3 and M4 were placed on a second pad 18 m apart and 335 m downgradient, and well M5 was placed on a third pad 550 m downgradient. The BKG well was located about 175 m upgradient of the tailings pile and about 30 m upgradient of the standing water pond (figure 3). The depths from ground level to the bottom of the PVC casing for each completion in the upgradient and downgradient wells are shown in table 3. Also shown in table 3 are the media (gravel or bedrock) in which the perforated section of the casing was located and the method of obtaining water samples. Well M3-5 never contained water and, therefore, was not used.

Table 3.-Background and downgradient monitoring wells ${ }^{\mathbf{1}}$

|  | Well ID | Depth, m | Completion media |
| :---: | :---: | :---: | :---: |
| M1-2 |  | 2.1 | Colluvial gravel. |
| M1-3 |  | 3.4 | Bedrock. |
| M1-8 |  | 8.5 | Bedrock. |
| M2-4 |  | 4.0 | Colluvial gravel. |
| M2-6 |  | 6.1 | Bedrock. |
| M2-12 |  | 12.5 | Bedrock. |
| M3-5 |  | 4.9 | Colluvial gravel. |
| M3-10 |  | 9.8 | Bedrock. |
| M4-5 |  | 5.2 | Colluvial gravel. |
| M4-7 |  | 7.3 | Bedrock, |
| M4-10 |  | 9.8 | Bedrock. |
| M5-4 |  | 4.0 | Colluvial gravel. |
| M5-23 |  | 22.9 | Bedrock. |
| M5-53 |  | 53.4 | Bedrock. |
| BKG-6 |  | 6.4 | Colluvial gravel. |
| BKG-20 |  | 20.1 | Bedrock. |
| BKG-43 | . . . . . | 43.3 | Bedrook. |

[^3]
## FIELD SAMPLING AND DATA COLLECTION

## SOLID SAMPLES

During well construction in the tailings, disturbed samples were obtained using a split-barrel sampler. The sampler was driven with a $63.6-\mathrm{kg}$ hammer and consisted of two standard $38-\mathrm{cm}$-long split tubes with $20-\mathrm{cm}$-long spacers at the top and the middle and a $9-\mathrm{cm}$-long shoe. It was possible to obtain a total of 116 cm (not counting the shoe space) of sample per drive. Continuous samples from the surface to the desired depth were collected from most holes. Below the water table, a rivet-type basket retainer was placed in the shoe of the sampler to aid in sample removal. Samples were obtained in 1987 and again in 1990 while installing additional monitoring wells (P3A, P3B, and P3C). The samples were used for detailed mineralogical analyses; determinations of grain size, specific gravity, clay content, and moisture content; sequential analyses of base-metal loading; and development of a detailed site cross section.

## WATER SAMPLES FROM BAT SAMPLERS

Before the field sampling trips, BAT sampling vials were flushed and then evacuated with an inert gas (helium), thereby washing out all atmospheric gases, such as oxygen and carbon dioxide. The vacuum evacuation system was one designed and constructed by USBM staff. After several evacuation cycles were completed, the vials were removed from needle connections while in a vacuum, the magnitude of which was indicated by an in-line pressure valve. Any remaining molecules of gas in the vials were helium, so the sampling vessel was completely
free of oxygen or carbon dioxide molecules. The system was designed with multiple ports so that six vials could be evacuated at once.

Collecting samples using the BAT system (figure 4A) yielded an independent airtight vial for each sample. One "purge volume" of liquid was always withdrawn prior to sampling and the contents discarded; this amount was a minimum of 10 mL , which constituted the "dead volume" inside the sampler, i.e., the volume that had resided in the vial since the previous sampling trip. Obtaining 40 mL of sample from the vadose zone using ceramic tips required 2 to 12 h . Thermoplastic tips, which have larger pores than the ceramic tips, yielded over 60 mL in 15 min from the saturated zone.

Liquid sampling vials were stored on ice for no more than 12 h before they were opened to analyze for Eh (using a platinum electrode) and pH (using a glass electrode). Electrical conductivity was not measured because none of the available probes could measure conductivities as high as those found in the pore waters. Bicarbonate titrations were not performed because all tailings pH values were already below the titration endpoint pH . Dissolved oxygen (DO) was not measured because the BAT sampling procedure exerts a strong negative pressure on water during sampling and has the potential to withdraw dissolved gases from solution. The omission of DO for these locations in the database is considered defensible because measured Eh was used as input to the computer code WATEQ4F. Sensitivity studies using this code indicated that the influence of DO on Eh status is insignificant in waters with low pH and large concentrations of dissolved iron.

After the Eh and pH measurements, the sample was immediately acidified with nitric acid for element analyses by an inductively coupled plasma emission spectra analyzer (ICP) in the laboratory. When time allowed, duplicate samples were collected for sulfate and chloride analyses using an ion chromatograph (IC). Separate aliquots from one sample run were preserved to a pH of 2 with hydrochloric acid for arsenic speciation analyses. Separate aliquots from two sampling trips were collected for laboratory iron speciation analyses.

Water samples taken with the BAT sampler were not filtered to $0.45 \mu \mathrm{~m}$ for several reasons. First, for the purpose of evaluating trends, the filtration capability of the ceramic tips (estimated by the manufacturer to be 1 to 2 $\mu \mathrm{m}$ ) would be adequate. Second, the in-line filtration apparatus has several points where atmospheric air is trapped prior to sampling. A priority of the experimental design was to prevent exposure to the atmosphere during sampling; therefore, it was concluded that one order of magnitude of filter size (the difference between 0.45 and $2 \mu \mathrm{~m}$ ) could be sacrificed to prevent compromising Eh , pH , and other parameters critical to sulfide oxidation. To verify this assumption, one complete sample run was filtered to $0.45 \mu \mathrm{~m}$ after being collected with a syringe-and-filter system (acquired after 1 year of sampling) to evaluate how the water quality data would compare with the data for the unfiltered ( 1 to $2 \mu \mathrm{~m}$, effective) samples. In no case did an element concentration differ by more than 9 pct , and in most cases, differences ranged from 0 to 4 pct.

## GAS SAMPLES FROM BAT SAMPLERS

Thermoplastic BAT sampler tips (which have larger pore sizes than the ceramic tips) were installed in the vadose zone to sample pore gas. The vials were flushed with helium and evacuated as described above. Only in rare instances, such as spring infiltration or installation into the capillary fringe, did these installations yield any liquid. The rest of the time, because these tips were installed dry, the pore entry pressure was so high that only gas could be sampled. The vials were maintained at cool temperatures until analyzed with a gas chromatograph.

## WATER SAMPLES FROM PVC MONITORING WELLS

Water samples from all PVC monitoring wells were collected in two ways. A peristaltic vacuum pump connected to dedicated $0.96-\mathrm{cm}$ tubing was used for the shallow wells and dedicated downhole bladder pumps were used for the deep wells. Prior to sampling, the water levels were measured and the wells purged. The purge
amount was generally at least two tubing volumes. However, because of the long recharge time (up to 12 h ) required for the tailings monitoring wells, only one tubing volume was purged for these wells. Duplicate $125-\mathrm{mL}$ samples, one acidified with nitric acid to a pH of 1.5 and the other not acidified, were collected from each well. Prior to collection, the samples were filtered through a prefilter, a $0.8-\mu \mathrm{m}$ filter, and a $0.45-\mu \mathrm{m}$ filter, all separated by mesh spacers. The sample containers were filled to the top and immediately capped for minimum exposure to oxygen.

## FIELD DATA COLLECTION

## Water Properties

On-site water measurements included $\mathrm{pH}, \mathrm{DO}$, conductivity, Eh, and temperature. Calomel electrodes and platinum-type electrodes with silver-silver chloride reference cells were used to measure pH and Eh . A Clarketype oxygen electrode and a flowthrough conductivity cell were used to measure DO and conductivity, respectively. When feasible, the electrodes, conductivity cell, and temperature probe were placed in a flowthrough chamber, and measurements were made as sample water passed through the chamber. When there was an insufficient amount of a sample to pass through the chamber, measurements were made in a small beaker. In some samples, alkalinity was measured using a field digital titration procedure.

## Tailings Temperature

Tailings temperature data were collected for possible identification of high-oxidation zones and for input to the equilibrium thermodynamic computer model used in this research. Thermocouples were pushed into saturated and vadose zones of the tailings at depths corresponding to the depths of the BAT sampler tips in both clusters, that is, $0.61,1.2,2.1$, and 4.9 m . The thermocouples were equipped with a surface connection to which a digital readout device had been attached to obtain the belowsurface temperatures. Temperature data were collected at each depth during each sampling trip. No high-oxidation zones were identified from the temperature data.

## Head and Pore Pressure

Pore pressures at the $B$ wells and water levels at the $P$ and $M$ wells were measured on each sampling trip prior to collecting samples. At the $P$ and $M$ wells, depth to water was measured with an electronic tape. All positive heads were normalized to sea level. At the B wells, a BAT
downhole pressure transducer was used to measure pressure. Prior to installing the sampling vial (figure 4A), the pressure transducer (figure $4 B$ ) was lowered down the access tube and connected hydraulically to the downhole septum with the same type of spring-loaded hypodermic needle used for sampling. The BAT sampler pressure transducer is capable of measuring negative gauge pressures in the vadose zone, in the manner of a tensiometer. Negative gauge pressures are interpreted relative to phreatic surface where water pressure equals atmospheric pressure. Saturated zone B wells were monitored for positive pressure data using the same transducer.

## In Situ Moisture and Density

A Campbell-Pacific Nuclear (CPN) 503 moisture density probe was used to measure moisture content and total density over continuous depth profiles at 12 locations on the tailings impoundment. Measurements were taken in June and August 1990 and in March 1991 and were made at $7.6-$ to $30.5-\mathrm{cm}$ intervals down the access tubes. Of the 12 access tubes used with the CPN moisture density probe at the tailings impoundment, six were BAT sampler access tubes (stainless steel) and six were access tubes (aluminum) installed next to monitoring wells P1, P2, P3, P4, P5, and P6. The CPN 503 moisture density probe has two radioactive sources. The first is a cesium source that emits gamma rays, or photons. The more energy reflected back to the detector, the less the wet (solid plus liquid) density of the soil.

The second radioactive source is composed of americium and beryllium and emits "fast" neutrons. The detector only measures the return of "slow" electrons. A fast neutron must hit something of equal mass, such as a hydrogen nucleus, in order to be slowed to a speed measurable by the neutron detector. The usual substances in soil that contain hydrogen atoms are water, plant organic material (which is primarily water), and hydrocarbons. Therefore, as long as negligible organic material and hydrocarbons exist in the soil, the detector measurement is correlated to moisture content. If the soil is high in boron, there may be an interference problem because the boron nucleus is about the same mass as a hydrogen nucleus. Generally water is the only significant hydrogen source in a soil and boron is rarely present.

## Hydraulic Conductivity

The BAT sampler system was designed for in situ point measurements of hydraulic conductivity. The theoretical basis for the test is Hvorslev's solution for a variable head (rising or falling) test for radial flow from an open standpipe. BAT Envitech has adapted the solution for its system (Petsonk, 1984). In particular, incorporation of

Boyle's gas law, which relates volume to pressure, is necessary because the testing procedure includes positive or vacuum pressurization, depending upon whether one is doing an outflow or an inflow test. Other adaptations of the formula include corrections for (1) variations in crosssectional area over the length of the testing apparatus and (2) geometry of the filter tip. BAT Envitech has written software to perform these calculations (Petsonk, 1984).

To perform a hydraulic test, a double-ended sampling vial is used in series with a pressure transducer. The vial is lowered down the access tube to establish hydraulic connection with the filter tip when the spring-loaded hypodermic needle pierces a septum in the vial and another septum at the top of the filter tip. The filter tip must be more permeable than the formation. For this reason, only the completions in the saturated zone with the large-pore-sized thermoplastic tips were used. This way, the filter tip would not limit hydraulic conductivity. When the vial, extension pipe, and pressure transducer unit are charged with a known volume of water and a known volume of positively pressurized gas, the system will force fluid into the tailings pores when hydraulic connection is established (outflow test). If the vial is evacuated, an inflow test is performed. The hydraulic conductivity is calculated repeatedly during the test until a consistent value is reached. However, it is important to ensure that all the water in the vial is not forced into the tailings pores, which would force gas into the tip. To safeguard against this possibility, the BAT software calculates the pressure at which all the water would be forced from the vial and reports a pressure within 80 pct of that value as a safety threshold at which to stop the process.

## Groundwater Flow Direction and Velocity

A sodium chloride tracer test was performed to determine the groundwater flow and direction in the colluvium downgradient of the tailings. In this test, a solution of sodium chloride was gravity fed into well M2, and an attempt was made to trace the salt plug downgradient on preestablished grid lines using electromagnetic terrain conductivity equipment. In the initial test, the salt plug was traced only 76.2 m downstream. After that, no conductivity differential could be detected. Because of this short distance from the injection point, the results were deemed too high because of the influence of the gravity injection pressure (about 2.4 m of head) of the sodium chloride solution, and a second test using a different method was used.

In the second test, a borehole-to-surface electrical test was performed. The field test was conducted by personnel from the Department of Geophysical Engineering of the Montana College of Mineral Science and Technology, Butte, MT. For this test, a current electrode was
positioned within the borehole at the depth of interest and another placed at electrical infinity. A radial array of equally spaced potential electrodes were placed on the surface. An electrolytic solution was injected into the zone of interest, and as the solution plume was mobilized by the groundwater flow, a direct current from the downhole electrode was introduced into the conductive region. The recorded potential differences measured on the surface were used to compute apparent resistivity, electrical plume length, actual plume length, and groundwater velocity. ${ }^{4}$

## LABORATORY DATA COLLECTION

## Water Analysis

Water samples brought in from the field were analyzed for total silver, aluminum, barium, boron, cadmium, calcium, copper, iron, lead, magnesium, manganese, nickel, potassium, silicon, sodium, sulfur, and zinc on the ICP at the USBM's Spokane Research Center (SRC) chemistry laboratory. The ICP was used to measure concentrations of the anions sulfate and chloride. Samples were diluted when necessary so that concentrations fell within the linear operating ranges of both the instruments and available standards.

## Pore Gas Analysis

A Nuclear-Chicago gas chromatograph (model 5341) was used to measure pore gas concentrations of oxygen and carbon dioxide. Samples were withdrawn by syringe needle from the BAT sampling vial and injected into the gas chromatograph through a septum port.

Column 1 was packed with a $60 / 80$ molecular sieve to measure oxygen, nitrogen, and composite peaks. Column 2 was filled with $80 / 100$ Chromosorb packing material to measure carbon dioxide and composite peaks. Experiments with flow rates of carrier gas, column temperature, and volume of sample injected were performed to yield a range of operation wherein retention times of peaks were consistent, peaks were well separated, and instrument sensitivity was optimized for the concentrations of oxygen and carbon dioxide expected.

The operating parameters used were as follows:

1. Carrier gas volume flow rate for Column 1 (oxygen) was $20 \mathrm{~mL} / \mathrm{min}$ and $4 \mathrm{~mL} / \mathrm{min}$ for Column 2 (carbon dioxide).

[^4]2. Temperature (both columns) was 30 to $32^{\circ} \mathrm{C}$.
3. Sample injection volume was $40 \mu \mathrm{~L}$.

The gas chromatograph was calibrated for each session by an analysis of "specialty gases" of known concentrations that were made up to requested mixes. A calibration line was generated for both carbon dioxide and oxygen during each chromatography session using air as one point and either 0.5 pct carbon dioxide in nitrogen or 2.0 pct oxygen in nitrogen as the other point.

## Mineral, Chemical, and Physical Properties

Two separate mineral analyses were performed on splits of tailings samples taken in the field. Microscopic examinations were performed by the USBM's Western Field Operations Center, Spokane, WA, to determine the predominant constituents, especially the sulfide content, and a more detailed examination was performed by the U.S. Geological Survey (USGS) to determine sulfate reduction and secondary sulfide formation in the tailings base and subbase material. In the latter tests, polished sections were examined using a reflected-light microscope and a scanning electron microscope (SEM) with energydispersive scanning (EDS) capabilities. Photomicrographs were also taken.

Chemical analyses of solid samples below the tailings were performed under contract by IGAL, Inc. A modified sequential extraction procedure was used to help clarify the issue of metal fixation in the sediments below the tailings.

Grain size, specific gravity, plasticity indices, and moisture content [American Society of Testing and Materials (ASTM) designations D422-63, D854-83, D4318-84, and D2216-80, respectively] of the tailings, organic layer below the tailings, and volcanic ash deposit below the tailings were determined at SRC's soils laboratory. A Micrometrics Instrumentation Corp. Sedigraph 5000 particle-size analyzer was used to determine fine grain-size distribution.

## Iron and Arsenic Speciation

The speciation of iron and arsenic in an aqueous solution depends strongly on the Eh potential of the system and also on pH (Hem, 1985). Therefore, iron and arsenic speciation is often determined for systems where oxidation is important. Iron speciation was performed on water samples taken from the vadose and saturated zones of the tailings by a USBM chemist.
Arsenic speciation for this research was performed by IGAL, Inc., using a simultaneous extraction procedure developed by Mok and Wai (1987). Although dissolved arsenic concentrations were too low for accurate
measurement by ICP, trace concentrations exist in the pore water. The Mok and Wai procedure includes an extraction step that concentrates the sample, making it possible to measure concentrations that were originally below detection limits. An atomic absorption graphite
furnace was used for the final measurements of elemental arsenic.

Because they are beyond the scope of this RI, results of the iron and arsenic speciation tests are not included.

## DATA ANALYSIS AND RESULTS

## PRESSURE AND HEAD MEASUREMENTS IN TAILINGS

Figure 5 shows gauge pressure data for the vadose zone, plotted throughout the 4 years of the field study. The pressures range from 0 (i.e., atmospheric pressure) to negative pressures of slightly less than -2 m . The pressures in the vadose zone are closest to atmospheric (saturated) pressure conditions immediately after the spring snowmelt during April and May. The gauge pressure data were measured to chart relative changes in moisture content. The matric suction in the vadose zone becomes less negative as the moisture content increases, reaching zero when the soil is saturated.

Gauge pressure was measured most often during 1988, so that year is best for comparing changes in relative moisture content in the shallow tips with those from the deeper tips at well clusters B1 and B2. As the snow melted in the spring, there was a 1 -month lag in peak gauge pressures (and therefore moisture content) between the shallow tip at well B1-4c, ${ }^{4}$ ( 1.2 m ) and the deeper tip at well B1-7c ( 2.1 m ). A 1-month lag in peak readings was also discernable between the 1.2 - and $2.4-\mathrm{m}$ sampling depths at wells B2-4c and B2-8c.

The 1989 measurements for three of the four vadose zone tips show a distinct increase in pressure, and therefore in moisture content, during the autumn months. This is probably because there was significantly more rainfall in the region during the autumn of 1989 than during the autumn of 1988. It is not obvious why the heads at the tip at well B1-7c did not follow this trend.

Figure 6 shows the head measurements collected in the piezometers and BAT sampler tips in the saturated zone. A seasonal trend is obvious for all samples, whereby heads in the impoundment are highest in the spring after snowmelt and lowest in the winter. A trend in head pressure is apparent among the sampling locations: The most upgradient wells in the tailings (wells P6, P5, P4, and B1-16) have the highest heads, followed by well B2-16, which is farther downgradient in the tailings.

[^5]
## GAS CONCENTRATIONS IN TAILINGS PORE SPACES

The percentages of oxygen and carbon dioxide in the gas phase in vadose zone pore spaces are presented graphically in figure 7. The approximate depths from ground level at each location are shown in table 2.

## Oxygen

In wells at both well cluster B1 and well cluster B2, the concentrations of oxygen decreased with depth (table 4). This finding is similar to the findings of two other studies, one in a sulfidic uranium tailings impoundment (Cherry and others, 1980) and one in sulfidic tailings and alluvium at the Homestake Mine in Lead, SD (Cherry and others, 1986). In the first study (Cherry and others, 1980), oxygen concentrations at depths of 46 cm varied from 9 to 12 pct while oxygen concentrations at depths of 274 cm varied from 1 to 3 pct. In the second study (Cherry and others, 1986), oxygen pore gas profiles were compiled from the vadose zone at two locations in meander deposits of tailings and at two locations in a tailings impoundment. At a depth of 61 cm , concentrations of oxygen varied from 5 to 20 pct, while at a depth of 244 cm , oxygen concentrations varied from 1 to 10 pct.

Table 4.-Average concentrations of oxygen and carbon dioxide as a function of depth in vadose zone pore spaces, percent by volume

| Gas | Well cluster B1 |  | Well cluster B2 |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: |
|  | 0.6 m | 1.2 m | 0.6 m | 1.2 m | 2.4 m |
| 0 | 20.0 | 3.1 | 11.0 | 3.3 | 3.0 |
| $\mathrm{CO}_{2}$ | 0.0 | 0.6 | 0.2 | 1.1 | 2.8 |

The decrease of oxygen with depth indicates that gaseous oxygen is consumed in the vadose zone. Cherry and others (1986) propose that the oxygen consumption is represented by

$$
\mathrm{FeS}_{2}+(7 / 2) \mathrm{O}_{2}+\mathrm{H}_{2} \mathrm{O} \rightarrow \mathrm{Fe}^{2+}+2 \mathrm{SO}_{4}^{2-}+2 \mathrm{H}^{+}(\mathrm{A})
$$

when ferrous iron $\left(\mathrm{Fe}^{2+}\right)$ remains in solution, and by

$$
\begin{align*}
\mathrm{FeS}_{2}(\mathrm{~s})+ & (15 / 4) \mathrm{O}_{2}+(7 / 2) \mathrm{H}_{2} \mathrm{O} \rightarrow \mathrm{Fe}(\mathrm{OH})_{3}(\mathrm{~s}) \\
& +2 \mathrm{SO}_{4}^{2-}+4 \mathrm{H}^{+} \tag{B}
\end{align*}
$$

when iron hydroxide ( FeOH ) precipitates from excess ferric iron.

## Carbon Dioxide

Concentrations of carbon dioxide gas in pore spaces of the vadose zone increase with depth (table 4). These findings are similar to those presented in Cherry and others (1980) in a study of the vadose zone of sulfidic uranium tailings. In this study, carbon dioxide gas concentrations rose from 0.3 to 0.8 pct at depths of 46 cm below the surface to 1.0 to 1.5 pct at depths of 274 cm . Cherry and others surmised that the high carbon dioxide concentrations in the deeper vadose zone were the result of root respiration and the decay of organic matter. This hypothesis offers only a partial explanation for the study site discussed here, which is poorly vegetated by grasses and supports brush and saplings only near the site perimeter. Also, grass root respiration is unlikely to extend to depths of 2.4 m . Another source of carbon dioxide could be microbial respiration (Wood and others, 1993). A 1992 bacterial identification study at the site showed the presence of the sulfate-reducing bacteria Thiobacillus, acidophilic heterotrophs, and aerobes at depths of 245 to 520 cm . No carbonates were found in the mineralogical analyses of surface samples, but near the surface, carbonates would have been consumed by acid early in the life of the impoundment.

## HYDROLOGIC AND PHYSICAL PROPERTIES OF TAILINGS

The hydrologic, physical, and chemical conditions of the waste impoundment and the sediments immediately beneath the impoundment strongly influence the release and attenuation of contaminants. Water in the saturated tailings comes from precipitation, which seeps downward through the vadose zone; this water then flows into the groundwater below the tailings in the hydraulically connected underlying aquifer. Evidence also suggests groundwater may flow upward into the sediments beneath and possibly into the tailings through fractures in the bedrock below the colluvium.

## Grain-Size Distribution

The vertical and horizontal seepage rates of water in the tailings may be influenced by the great reduction in grain size with depth. Grain-size distributions in composite samples at depths between 1.5 and 2.1 m and
between 4.9 and 5.8 m near well P3 are shown in figure 8. At well P3 and at least two other locations, a layer of tailings containing silt-sized particles 60 to 90 pct finer than 0.02 mm lies at the base of the impoundment. The higher percentage of fines at increased depth may exist for many reasons.

1. A greater portion of fines in the vadose zone may already have been dissolved.
2. Some portion of the fines in the saturated zone may be precipitated oxidation products from constituents leached out of the overlying material.
3. Some of the fines in the vadose zone may have been cemented into larger, agglomerated particles.
4. Some portion of the fines resulting from weathering in the vadose zone may have been transported downward with time.

The change in grain-size distribution with depth may be correlated to the fact that water samples from the saturated zone have higher concentrations of many key elements than do samples from the vadose zone. Because finer materials have more surface area available for chemical interaction, which leads to more rapid dissolution, highly soluble fines in the vadose zone have probably already been dissolved.

It is important to note that the increase in the percentage of fines with depth in the impoundment will reduce hydraulic conductivity with depth.

## Density and Moisture

Analysis of the data from the moisture and density profiles shows four distinct zones of moisture in and below the tailings. These zones are the vadose zone, the capillary fringe zone, the saturated zone in the tailings, and the saturated organic layer-silt zone below the tailings. The average in situ moisture, expressed as weight of water per weight of dry solids, of each zone is summarized in table 5. Based on moisture content, the vadose zone ranges from 1.5 m deep at well $\mathbf{P} 6$ to 2.7 m at well $\mathbf{P}$. This zone was about 34 pct saturated in June and about 30 pct saturated in August. The capillary fringe zone, identified as the zone above the water table in which the moisture content equals or exceeds the lowest moisture content reading below the water table, ranges from 0.9 to 1.8 m above the water table. Evaporation effects result in upward capillary flow and a reduction of average moisture content in the vadose zone between June and August. Evaporation effects could be seen to a depth of about 1.5 m , after which very little, if any, moisture changes occurred between spring and late summer.

Obtaining in situ moisture and density data at various locations allows the identification of zones or layers with

Table 5.-Average moisture content in various zones in and below tailings, percent ${ }^{1}$

| Well ID | Vadose zone |  | Capillary fringe June | Saturated zone June | Organic silt zone ${ }^{2}$ June |
| :---: | :---: | :---: | :---: | :---: | :---: |
|  | June | August |  |  |  |
| P1 | 9.9 | 9.7 | ND ${ }^{3}$ | ND | ND |
| P2 | 12.6 | 11.4 | 27.4 | 26.5 | ND |
| P3 | 11.1 | 9.5 | 26.5 | 27.1 | 46.9 |
| P4 | 9.4 | 8.1 | 27.6 | 27.7 | ND |
| P5 | 8.0 | 6.7 | 26.1 | 26.1 | ND |
| P6 | 8.6 | 7.5 | 22.1 | 21.9 | ND |
| B1-4 | 11.6 | 9.1 | ND | ND | ND |
| B2-4 | 10.2 | 10.4 | ND | ND | ND |
| B1-7 | 9.1 | 8.3 | ND | ND | ND |
| B2-8 | 12.1 | 10.5 | ND | ND | ND |
| B1-16 | 9.4 | 7.5 | 26.1 | 26.1 | ND |
| B2-16... | 12.4 | 10.9 | ( ${ }^{4}$ ) | 29.4 | ND |

${ }^{1}$ Moisture content as a percentage is defined as the weight of water divided by the weight of dry solids times 100. Moisture contents in the perched water zones identified in wells P1, P2, P5, B1-16, and B2-16 are not included in the average.
${ }^{2}$ The organic-silt zone is a zone of material below the tailings. This zone has higher moisture content and lower density than the tailings.
${ }^{3} \mathrm{ND}$ No data. In all cases, the access tubes for in situ moisture measurements were not driven to these zones at these wells.
${ }^{4}$ All moisture contents above the water table were less than any measured below the water table.
excessively high or low moisture contents or densities. These zones could indicate perched water, different material types, layers, or other anomalies that might influence the downward migration of contaminants.

## Tailings Layering

Physical and chemical heterogeneities are not uncommon in milled tailings impoundments, and this study site was no exception. Spatial variations in physical property values in tailings piles can result from differences in ore mineralogy, short-term changes in milling processes, depositional history, or weathering after deposition. The tailings at the study site are layered, and layers differ on the basis of color, texture, grain size, density, and moisture content. The influence of these physical heterogeneities on water chemistry and water movement may vary depending on locality.

The moisture content and density profile in figure 9 at well B2-4c shows an isolated layer of high moisture and low density in the vadose zone about 46 cm below the surface. A tailings sample (B-2) was collected from the surface to a depth of 61 cm through this layer near well $\mathrm{B} 2-4 \mathrm{c}$ and examined. In the middle of the sample was a hardpan layer. The hardpan sample did not soften or decompose when it was exposed to water or concentrated acid in the laboratory. The tailings above the hardpan appeared to be more oxidized, much lower in moisture content, and coarser in grain size than the tailings below the hardpan.

The grain-size distributions of samples above and below the hardpan are shown in figure 10. A dramatic reduction in grain size between the top and bottom of sample B-2 can be seen. The explanation of this large difference, although not clear, possibly relates to the chemical and physical weathering of particles, or perhaps the cementation of particles above the hardpan but not below.

The hardpan in sample B-2 divides coarse and fine tailings, probably restricts the downward flow of atmospheric oxygen, and reduced water seepage velocity. This has two effects on contaminant migration and attenuation. First, because oxidation is required in the acid-generation process, acid generation below the hardpan is slowed. Second, the hardpan appears to influence pore water quality. The data in table 6 show that concentrations of most metals in solution increase with depth in well cluster B1 but decrease with depth in well cluster B2. This difference may be related to the hardpan within the well cluster B2. Because the seepage velocity is lower through the hardpan and the finer material below, the $\mathrm{H}^{+}$ion may be given enough residence time to consume the neutralizing agents resulting from silicate and aluminosilicate mineral dissolution, resulting in more sulfide oxidation products in solution at the $1.2-\mathrm{m}$ level. At well cluster B 1 , where there is no hardpan, the sulfide oxidation products and $\mathrm{H}^{+}$appear to move frecly downward, resulting in higher metal concentrations and lower pH with depth.

Similar findings were reported at the Heath Steele Mine's tailings dump in New Brunswick (Boorman and

Table 6.-Average constituent concentrations in well clusters B1 and B2, parts per million

| Constituent | Well cluster B1 |  |  | Well cluster B2 |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  | 1.2 m | 2.1 m | 4.8 m | 1.2 m | 2.4 m | 4.8 m |
| pH | 3.76 | 3.73 | 3.49 | 3.16 | 3.74 | 3.89 |
| Element: |  |  |  |  |  |  |
| Al | 55 | 582 | 2,479 | 552 | 501 | 147 |
| Ca | 96 | 466 | 531 | 428 | 451 | 458 |
| Cu | 15 | 113 | 16 | 137 | 102 | 50 |
| Fe | 75 | 811 | 12,864 | 2,013 | 1,194 | 763 |
| K | 12 | 4 | 59 | 2 | 6 | 4 |
| Mg | 93 | 372 | 2,429 | 329 | 416 | 155. |
| Mn | 2 | 9 | 159 | 8 | 12 | 8 |
| Na | 6 | 36 | 38 | 17 | 29 | 17 |
| Pb | 0.20 | 0.40 | 5 | 0.70 | 0.70 | 2 |
| S | 366 | 2,303 | 15,614 | 3,013 | 2,531 | 1,317 |
| Si | 70 | 49 | 41 | 100 | 34 | 32 |
| Zn ........... | 7 | 46 | 1,539 | 140 | 178 | 78 |

NOTE.-Averages are calculated on analysis of 14 to 16 different water samples taken over 2 years. Well cluster B2 is about 46 m southeast of well cluster B1. Depths are from ground level to the center of the porous sampling tip.

Watson, 1976). The Canadian researchers describe the hardpan as being 5 to 10 cm thick, lying 25 to 50 cm below the surface between the oxidation zone and the reduction zone, and consisting of tailings cemented with iron hydroxides, oxides, and gypsum. In addition, the hardpan contained high levels of copper and zinc that precipitated as a result of chemical reactions. In 1985, the pore water chemistry at the Heath Steele tailings dump was found to be about the same as it was in 1976. The consistency of the geochemistry over the 9 -year period was attributed to the effect of the hardpan (Blowes and others, 1987).

## Hydrologic Characteristics

Based on three-point solutions of average potentiometric elevations among wells P4, P5, and P6, and among wells P4, P5, and P1, the direction of the horizontal component of flow from well P5 was determined (shown by an arrow on figure 3). The potentiometric surface in the direction of flow dips about 0.78 m over a distance of about 140 m between well P6 and well P1, resulting in a relatively flat horizontal hydraulic gradient of $5.6 \times 10^{-3}$ $\mathrm{m} / \mathrm{m}$. This measurement was compared with an even flatter horizontal gradient of $6.0 \times 10^{-4} \mathrm{~m} / \mathrm{m}$ from well P5 to well P4. Downgradient horizontal hydraulic gradients were $3.9 \times 10^{-2} \mathrm{~m} / \mathrm{m}$ and $2.2 \times 10^{-2} \mathrm{~m} / \mathrm{m}$ between the shallowest piezometers of well M2 and well M4 and between the shallowest piezometers of well M4 and well M5, respectively. Spacings between wells in the saturated tailings were inadequate for determining the vertical component of the hydraulic gradient. However, in the multiple-completion background and downgradient wells, the vertical component of flow direction and vertical hydraulic gradients were determined at wells BKG, M2, M4, and M5 and are shown in table 7. In situ
measurements determined with the BAT system indicated an average hydraulic conductivity in the saturated tailings of $2 \times 10^{-5} \mathrm{~cm} / \mathrm{s}$.

Other hydrologic properties that affect downgradient contaminant transport at the study site are advection and dispersion. Based on the difference in estimated horizontal groundwater flow velocities $\left(2.7 \times 10^{-4} \mathrm{~m} / \mathrm{d}\right.$ in the saturated tailings and $0.6 \mathrm{~m} / \mathrm{d}$ in the downgradient aquifer) (Stewart and others, 1990), ${ }^{5}$ the transport of contaminants by flowing groundwater (advection) is much greater in the downgradient aquifer than in the tailings. Because the shallow aquifer at this site is narrow, transverse dispersion is probably constrained and only longitudinal dispersion occurs freely.

From a positive environmental aspect, the decrease in hydraulic conductivity and the relatively flat gradient through the tailings results in a very slow and naturally controlled release of soluble metals from the tailings into the downgradient environment, allowing for maximum dilution and chemical precipitation. However, the long periods over which the pore water is in contact with the tailings facilitates long-term mechanical weathering and allows completion of slower kinetic chemical reactions.

The vertical component of gradient in wells BKG and M5 indicates an upward flow direction between the intermediate and the shallow completions in the spring and late summer, indicating a more continuous recharge in the shallow alluvium. At well M2, the direction of the vertical flow component appears to go upward in the spring and downward in late summer. At well M4, the flow direction is downward even during the spring recharge, possibly indicating discharge into a bedrock fracture.

[^6]Table 7.-Vertical component of hydraulic gradient and flow direction for background and downgradient multiple-completion wells.

| Well ID | Season | Vertical flow direction | Horizontal gradient, $\mathrm{m} / \mathrm{m}$ |
| :---: | :---: | :---: | :---: |
| BKG-6 BKG-20 | Spring | Upward | 0.016 |
| BKG-6-BKG-20 | Late summer | Upward | 0.015 |
| BKG-20 $\rightarrow$ BKG-43 . | Spring | Downward | 0.002 |
| BKG-20-BKG-43 . | Late summer | Downward | 0.001 |
| M2-4-M2-6 | Spring | Upward | 0.004 |
| M2-4-M2-6 | Late summer | Downward | 0.007 |
| M2-6-M2-12 | Spring | Upward | 0.032 |
| M2-6-M2-12 | Late summer | Upward | 0.002 |
| M4-5 ${ }^{\text {M } 4-7 ~}$ | Spring . . . | Downward | 0.038 |
| M4-5 M 4 -7 | Late summer | Downward | 0.144 |
| M4-7 $\rightarrow$ M4-10 | Spring | Downward | 0.022 |
| M4-7-M4-10 | Late summer | Downward | 0.089 |
| M5-4-M5-23 | Spring | Upward | 0.092 |
| M5-4 ${ }^{\text {M }}$-23 | Late summer | Upward | 0.116 |
| M5-23 - M5-53 | Spring | Downward | 0.133 |
| M5-23 - M5-53 | Late summer | Downward | 0.132 |

## PROPERTIES OF SEDIMENTS BELOW TAILINGS

## Hydrologic and Physical Characteristics

Solid samples collected during initial drilling clearly indicate that the tailings were deposited in a shallow, swampy lake basin. Below the tailings is an organic-rich silt layer 30 to 60 cm thick containing abundant snail shells. Below this layer is a layer of silt 3 to 4.5 m thick. Atterburg limit determinations indicate the silt has a liquid limit of 66.7 pct and a plasticity index of 7.2 . According to the Unified Soil Classification System (U.S. Bureau of Reclamation, 1963), this material is in the MH soil classification group, indicating it to be inorganic silts, micaceous or diatomaceous fine sandy or silty soil (elastic silt). MH soils are generally very absorptive, have low dry strength, and exhibit slow dilatancy. An EDS spectrum of this material showed abundant silicon and detectable amounts of aluminum, potassium, calcium, and iron. In addition, secondary kaolinite minerals could be present. Kaolinite is formed by weathering or hydrothermal alteration of aluminum silicates, particularly feldspar (Klein and Hurlbut, 1985).

Figure 11 illustrates that at a depth of 5.8 m , the silt zone has a lower density than the tailings and contains 1.7 times more water by weight per unit volume than the tailings. The average water content and bulk density of the silt below the tailings at well P3 (measured in June 1989) were 46.9 pct by weight and $1.17 \mathrm{~g} / \mathrm{cm}^{3}$, respectively. By comparison, the average water content and bulk density in the saturated tailings at well P3 were 27 pct and $1.60 \mathrm{~g} / \mathrm{cm}^{3}$, respectively. Using the average bulk densities measured in June 1989 and the average specific gravity of solids in each zone (determined by specific gravity tests on samples collected at the study site), the porosity for the
saturated tailings was 42.8 pct and 54.4 pct for the saturated silt. These measurements were consistent with the presence of the organic material underlain by lacustrine silt, as identified during drilling.

## Mineral Analysis

To get a better understanding of the fate of the concentrated contaminants that exist in the tailings, a detailed mineral analysis of the organic-rich layer and other sediments below the tailings was undertaken. This work was performed under contract by Dr. Charles Alpers of USGS. The objective of the analysis was to determine if the organic-rich layer was causing any attenuation of metals migrating from the tailings. To investigate this possibility, evidence was sought for sulfate reduction and secondary sulfide formation in the organic-rich layer. Several samples of the organic-rich material were prepared and examined using a reflected-light microscope and SEM with EDS capabilities. A description of each sample observed by Dr. Alpers is found in appendix C. The following is a summary of Dr. Alpers' report to the USBM:

Sediment samples from the field site were scanned in two batches, one collected during 1988, the other during 1990. The 1988 samples (eight in all) consisted of dried powders taken from various depths while drilling monitoring wells P 4, P 5, and P6. Polished sections were prepared of the fine-grained fraction of these samples by first screening the samples at 60 mesh and then mounting the fine-sized fraction in 1 -in-diam epoxy blocks. These polished sections were examined using a reflected-light microscope and a SEM with EDS capabilities.

The 1990 samples were delivered in frozen state as sections of intact, split barrel samples collected while drilling monitoring wells B2A, P3A, and P3C. The cores arrived wrapped in cellophane and aluminum foil. The sampling strategy was to sample the organic-rich layer near to the tailings-sediment interface in each core as well as other locations at approximately $30-\mathrm{cm}$ intervals. These samples were dried in an oven overnight at about $90^{\circ} \mathrm{C}$, and then were mounted on aluminum disks for SEM analysis. No polished sections were prepared for the 1990 samples.

Results indicate the organic-rich layer is host to numerous framboidal spheres composed of Fe and S and assumed to be pyrite. This indicates a strong reducing environment, where bacteria are able to reduce aqueous sulfate to aqueous hydrogen sulfide, in the presence of sufficient iron to produce solid iron sulfides. This process is only possible where the sulfate-reducing bacteria have sufficient sources of aqueous sulfate, organic carbon, iron, and nutrients, such as ammonia and phosphate (Goldhaber and Kaplan, 1982).

Rates of sulfate reduction are highly variable; complete sulfate removal in marine sediments can take hundreds of years (Goldhaber and Kaplan, 1982). In some marine sites of rapid burial, significant sulfate reduction can take place in years to tens of years (Chanton, Martens, and Goldhaber, 1987). If none of the crucial ingredients are limiting, sulfate reduction can proceed in relatively fast rates, and it would be possible to produce the observed framboids in their entirety after the disposal of the tailings in the 1930's and following years. However, it is more likely that the framboidal pyrite was present prior to the introduction of the tailings.

One possibility with respect to metal mobilization at this tailings site is that the reducing environment represented by the neo-formed sulfides could be a site of metal fixation. Thus, metals leached from the oxidized tailings could be fixed in the organic-rich, sulfide-bearing layer.

However, other than the pyrite framboids, no secondary base-metal sulfides were observed. If metals leached from the tailings had been actively reduced, coatings on the framboids consisting of minerals such as chalcocite, covellite, and digenite (Cu-sulfides) or sphalerite ( Zn -sulfide) might be expected. These minerals are commonly observed in zones of sulfide enrichment, formed below the water table in actively oxidizing base metal sulfide systems
(Alpers and Brimhall, 1989). Given that no such secondary base-metal sulfides were observed, it seems that any metals that are being fixed because of flow through the sulfide-rich organic layer are indeed being fixed by adsorption onto organic material.

## Chemical Analysis

To help clarify the issue of metal fixation in the sediments below the tailings, chemical analyses using a modified sequential extraction procedure were performed on samples collected near the base of the tailings and up to 150 cm below the base. The samples were obtained during the 1990 drilling of wells P3A, P3C, and P2A and were taken at 15 to 61 cm below the tailings in the organic layer (P3A), 122 cm below tailings and below the organic layer (well P3C), 15 to 61 cm above the base of tailings and above the organic layer (well P2A), and 15 to 61 cm below the tailings in the organic layer (well P2A). These tests were performed, under contract, by IGAL, Inc.

In the sequential extraction procedure used, five fractions were chosen that were likely to have been affected by various environmental conditions. These were fraction 1, exchangeable; fraction 2 , bound to carbonates; fraction 3 , bound to iron and manganese oxides; fraction 4 , bound to organic matter; and fraction 5, bound to sulfides. Six elements (silicon, aluminum, iron, manganese, copper, and lead) in all five fractions were analyzed by atomic absorption spectrometry. Calcium and magnesium were determined by ICP analysis.

Results of the sequential extraction tests are shown in appendix D. These results indicate that solid-phase lead and copper were not present to any great extent in the organic-rich layer or silt zone below the tailings, but were present in the base of the tailings. Lead was bound primarily in the sulfide-residual and oxide phases at the tailings base, and copper was bound primarily in the sulfide-residual phase at the tailings base. Both did not appear to be remobilizing below the tailings. Solid-phase iron and manganese were abundant in the organic-rich layer and silt zone below the tailings. In the organic-rich layer, iron was present in the oxide, sulfide, and carbonate phases, with the oxide phase being the most dominant. A smaller, but significant, amount of iron was bound to organic matter in this layer. Iron was bound primarily to sulfides in the tailings base and to carbonates in the silts below the organic-rich layer. Manganese was also bound to carbonates. These data indicate that some of the reduction of iron and manganese in the pore water of the organic-rich layer and silts below the tailings is due to iron carbonate and manganese carbonate precipitation.

Although calcium and magnesium were present in several phases in the organic-rich zone, they appeared most abundant in the silts below the organic-rich layer, primarily in the carbonate form. Carbonate dissolution in this zone is probably the major source of calcium and magnesium in the gravel aquifer downgradient from the tailings impoundment.

## WATER QUALITY

Water quality data were collected upgradient from the tailings (BKG wells), from the vadose and saturated zones of the tailings ( B and P wells), from below the tailings, and from different distances downgradient of the tailings ( $M$ wells). The results of each sampling trip are shown in appendix $B$, and the averages are summarized in tables 8 through 10. Systematic errors, such as erratic measurements in all samples from one collection trip, do not appear. At most, two samples in one sample run were anomalous, and even in these instances, it was impossible to determine whether the samples were mislabeled, contaminated, misdiluted, or improperly analyzed by the ICP. Because no systematic reasons for rejection were identifiable, rejection decisions were made on a statistical basis. All data outliers were rejected on the basis of the Grubbs test (Taylor, 1990) using $\alpha=0.001$. This very small value of $\alpha$ ensured that only the most extreme data were rejected. The data were grouped by element at each sampling location across all sampling trips for detection of outliers.

Arsenic data are not reported because they were found to be below or near detection limits for the ICP, and the ICP does not provide accurate measurements of arsenic near the detection limit.

Many of the variations in concentration discussed in the following sections are described in terms of mineralogical solubility controls, which are briefly mentioned here because they may influence the relative concentrations of various constituents. Discussions will be limited to values from the tailings and Quaternary colluvium only. Values from the bedrock will not be discussed, except where there appears to be an effect of bedrock waters on tailings and shallow colluvium waters. Values from sediments immediately below the tailings are discussed in the section on "Water Quality Below Tailings."

## Eh and pH

There is no apparent seasonal (temporal) variation for either Eh or pH . The vadose zone is generally more acidic (with lower pH values) than the saturated zone. Similarly, the Eh values in the vadose zone are consistently oxidizing, whereas the saturated zone waters are more variable and less oxidizing. These findings were expected. Because the vadose zone has oxygen gas in the pore spaces, sulfides would be oxidized, producing sulfuric acid, which causes pH to decrease. As the waters percolate deeper, however, less oxygen but more (fresh) solids are available to react with the acid. Thus, Eh is likely to decrease and pH to increase. In the vadose zone, average pH and Eh are 3.6 and 540 mV , respectively, and in the saturated zone these values are 4.2 and 450 mV , respectively. Downgradient at well $\mathrm{M} 5-4, \mathrm{pH}$ gradually increases to 7.1, which is the background level shown at well BKG-6. This is a result of hydrogeochemical reactions, dilution, and dispersion. Downgradient, Eh averages 360 mV at well M5-4, a value that is only slightly lower than the average background Eh of 400 mV at well BKG-6.

Table 8.-Arithmetic means of analysis and chemical characteristics of tailings pore water from vadose zone

|  | B1-4 | B1-7 | B2-4 | B2-8 | Average |
| :---: | :---: | :---: | :---: | :---: | :---: |
| Eh, mV | 540 | 540 | 560 | 520 | 540 |
| pH | 3.80 | 3.70 | 3.20 | 3.70 | 3.60 |
| Element, mg/L: |  |  |  |  |  |
| Al | 59.00 | 450.00 | 650.00 | 430.00 | 400.00 |
| B | 0.25 | 2.10 | 7.10 | 2.90 | 3.10 |
| Ba | 0.02 | 0.02 | 0.01 | 0.01 | 0.02 |
| Ca | 100.00 | 450.00 | 400.00 | 460.00 | 350.00 |
| Cd | 0.02 | 0.20 | 0.98 | 1.10 | 0.58 |
| Cu | 12.00 | 98.00 | 140.00 | 91.00 | 85.00 |
| Fe | 80.00 | 700.00 | 1,900.00 | 1,000.00 | 920.00 |
| K | 10.00 | 4.00 | 2.70 | 5.90 | 5.70 |
| Mg | 90.00 | 320.00 | 320.00 | 360.00 | 270.00 |
| Mn | 2.00 | 8.30 | 8.10 | 10.00 | 7.10 |
| Na | 8.20 | 37.00 | 15.00 | 28.00 | 22.00 |
| Ni | 0.30 | 0.32 | 0.34 | 0,45 | 0.35 |
| Pb | 0.21 | 0.34 | 0.61 | 0.63 | 0.45 |
| S | 350.00 | 2,000.00 | 3,000.00 | 2,200.00 | 1,900.00 |
| Si | 63.00 | 48.00 | 94.00 | 33.00 | 60.00 |
| Zn | 7.20 | 40.00 | 139.00 | 160.00 | 87.00 |

Table 9.-Arithmetic means of analysis and chemical characteristics of tailings pore water from saturated zone

|  | P4 | P5 | P6 | B1-16 | B2-16 | Average |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| Conductivity, $\mu \mathrm{S} / \mathrm{cm}$ | 7,850 | 6,953 | >10,000 | NM | NM | NM |
| Eh, mV | 390 | 470 | 400 | 490 | 500 | 450 |
| pH | 4.70 | 4.10 | 4.70 | 3.50 | 3.90 | 4.20 |
| $\mathrm{SO}_{4}, \mathrm{mg} / \mathrm{L}$ | 23,000 | NM | NM | 39,000 | 3,900 | NM |
| Element, mg/L; |  |  |  |  |  |  |
| Al | 70.00 | 990.00 | 18.00 | 2,300.00 | 140.00 | 700.00 |
| B | 22.00 | 19.00 | 64.00 | 28.00 | 2.10 | 27.00 |
| Ba | 0.02 | 0.04 | 0.03 | 0.01 | 0.01 | 0.02 |
| Ca | 440.00 | 430.00 | 540.00 | 500.00 | 460.00 | 474.00 |
| Cd | 2.50 | 4.50 | 0.04 | 17.00 | 1.00 | 5.00 |
| Cu | 9.80 | 290.00 | 26.00 | 16.00 | 48.00 | 78.00 |
| Fe | 8,800.00 | 7,800.00 | 22,000.00 | 11,000.00 | 740.00 | 10,000.00 |
| K | 76.00 | 31.00 | 71.00 | 54.00 | 4.20 | 47.00 |
| Mg | 1,500.00 | 1,100.00 | 4,000.00 | 2,000.00 | 150.00 | 1,800.00 |
| Mn | 170.00 | 63.00 | 250.00 | 140.00 | 7.80 | 130.00 |
| Na | 45.00 | 18.00 | 24.00 | 39.00 | 17.00 | 29.00 |
| Ni | 1.90 | 1.20 | 4.40 | 3.20 | 0.19 | 2.20 |
| Pb | 2.40 | 3.20 | 5.00 | 5.20 | 2.20 | 3.60 |
| S | 7,900.00 | 8,000.00 | 21,000.00 | 13,000.00 | 1,300.00 | 10,000.00 |
| Si | 30.00 | 35.00 | 17.00 | 40.00 | 29.00 | 30.00 |
| Zn | 840.00 | 550.00 | 3,200.00 | 1,300.00 | 74.00 | 1,200.00 |

NM Not measured or only one measurement made.

## Sulfur, Iron, and Manganese

Iron and sulfur are presented together because they are the predominant dissolved constituents in all tailings water samples and the primary constituents of pyrite. The dissolved iron in this system is in the form of ferrous and ferric iron. Sulfate concentrations measured by IC for several sample runs verify the assumption that all dissolved sulfur measured by ICP is in the form of sulfate. While sulfate is the predominant anion in the tailings pore waters, small concentrations of chloride were also detected. Manganese is presented with sulfur and iron because manganese behaves in a manner similar to iron chemically and mineralogically. As is iron, manganese is influenced by redox in weathering environments (Hem, 1985); downgradient of the low- pH zone, manganese should form oxides that scavenge other metals that are included subsequently in the oxide mineral matrix.

The solubility of iron and sulfur minerals is controlled by Eh and pH . Iron and sulfur concentrations with depth are nearly identical, which reflects their high correlation as a result of pyrite oxidation. Concentrations are generally higher in the saturated zone than in the vadose zone. In the vadose zone, the mean concentrations of iron and sulfur are 920 and $1,900 \mathrm{mg} / \mathrm{L}$, respectively. In the saturated zone, the mean is $10,000 \mathrm{mg} / \mathrm{L}$ for both constituents. In
the acidic environment of the impoundment, the high concentrations of iron and sulfur are probably attributable to the solubility of metal sulfate minerals such as melanterite, which is a ferrous species, and the jarosites. The pale green color of the tailings pore water samples verifies the dominance of ferrous iron. In the impoundment, most of the manganese will occur as the manganous $\left(\mathrm{Mn}^{2+}\right)$ and sulfate $\left(\mathrm{SO}_{4}^{2-}\right)$ ion pair. The mean values for manganese in the vadose and saturated zones of the tailings are 7.1 and $130 \mathrm{mg} / \mathrm{L}$, respectively.

Downgradient, sulfur attenuates to only $390 \mathrm{mg} / \mathrm{L}$ at well M5-4, a level four times background ( $92 \mathrm{mg} / \mathrm{L}$ at well BKG-06). However, iron attenuates rapidly to $0.64 \mathrm{mg} / \mathrm{L}$ at well M5-4, a level below that of background ( $0.77 \mathrm{mg} / \mathrm{L}$ at well BKG-6). The difference in attenuation between the two is caused by the species that control solubility. In neutral-pH environments, such as found downgradient of the study site, the concentration of sulfur is often controlled by gypsum solubility, whereas downgradient concentrations of iron are probably controlled by solubility of ferric species (goethite and ferrihydrite). Manganese attenuates to a mean of $0.42 \mathrm{mg} / \mathrm{L}$ at well M5-4, a level that is 14 times background ( $0.03 \mathrm{mg} / \mathrm{L}$ at well BKG-6), but well below the mean impoundment value of $85 \mathrm{mg} / \mathrm{L}$. This reduction is probably controlled by coprecipitation with iron and by manganese-carbonate solubility.
Table 10.-Arithmetic means of analysis and chemical characteristics of downgradient and background water

|  | BKG-6 | BKG-20 | BKG-43 | M1-2 | M1-3 | M1-8 | M2-4 | M2-6 | M2-12 | M3-10 | M4-5 | M4-7 | M4-10 | M5-4 | M5-23 | M5-53 |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| Conductivity, $\mu \mathrm{S} / \mathrm{cm}$ | 490 | 960 | 930 | 1,000 | 1,200 | 1,300 | 1,600 | 1,400 | 1,200 | 830 | 2,400 | 1,800 | 2,600 | 1,800 | 450 | 450 |
| Eh, mV ........ | 400 | 210 | 220 | 410 | 250 | 190 | 370 | 350 | 280 | 200 | 410 | 360 | 280 | 360 | 340 | 170 |
| $\mathrm{HCO}_{3}{ }^{-1}, \mathrm{mg} / \mathrm{L}$ | 340 | NM | NM | NM | 505 | 647 | 240 | NM | NM | NM | 437 | 543 | NM | 421 | 176 | 128 |
|  | 7.10 | 7.50 | 7.60 | 5.90 | 7.10 | 7.10 | 6.40 | 6.50 | 6.90 | 7.20 | 6.80 | 6.90 | 7.10 | 7.10 | 7.60 | 8.40 |
| $\mathrm{SO}_{4}{ }^{-2}, \mathrm{mg} / \mathrm{L}$ | 230 | 310 | 300 | 2,500 | 720 | 720 | 870 | 880 | 600 | 460 | 2,200 | 1,900 | 1,900 | 1,000 | 220 | 160 |
| Element, mg/L: |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |
| A | 0.21 | 0.23 | 0.30 | 0.84 | 0.34 | 0.38 | 0.37 | 0.36 | 0.26 | 0.25 | 0.38 | 0.38 | 0.37 | 0.34 | 0.36 | 0.34 |
| B | 0.18 | 4.30 | 5.00 | 0.63 | 0.41 | 0.43 | 0.17 | 0.20 | 0.51 | 0.31 | 0.32 | 0.37 | 0.46 | 0.29 | 1.20 | 2.40 |
| Ba | 0.03 | 0.04 | 0.04 | 0.04 | 0.04 | 0.05 | 0.04 | 0.04 | 0.04 | 0.04 | 0.04 | 0.04 | 0.05 | 0.06 | 0.08 | 0.05 |
| Ca | 140.00 | 47.00 | 36.00 | 480.00 | 260.00 | 290.00 | 290.00 | 280.00 | 270.00 | 220.00 | 610.00 | 625.00 | 530.00 | 390.00 | 74.00 | 12.00 |
| Cd | <0.01 | <0.01 | 0.03 | <0.01 | <0.01 | <0.01 | <0.01 | <0.01 | $<0.01$ | $<0.01$ | <0.01 | <0.01 | <0.01 | <0.01 | <0.01 | <0.01 |
| Cu | 0.05 | 0.05 | 0.05 | 0.24 | 0.08 | 0.05 | 0.05 | 0.07 | 0.07 | 0.05 | 0.18 | 0.13 | 0.10 | 0.08 | 0.06 | 0.05 |
| Fe | 0.77 | 0.93 | 0.64 | 260.00 | 14.00 | 13.00 | 1.20 | 4.50 | 1.40 | 3.40 | 0.57 | 1.60 | 2.70 | 0.64 | 1.30 | 0.52 |
| K | 2.30 | 2.30 | 2.60 | 14.00 | 3.50 | 3.20 | 6.50 | 6.20 | 2.20 | 2.20 | 8.70 | 2.00 | 5.10 | 4.30 | 0.70 | 0.20 |
| Mg | 29.00 | 27.00 | 19.00 | 280.00 | 79.00 | 71.00 | 96.00 | 91.00 | 66.00 | 37.00 | 210.00 | 180.00 | 140.00 | 120.00 | 11.00 | 0.50 |
| Mn | 0.03 | 0.15 | 0.03 | 31.00 | 5.60 | 3.50 | 22.00 | 22.00 | 4.70 | 2.00 | 1.90 | 1.00 | 1.10 | 0.42 | 0.11 | 0.03 |
| Na | 20.00 | 180.00 | 210.00 | 23.00 | 72.00 | 31.00 | 25.00 | 25.00 | 45.00 | 23.00 | 30.00 | 59.00 | 210.00 | 53.00 | 100.00 | 120.00 |
| Ni | <0.05 | <0.05 | <0.05 | 0.21 | <0.05 | <0.05 | <0.05 | <0.05 | <0.05 | <0.05 | <0.05 | <0.05 | <0.05 | <0.05 | <0.05 | <0.05 |
| Pb | 0.06 | 0.06 | 0.07 | 0.11 | 0.07 | 0.09 | 0.08 | 0.07 | 0.07 | 0.07 | 0.09 | 0.09 | 0.08 | 0.07 | 0.06 | 0.06 |
| S | 92.00 | 110.00 | 210.00 | 920.00 | 290.00 | 260.00 | 290.00 | 290.00 | 270.00 | 140.00 | 730.00 | 700.00 | 650.00 | 390.00 | 95.00 | 58.00 |
| Si | 14.00 | 10.00 | 10.00 | 23.00 | 9.30 | 11.00 | 14.00 | 14.00 | 12.00 | 11.00 | 19.00 | 16.00 | 21.00 | 15.00 | 13.00 | 6.40 |
| $\mathrm{Zn} \ldots$ | 0.11 | 0.08 | 0.07 | 56.00 | 0.38 | 0.14 | 0.21 | 0.16 | 0.08 | 0.09 | 0.39 | 0.12 | 0.12 | 0.16 | 0.14 | 0.09 |

## Lead and Nickel

Based on electronic configuration of their atoms, lead is a representative element and nickel is a transition element. Lead generally has a low solubility and is only superficially attacked by dilute sulfuric acid. Lead concentrations may frequently be less than that predicted by solubility conditions for a given pH . Hem (1976) believes much of this discrepancy can be attributed to cation exchange. However, the strong sorbtion characteristics of lead may also be a contributing factor. Nickel often substitutes for iron and consequently its major source in the tailings is probably pyrite. The mobility of both elements tends to be low and controlled by coprecipitation with iron and manganese oxides. The mean values of lead and nickel in the vadose zone of the study area are 0.45 and $0.35 \mathrm{mg} / \mathrm{L}$, respectively, and in the saturated zone are 3.6 and $2.2 \mathrm{mg} / \mathrm{L}$, respectively. Downgradient, lead attenuates to $0.07 \mathrm{mg} / \mathrm{L}$ at well M5-4, very near background levels of $0.06 \mathrm{mg} / \mathrm{L}$ at well BKG-6. Nickel levels are at or below background levels of $0.05 \mathrm{mg} / \mathrm{L}$ at well M5-4.

## Cadmium and Zinc

Cadmium is a common replacement cation for zinc in the sphalerite lattice and would be released with zinc during dissolution within the impoundment. Both are soluble in dilute acidic, oxidizing conditions, such as in the impoundment, and can have rapid reactions with these acids when associated with other, less reactive metals as a result of couple action. Both zinc and cadmium precipitate as hydroxides and carbonates in the presence of equivalent amounts of alkali or are adsorbed by the soil solid phase. The mean values of cadmium and zinc in the vadose zone of the tailings are 0.58 and $87 \mathrm{mg} / \mathrm{L}$, respectively, and in the saturated zone are 5.0 and 1,200 $\mathrm{mg} / \mathrm{L}$, respectively. Downgradient concentrations at well M5-4 are less than 0.01 and $0.09 \mathrm{mg} / \mathrm{L}$, respectively, both equal to or below background concentrations.

## Barium and Boron

Boron is a common trace constituent in feldspars and micas, and the borate ions are most soluble under acidic, oxidizing conditions, such as in the impoundment. The high boron concentrations found in the impoundment are unusual and probably result from the acid dissolution of borosilicates. Unlike boron, barium in the sulfate form is extremely insoluble and will tend to precipitate in the tailings. This is evidenced by the low concentrations of barium in the tailings pore water samples and by the abundance of barite in the solid tailings as determined by SEM. Mean concentrations of boron and barium in the
vadose zone are 3.1 and $0.02 \mathrm{mg} / \mathrm{L}$, respectively, and in the saturated zone are 27 and $0.02 \mathrm{mg} / \mathrm{L}$, respectively. Downgradient, boron attenuates to $0.29 \mathrm{mg} / \mathrm{L}$ at well M54, slightly higher than background levels of $0.18 \mathrm{mg} / \mathrm{L}$ at well BKG-6. Barium levels stay relatively constant, with an average of $0.06 \mathrm{mg} / \mathrm{L}$ at well M5-4 and an average background level of $0.03 \mathrm{mg} / \mathrm{L}$ at well BKG-6.

## Aluminum and Copper

These metals are presented together because they exhibit slightly different behaviors than the metals discussed previously. The behavior of aluminum is unique because saturated zone concentrations (with the exception of concentrations from well B1-16) are approximately equal to those in the vadose zone. Below pH 4.5, aluminum concentrations are limited by solubilities of basic aluminum sulfate minerals. Between pH 4.5 and 4.9, jurbanite may limit solubility. Aluminum solubility in waters of pH greater than 4.9 is reported to be controlled by the gibbsite solubility product (Nordstrom and Ball, 1986), and gibbsite is more likely to precipitate with increasing pH . Gibbsite solubility may be the factor that causes aluminum to have a relatively constant concentration across the transition zone. The mean concentration of aluminum in the vadose zone is $400 \mathrm{mg} / \mathrm{L}$ and in the saturated zone is $700 \mathrm{mg} / \mathrm{L}$. Downgradient at well M5-4, the mean value is $0.34 \mathrm{mg} / \mathrm{L}$, slightly higher than the mean background level of $0.21 \mathrm{mg} / \mathrm{L}$ at well BKG-6.

Copper has concentrations similar to those of aluminum in the saturated and vadose zones of the tailings. In view of the fact that the tailings are from a copper mine, the concentrations of copper are extremely low. Hem (1985) notes that if copper concentrations are less than those predicted by pH -Eh diagrams (thermodynamic chemical equilibria), then the lower concentrations are probably caused by the coprecipitation of oxides (such as iron or manganese oxides) or adsorption onto mineral surfaces. This appears to be the case at the study site. Assays have shown amounts of solid copper in the 1,000 to $3,000 \mathrm{ppm}$ range in the vadose and saturated portions of the tailings, but generally below the zone of oxidation. The mean concentration of dissolved copper in the pore water of the vadose zone is $85 \mathrm{mg} / \mathrm{L}$ and in the saturated zone is 78 $\mathrm{mg} / \mathrm{L}$. Mean downgradient level of copper at well M5-4 is $0.08 \mathrm{mg} / \mathrm{L}$, which is only slightly higher than the mean background level of $0.05 \mathrm{mg} / \mathrm{L}$ at well BKG-6.

## Calcium and Magnesium

Calcium and magnesium are alkaline-earth metals. Anorthite from the tailings and calcium carbonate from the snail shells in the lake sediments below the tailings are the possible sources of calcium at the field study site. The behavior of calcium in sulfate-dominated systems is
generally governed by the gypsum solubility product. Magnesium is similar to and tends to mimic the chemical behavior of calcium. Most magnesium minerals do not precipitate unless considerably supersaturated. The major source of magnesium in the impoundment is probably chlorite, common in propyllitized andesite.

Calcium and magnesium have comparable concentrations and behavior in the vadose zone, but in the saturated zone their behaviors diverge. That is, calcium concentrations do not increase appreciably in the saturated zone, whereas magnesium concentrations do. In the vadose zone, average pore water concentrations of calcium and magnesium are 350 and $270 \mathrm{mg} / \mathrm{L}$, respectively. In the saturated zone, the averages are 474 and $1,800 \mathrm{mg} / \mathrm{L}$, respectively. Calcium increases downgradient, but then decreases to $390 \mathrm{mg} / \mathrm{L}$ at well M5-4. Magnesium levels at well M5-4 attenuate only to $120 \mathrm{mg} / \mathrm{L}$. Background levels of calcium and magnesium at well BKG-6 average 140 and $29 \mathrm{mg} / \mathrm{L}$, respectively.

## Potassium and Sodium

Potassium is probably derived from dissolution of potassic feldspars and sodium from the dissolution of the albite feldspars. Sodium is an ion of small radius and is strongly hydrated. Once sodium enters into solution, there are no dominant precipitation reactions that control its solubility (Hem, 1985). Potassium may be controlled by being incorporated into clay structures and adsorbed (Hem, 1985). Potassium concentrations are higher in the saturated zone than in the vadose zone, like the majority of other cations, but sodium concentrations are not. Mean concentrations of potassium and sodium in the vadose zone are 5.7 and $22 \mathrm{mg} / \mathrm{L}$, respectively, and in the saturated zone are $47 \mathrm{mg} / \mathrm{L}$ and $29 \mathrm{mg} / \mathrm{L}$, respectively. Downgradient at well M5-4, potassium attenuates to $4.3 \mathrm{mg} / \mathrm{L}$, slightly above background concentrations of $2.3 \mathrm{mg} / \mathrm{L}$ at well BKG-6. Sodium concentrations increase downgradient to an average of $53 \mathrm{mg} / \mathrm{L}$ at well M5-4, about 2.5 times higher than the background level of $20 \mathrm{mg} / \mathrm{L}$ at well BKG-6.

## Silicon

Silicon is often referred to as the dissolved oxide species silica $\left(\mathrm{SiO}_{2}\right)$ in natural waters, but its actual form is usually one of the more hydrated uncharged ions based on the tetrahedron form $\mathrm{SiO}_{4}{ }^{4}$, such as silicic acid $\left(\mathrm{H}_{4} \mathrm{SiO}_{4}\right)$.

The average concentration of silicon in the vadose zone pore water is $60 \mathrm{mg} / \mathrm{L}$ and in the saturated zone is $30 \mathrm{mg} / \mathrm{L}$. Silicon is the only dissolved constituent for which average concentrations are higher in the vadose
zone. Silicon solubility at cool temperatures is generally controlled by the mineral referred to as amorphous silica (Hem, 1985) and may also be controlled by such aluminosilicate minerals as kaolinite and montmorillonite. Silicon concentrations in the two zones appear to differ in correlation to the different redox status, but the thermodynamics of silica suggest that the differing concentrations are not a result of acid dissolution. It is possible that the higher silicon concentration in the vadose zone results from the sparse vegetation; Drees and others (1989) note that production of organic complexes increases the dissolution rate of silica by complexing monosilicic acid. Drees and others also note that the dynamic changes in moisture content caused by wet-dry cycles may influence silica concentration more than other processes, such as dissolution-precipitation reactions. In downgradient well M5-4, the mean concentration is $15 \mathrm{mg} / \mathrm{L}$, or nearly equal to the average background concentration at well BKG-6 of $14 \mathrm{mg} / \mathrm{L}$.

## Water Quality Below Tailings

To determine contaminant concentrations below the tailings, three additional wells were drilled in the vicinity of well P3. These wells, P3A, P3B, and P3C, were drilled to 6.5 m (about 30 cm below the tailings), 5.9 m (base of the tailings), and 7.1 m (about 90 cm below the tailings), respectively. Well P3 (drilled in 1987) was drilled to 9.1 m , about 3 m below the tailings. Average concentrations of metal ions in these wells are shown in table 11.

Fifty years after the tailings were deposited onto the silts, concentrations of every element determined (except barium) were lower in the pore water of the silts 30 to 90 cm below the tailings than in the pore water at the base of the tailings (table 11) and much lower than in the pore water in the core of the saturated tailings (table 9). This could mean that water with very low concentrations of measured constituents is flushing the porous silts and perhaps the base of the tailings. At the P3 cluster wells (P3, P3A, P3B, and P3C), the vertical component of gradient indicated a weak upward flow in the lacustrine sediments during the spring, a time of high groundwater recharge.

Another explanation for low metal concentrations in the silts below the tailings is that tailings pore water may not be seeping into the silts to any significant degree, but may flow horizontally as a result of lower hydraulic conductivity at the base of the tailings. If substantial horizontal flow does occur at the base of the tailings, then pore water from the tailings may eventually enter the gravels at the edges of the impoundment, bypassing the organic material and silts. The degree of mixing between tailings pore water and colluvial water is unknown.

Table 11.-Average consttuent concentrations below tailings

| Constituent | P3B | P3A | P3C | P3 |
| :---: | :---: | :---: | :---: | :---: |
| Conductivity, $\mu \mathrm{S} / \mathrm{cm}$. | 3,448 | 2,456 | 1,630 | 1,788 |
| Eh, mV ........ | 230 | 215 | 181 | 220 |
| $\mathrm{HCO}_{1-3}, \mathrm{mg} / \mathrm{L}$ | 473 | 674 | 574 | 553 |
| pH | 6.10 | 6.40 | 6.60 | 6.90 |
| Element, mg/L: |  |  |  |  |
| Al | 1.25 | 0.57 | 0.33 | 0.30 |
| B | 2.60 | 0.69 | 0.56 | 0.30 |
| Ba | 0.04 | 0.07 | 0.08 | 0.09 |
| Ca | 536.00 | 508.00 | 391.00 | 363.00 |
| Cu | 0.58 | 0.17 | 0.09 | 0.07 |
| Fe | 968.00 | 233.00 | 197.00 | 9.20 |
| K | 54.30 | 22.80 | 12.40 | 1.90 |
| Mg | 610.00 | 361.00 | 145.00 | 127.00 |
| Mn | 74.00 | 22.00 | 6.50 | 0.80 |
| Na | 65.00 | 38.00 | 25.00 | 38.00 |
| Pb | 0.21 | 0.11 | 0.10 | 0.06 |
| S | 1,887.00 | 893.00 | 504.00 | 354.00 |
| Si | 21.00 | 16.00 | 18.00 | 25.00 |
| Zn | 4.50 | 2.80 | 0.93 | 0.35 |

A third explanation for the low concentrations in the silts below the tailings is that the neutralizing capacity of the calcareous, carbonaceous silt could be inducing precipitation, which would decrease metal concentrations in the silt pore water.

## Discussion and Summary of Water Quality Data

The following statements summarize the observed findings regarding the dissolved chemical constituents.

1. The vadose zone is more oxidizing (has higher Eh values) and is more acidic (has lower pH values) than the saturated zone.
2. Several dissolved constituents (sulfur, iron, manganese, lead, zinc, nickel, boron, cadmium, magnesium, and potassium) have higher average concentrations in the saturated tailings than in the vadose tailings. Several possible explanations exist. (a) Some redox species are more soluble under oxidizing conditions, and the oxidation products of easily dissolved minerals have been flushed from the vadose zone, while the presence of remaining sulfides continues to depress the pH ; (b) the percentage of fines increases with depth (finer materials tend to have more surface area available for chemical interaction, and may, therefore, cause more dissolved materials to be in solution in the deeper saturated zone); (c) different mineral assemblages may have been mined over time, in which case the corresponding wastes would have depthdependent changes in properties; or (d) different milling procedures might have been employed at the mill over
time, leading to corresponding depth-dependent changes in tailings composition.

The first explanation, offered by Dubrovsky and others (1985), is also supported by the work of Blowes and Jambor (1990). The second explanation, regarding the correlation to grain size, is plausible. Goss and others (1973) demonstrated with radioactively tagged clays that particulate material is transported downward through the vadose zone during infiltration. The third and fourth explanations regarding changes in depth corresponding to changes in depositional history are also possible because of mining (and milling) mineralogically different zones in the ore body, accidental mill reagent (lime, soda ash, crsylic acid, etc.) overdoses, and longer drying-out periods (oxidation exposure) for some portions of the tailings.
3. Concentrations of sodium, calcium, copper, aluminum, and barium tend to be the same for each element throughout both zones. Sodium, calcium, and aluminum are generally not considered redox species; therefore, they would not be influenced differently by the two zones. Phase diagrams for copper and super-sulfate systems indicate that copper is in equilibrium as $\mathrm{Cu}^{2+}$ over the range of pH and Eh encountered in both zones. Barium generally has a very low solubility in natural waters.
4. Concentrations of silicon tend to be slightly higher in the vadose zone than in the two saturated zones. Because redox thermodynamics are not likely to control silicon solubility, the higher solubility in the vadose zone is likely to be the result of organic complexing from roots and the influence of wet-dry cycles.
5. Downgradient profiles of average hydrologic and chemical parameters at the field site are shown in figure 12. Groundwater quality dramatically improves in the gravel downgradient of the tailings. Aluminum, copper, iron, lead, silicon, zinc, and pH attenuate rapidly in the first 76 m downgradient from the tailings and reach background levels of $0.3,0.5,0.2,0.03,15,0.05 \mathrm{mg} / \mathrm{L}$ and 7.0 , respectively, at well M5, which lies 550 m from the tailings. Potassium, manganese, magnesium, and sulfate attenuate but do not reach background levels. Downgradient calcium levels remain at the same value as the tailings pore water, and sodium is near background levels in the tailings pore water but increases above background levels downgradient. Also at well M5, pH is up to background levels of 7.0 .
6. Two key components, calcium and sulfate, were four times more concentrated downgradient than background. The presence of a significant concentration of sulfate in the tailings coupled with the solubilities of secondary sulfate minerals are major influences on the concentrations of many contaminants. Also, the presence of a significant calcium source in the sediments below the tailings has a major impact on attenuation. Iron is one of the major constituents released during oxidation of sulfide tailings. Downgradient attenuation of iron, as well as other trace metals, such as copper, lead, and zinc, is extremely rapid upon leaving the tailings.

## CONCLUSIONS

This report addresses acid production, leaching, transport, and attenuation of dissolved metals at an oxidized, acid-producing tailings impoundment in north-central Washington. This report describes the monitoring, physical properties, and on-site data collection necessary to characterize the site and to determine existing hydrological, physical, and geological conditions. Related reports present multivariate statistical analyses of vadose and saturated pore waters, and hydrological and hydrogeochemical investigations and modeling, (Lambeth, 1992; Williams, 1992). Forty-two monitoring wells were installed upgradient, within, below, and downgradient of the tailings impoundment. During a period of 3 years, pore water samples were taken approximately every 5 weeks and analyzed for dissolved constituents, $\mathrm{pH}, \mathrm{Eh}$, conductivity, temperature, DO, and alkalinity. In addition, pore gas samples were collected and water table elevation, tailings temperature, moisture and density, hydraulic conductivity, and groundwater flow velocity measurements were made. Solid samples were collected for mineralogic and chemical analyses and for determination of physical properties.

In the 50 years since deposition of milled tailings ended at the study site, acidic conditions have developed, resulting in high concentrations of dissolved heavy metals and other contaminants in the tailings pore water. Physical observation of the solid samples collected during monitoring well drilling show zones, from top to bottom, of unsaturated tailings, saturated tailings, lake sediments grading into volcanic silts, colluvial gravels, and fractured bedrock. The lake sediments immediately below the tailings consist of 30 to 60 cm of organic-rich material intermixed with silts containing large amounts of snail shells.

These below-tailings sediments are instrumental in the geochemical behavior of released tailings pore water. The vadose and saturated zones in the tailings and the saturated lake sediments and silts below the tailings were verified by measured differences in moisture content and density using a downhole neutron probe at eight locations in the tailings pile. Two of the neutron probe profiles showed layers of high moisture in the vadose zone, about 46 cm below the surface. A $61-\mathrm{cm}$ sampling tube pushed through one such layer showed a 2.5 - to 5 -cm-thick hardpan in the center of the sample. The tailings below the hardpan were much wetter and finer than the tailings above. The hardpan contained high concentrations of iron (from an acid-leaching test) and may reduce the water seepage velocity, alter the direction of flow, and possibly act as an oxidation barrier, slowing the pyrite oxidation process.

Groundwater is in contact with the tailings year around. Piezometric elevations in two multiple-completion wells indicate that groundwater from deeper fractured bedrock upwells into the sediments and possibly the tailings during part of the year. Water from the sediments probably flows into the fractured bedrock during other parts of the year. This water is supplemented by rain and snowmelt that filter through the vadose zone. The low slope of the phreatic surface ( $5.6 \times 10^{-3}$ ), coupled with the relatively low hydraulic conductivity ( $10^{-5} \mathrm{~cm} / \mathrm{s}$ ) of the tailings material, results in extremely slow downgradient groundwater flow rates through the tailings and long residence times for mechanical and chemical weathering and reactivity. In addition, grain-size comparisons between vadose and saturated zone samples taken from well P3A showed eight
times more $0.01-\mathrm{mm}$-sized particles in the saturated zone than in the vadose zone. This may be correlated to the large amount of dissolved constituents in the saturated zone because finer materials have more surface area available for chemical reaction.

SEM analysis of the tailings base and sediments below the tailings indicate abundant barium sulfate (barite) in the deep tailings, with detectable amounts of K-feldspar, quartz, and iron oxide. In the organic-rich layer below the tailings, numerous framboidal spheroids composed of iron and sulfur and a mineral assumed to be pyrite were found intermixed with abundant radiolarian debris, alga cysts, and snail shell fragments. The snail shells showed only calcium on the EDS spectrum. Given this type of reducing environment, secondary base-metal sulfides such as chalcocite, covellite, digenite, or sphalerite were expected to exist as coatings on the framboids. However, no secondary base metals were observed with SEM in the organic-rich layer. An EDS spectrum of the silts below the organicrich layer showed silicon, aluminum, potassium, and calcium, some of the major elements in dacitic-to-rhyolitic glass from volcanic ash falls.

Chemical analyses of the tailings base and sediments below the tailings indicate that solid phase lead and copper are present in the base of the tailings, but not in the organic-rich layer below the tailings, and do not appear to be remobilizing below the tailings. At the base of the
tailings, iron is bound primarily to sulfides and oxides, and in the organic-rich layer, iron is bound to oxides, sulfides, carbonates, and organic matter. In the silts below the organic-rich layer, iron and manganese are bound primarily to carbonates. Calcium and magnesium are very abundant in this zone, also in the carbonate form.

Long-term water quality monitoring at the field study site indicates that the vadose zone is more acidic than the saturated zone and appears to have been more aggressively chemically weathered than the saturated zone. Silicate and aluminosilicate dissolution is more advanced in the vadose zone than in the saturated zone. Because the water quality improves dramatically with depth below the tailings, the soluble contaminants in the tailings pore water are not penetrating the base of the tailings into the organic-rich layer and silts below to any great extent, but are probably being transported slowly downgradient through the tailings and are discharged near the southeast end of the tailings pile, where the colluvial gravels are in direct contact with the tailings. After the water leaves the impoundment, several processes aid in downgradient attenuation. These include hydrogeochemical reactions, dilution, advection, and dispersion. At a distance of 550 m downgradient from the impoundment, all measured dissolved constituents naturally attenuate to near-background concentrations except calcium, magnesium, manganese, sodium, and sulfur.

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Figure 1


Low-angle photograph of study site looking downgradient.

Figure 2


|  | LEGEND |
| :---: | :---: |
| 6 | Tailings |
| 格 | Organic-rich silt |
|  | Silt |
| 48:9] | Quaternary colluvium |
| $\nabla$ | Water table |



Cross section of tailings impoundment and stratigraphy below impoundment.

Figure 3


Plan view of reseanch site and monitoring well locations.

Figure 4


Cross section of BAT sampler. A, Sample vial; B, pressure transducer.

Figure 5


Gauge pressure data from vadase zone. A, B1-4c; B, B2-4c; C, B1-7c, D, B2-8c.

Figure 6


Head data from saturated zone sampling locations plotted against time.

Figure 7


Oxygen and carbon dioxide content at vadose zone sampling locations plotted against time.

Figure 8


Grain-size distribution of samples from vadose zone (solid line) and saturated zone (dotted line), well P3A.

Figure 9


Moisture and density profiles in vadose zone, well B2-4c.

Figure 10


Grain-size distribution in samples above and below hardpan. The samples were collected in a zone extending from the surface to a depth of 76 cm near well B2-2c.

Figure 11


Moisture and density profiles in tailings and silts below tailings near well P3. Changes between the two units ane noticeable at 5.8 m .

Figure 12


Changes in elevation, pH, Eh, and metal concentrations in shallow groundwater from background ( -400 m ), through the tailings ( 0 m ), to three locations downgradient (76, 335, and 550 m ).

Figure 12-Continued


Changes in elevation, $\mathrm{pH}, \mathrm{Eh}$, and metal concentrations in shallow groundwater from background ( -400 m ), through the tailings ( 0 m ), to three locations downgradient (76, 335, and 550 m ).

Figure 12-Continued


Changes in elevation, $\mathrm{pH}, \mathrm{Eh}$, and metal concentrations in shallow groundwater from background ( -400 m ), through the tailings ( 0 m ), to three locations downgradient ( 76,335 , and 550 m ).

## APPENDIX A.-WELL COMPLETION REPORTS FOR P, M, AND BKG WELLS

RESOURCE PROTECTION WELL REPORT

| PROJECT NAME: <br> Attydrogeologic Phonomence - <br> nai uobs Mana ement |
| :---: |
| WELL IDENTIFICATION No. $P$ l |
| drilling method: Hollow Stem Auger |
| DRILLER: |
| FIRM: U.S.R,M. |
| SIGNATURE: |
| CONSULTING FIRM: |
| REPRESENTATIVE: |

StART CARD No. $\qquad$
countr: okanogan
LOCATION: SE $1 / 4$ SE $1 / 4$ Sec 18 Twn 33N R 22E STREET ADDRESS OF WELL: $\qquad$
WATER LEVEL ELEVATION:
GROUND SURFACE ELEVATION: $1859.8^{\prime} \mathrm{A}$ bove Sou lead.
INSTALLED: $10 / 1 / 87$
DEVELOPED; $\qquad$
$\square$ OF $\qquad$

RESOURCE PROTECTION WELL REPORT


ECY 050-12 (Rev. 11/89)

RESOURCE PROTECTION WELL REPORT
START CARD NO. $\qquad$

PROJECT NAME: Hydrogcologic Phenomena
Mine waste Manugenent WELL IDENTIFICATION NO. PB
dRILL IN MEthod: Hollow Stem Auger DRILLER: $\qquad$ FIRM: U.S.B.M.
sIGNATURE: $\qquad$ CONSULTING FIRM: $\qquad$
REPRESENTATIVE: $\qquad$ county: okanogan LOCATION: SE $1 / 4$ SE $1 / 4$ Soc 18 Twi $33 \mathrm{~N}^{2}$ RILE StREET ADDRESS OF WELL: $\qquad$
WATER LEVEL ELEVATION: $\qquad$ GROUND SURFACE ELEVATION: $1858.4^{\prime}$ Agar S.L. INSTALLED: $\qquad$ developed: $\qquad$


ECY 050-12 (Rev. 11/89)

RESOURCE PROTECTION WELL REPORT

Hydruguologic phonaman -
PROJECT NAME: Ming Wast Monc;icment
WELL IDENTIFICATION NO. P3A
DRILLING METHOD: Hollow Stem Au jor
DRILLER:
FIRM: U.S.B.M
SIGNATURE:
CONSULTING FIRM:
REPRESENTATIVE:

START CARD NO. $\qquad$
county: OKanogan
LOCATION: SE $1 / 4$ SE $1 / 4$ Sec 18 Pwn 33N R Z2E STREET ADDRESS OF WELL: $\qquad$

WATER LEVEL ELEVATION: $\qquad$
ground surface elevation: No elev. taken.
INSTALLED: $\qquad$ $5 / 1 / 90$ DEVELOPED: $\qquad$


## RESOURCE PROTECTION WELL REPORT

## Hytrogeologic Phenomena - start card no.

$\qquad$ county: OKanogan LOCATION: SEE $1 / 4$ SE $1 / 4$ Sec 18 Pwn 33N R 22E STREET ADDRESS OF WELL: $\qquad$
 DRILLING METHOD: Hollow Stem Anger FIRM: U.S.B.M. sIgnature: $\qquad$ CONSULTING FIRM: $\qquad$

WATER LEVEL ELEVATION: ground surface elevation: No. elev. taken INSTALLED: $\quad 5 / 1 / 90$ developed: $\qquad$

[^9]
## RESOURCE PROTECTION WELL REPORT

 project name: mine Waste management well identification no. P3C drilling method: Hollow Stem Auger DRILLER:
$\qquad$
FIRM: U.S.B.M.
SIGNATURE:
CONSULTING FIRM: $\qquad$ REPRESENTATIVE: $\qquad$
country: OKanogan
START CARD NO. $\qquad$ LOCATION: SE $1 / 4$ SE $1 / 4$ Sec 18 Twi 33N R 22E STREET ADDRESS OF WELL: $\qquad$
WATER LEVEL ELEVATION: $\qquad$
$\qquad$ INSTALLED: $\quad 5 / 1 / 90$ DEVELOPED: $\qquad$


[^10]
## RESOURCE PROTECTION WELL REPORT

Hydro geoloque Phenomena -
PROJECT NAME: Mim WAste Monagemant
WELL IDENTIFICATIONNO. PL
DRILLING METHOD: Hollow STEm Puget
DRILLER:
FIRM: $4 . S$ BM
SIGNATURE:
CONSULTING FIRM:
REPRESENTATIVE:

START CARD NO. $\qquad$
county: okanogan LOCATION: SE $1 / 4$ SE $1 / 4$ Soc 18 Twn 33N R22E STREET ADDRESS OF WELL: $\qquad$

WATER LEVEL ELEVATION: ground surface elevation: 1857,3 shove Sen luce INSTALLED: $10 / 6 / 87$ DEVELOPED: $\qquad$
SCALE: $1=-5$
PAGE $\qquad$ of $\qquad$

ECY 060-12 (Rev. 11/89)

RESOURCE PROTECTION WELL REPORT

Hydrogeologic phanomana-
PROJECT NAME: Minos Wont Management
WELL IDENTIFICATION NO. dRILLING METHOD: Hollow Ste Auger DRILLER:
FIRM: U S.B.M
SIGNATURE:
CONSULTING FIRM:
REPRESENTATIVE: $\qquad$
$\qquad$
COUNTY: OMan logan
LOCATION: SE $1 / 4$ SE $1 / 4$ Sec 18 Tun 33N R22E STREET ADDRESS OF WELL: $\qquad$
WATER LEVEL elevation: $\qquad$ GROUND SURFACE ELEVATION: 1858.6 Above Select installed: $10 / 7 / 87$
DEVELOPED: $\qquad$


SCALE: 1" = $\qquad$ PAGE $\qquad$ of
ECY 050-12 (Rev. 11/89)

RESOURCE PROTECTION WELL REPORT

Hydrogeologis phenomena-
Miss West monagemant
PROJECT NAME: Mint Well e IDENTIGATIONNO. Pl
DRILING METHOD: Hollow Stem Auger
DRILLER:
FIRM: U.S.B.M.
SIGNATURE:
CONSULTING FIRM:
REPRESENTATIVE:

START CARD NO. $\qquad$
country: OK ono gam
LOCATION: SE $1 / 4$ SE (V/4 Soc 18 TwI 33N R $22 E$ STREET ADDRESS OF WELL: $\qquad$

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RESOURCE PROTECTION WELL REPORT

Hydrogeologic phenomena
projectaname: Mia Waste management
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FIRM: U.S.D.M,
sIGNATURE: $\qquad$ CONSULTING FIRM: $\qquad$
REPRESENTATIVE: $\qquad$
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START CARD NO.
LOCATION:NE1/4 NE $1 / 4$ Sec 19 Twi 33N R L2E
STREET ADDRESS OF WELL: $\qquad$
WATER LEVEL ELEVATION: $\qquad$
GROUND SURFACE ELEVATION: $\qquad$
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## RESOURCE PROTECTION WELL REPORT

Hydrogeologic phonomema PROJECT NAME: Mive Doste Management WELL IDENTIFICATION NO. M2 $(13,0,41)$ dRilling method: Air Potary whown hole kammer DRILLER:
FIRM: U.S.BM.
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REPRESENTATIVE: $\qquad$
cOUNTY: OKonogon
LOCATION: N巨 $1 / 4$ NS $1 / 4$ Sec $19 \mathrm{Twn}^{3} 3 \mathrm{~N}$ R 22 E street address of Well:

WATER LEVEL ELEVATION: GROUND SURFACE ELEVATION: $\qquad$
INSTALLED: $\quad 7 / 7 / 87$
DEVELOPED: $\qquad$


ECY 050-12 (Rev. 11/89)

## RESOURCE PROTECTION WELL REPORT

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representative: $\qquad$
COUNTY: OKanogon
 STREET ADDRESS OF WELL: $\qquad$
water level elevation: GROUND SURFACE ELEVATION: installed: $\quad 7 / 14 / 8 \eta$
DEVELOPED: $\qquad$


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RESOURCE PROTECTION WELL REPORT
Hydrogeologic phenomena -
Hydrogeologic phenomena
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PROJECT NAME: $n$ ind Waste Management)
WELL IDENTIFICATION NO. $r 74(17,24,32)$
DRILLING METHOD: Airkotary w/ Dounhile Homers DRILLER:
FIRM: U.S.B.M
SIGNATURE:
CONSULTING FIRM: tr
REPRESENTATIVE: $\qquad$
START CARD NO. $\qquad$
COUNTY: OKamogon
LOCATION: NW $1 / 4$ Nu) $1 / 4$ Sec 20 Twi 33N R $22 \sqrt{2}$
STREET ADDRESS OF WELL: $\qquad$
WATER LEVEL ELEVATION: $\qquad$ GROUND SURFACE ELEVATION: $\qquad$
INSTALLED: $\qquad$ DEVELOPED: $\qquad$


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ECY 050-12 (Rev. 11/89)

RESOURCE PROTECTION WELL REPORT

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PROJECT NAME: Min. White management WELL IDENTIFICATIONNO. MS ( $13,45,175$ ) DRILLING METHOD: Pinot air Rotary
DRILLER:
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country: GKonogan
LOCATION: NW $1 / 4 \mathrm{NW}$ So 20 Twi 33 N R 22 E STREET ADDRESS OF WELL: $\qquad$
WATER LEVEL ELEVATION: $\qquad$
GROUND SURFACE ELEVATION: $\qquad$
installed: $\qquad$ 10/23/87
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ECY 060-12 (Rev. 11/89)

## RESOURCE PROTECTION WELL REPORT



START CARD NO. $\qquad$
COUNTY: OKOnogan
LOCATION: SE $1 / 4$ SE $1 / 4$ Soc 18 TwI 33NR22E STREET ADDRESS OF WELL:

WATER LEVEL ELEVATION: GROUND SURFACE ELEVATION:
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ECY 060-12 (Rev. 11/89)

# APPENDIX B．－WATER QUALITY DATA FROM SAMPLING TRIPS BETWEEN 1988 AND 1991 






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| M5－53 | 05／3088 | 13.4 | 8.9 | ND | ND | ND | 4.011 | 542.045 | ND | ND | 0.03 | 2.688 | 0.061 | 13 | 0.000 |
| M5．53 | 05／20／88 | 18.3 | 8.0 | ND | 210 | ND | 4.103 | 541.953 | ND | ND | 0.18 | 2833 | 0.054 | 14 | 0.000 |
| M5－53 | 07125／88 | 11.8 | 7.4 | ND | 297 | 0.6 | 4.630 | 541.426 | ND | ND | 0.00 | 2.350 | 0.000 | 9 | 0.002 |
| M553 | 08122788 | 12.0 | 8.9 | ND | 72 | 1.1 | 4.984 | 541.072 | ND | ND | 0.38 | 2.454 | 0.000 | 10 | 0.000 |
| M5－53 | 09／19188 | 11.3 | 7.8 | ND | 102 | 0.8 | 5.258 | 540．798？ | ND | ND | 0.75 ？ | 2.471 | 0.037 | 6 | 0.000 |
| M5－53 | 1017788 | 9.5 | 7.9 | ND | 270 | 1.8 | 5.474 | 540.582 | ND | ND | 0.04 | 2.178 | 0.002 | 10 | 0.000 |
| M5－53 | 11／14／88 | 8.2 | 8.7 | ND | 203 | 2.8 | 5.517 | 540.539 | ND | ND | 0.11 | 2.470 | 0.051 | 13 | 0.000 |
| M5＿53 | 01／09／89 | 10.5 | 7.9 | ND | 113 | 1.2 | 5.486 | 540.569 | ND | ND | 0.00 | 2.536 | 0.018 | 10 | 0.000 |
| M5－53 | 03106189 | ND | ND | ND | ND | ND | 5.392 | 540.664 | ND | ND | ND | ND | ND | ND | ND |
| M5．53 | 0410189 | 9.7 | 9.3 | 805 | 54 | －0．0 | 3.941 | 542.115 | ND | ND | 0.14 | 2.418 | 0.042 | 8 | 0.000 |
| M5．53 | 05／2289 | 9.5 | 8.8 | 787 | 73 | 0.3 | 3.524 | 542.532 | ND | ND | 0.56 | 3.610 | 0.062 | 12 | 0.000 |
| M5－53 | 06／06／89 | ND | ND | ND | ND | ND | 3.655 | 542.401 | ND | ND | ND | ND | ND | ND | ND |
| M5＿53 | 06／27789 | ND | ND | ND | ND | ND | 3.816 | 542.240 | ND | ND | ND | ND | ND | ND | ND |
| M5－53 | 08／21／89 | 12.7 | 7.9 | 944 | 195 | 0.4 | 4.691 | 541.365 | ND | ND | 0.56 | 1.850 | 0.015 | 17 | 0.010 |
| M5－53 | 10／30／89 | 9.5 | 8.7 | 798 | 125 | 0.1 | 5.410 | 540.646 | ND | ND | 1.54 | 2.250 | 0.062 | 11 | 0.000 |
| M5．53 | 03／12900 | 9.5 | 8.7 | 805 | 137 | 0.0 | 4.977 | 541.078 | ND | ND | 1.03 | 1.930 | 0.168 | 10 | 0.010 |
| M5－53 | 04130／90 | 11.4 | 8.7 | 565 | ND | ND | 4.328 | 541.728 | ND | ND | 0.89 | 2.030 | 0.064 | 11 | 0.000 |
| M5－53 | 06／18／90 | 13.5 | ND | 612 | ND | 3.3 | 4.237 | 541.819 | ND | ND | ND | ND | ND | ND | ND |
| M5＿53 | 03／11／91 | 8.5 | 8.2 | 616 | ND | 2.3 | 5.008 | 541.048 | ND | 128.1 | 0.00 | 2.220 | 0.122 | 11 | 0.000 |

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# APPENDIX C.-SUMMARY OF SEM ANALYSIS OF SAMPLES TAKEN AT BASE OF AND BELOW TAILINGS 

## 1988 SAMPLES

Photomicrographs from SEM examination of polished sections of the 1988 and 1990 samples were taken. The actual photographs are not included in this RI but are available by contacting any of the authors. In this appendix, the SEM observations are described for each sample, including observations that were not recorded by photomicrograph.

Sample P-4A (From well P4, 0 to 7.6 cm below tailings.)
Barium sulfate (the mineral barite) is a fairly common constituent of the fine-grained fraction of sample P-4-A. Numerous barite grains, 2 to $8 \mu \mathrm{~m}$ in size, in a matrix rich in iron, aluminum, and silicon (perhaps an amorphous precipitate?) were observed. Elsewhere on this sample, rectangular gypsum crystals were found, as was a grain of iron-titanium oxide in a matrix of silica.

Sample P-4-B (From well P4, 7.6 to 22.9 cm below tailings.)
Framboidal spheroids composed of iron and sulfur were observed in sample P-4-B. Although the mineralogy of these spheroids has not been determined, they are assumed to be pyrite based on results of numerous other studies (e.g., Berner, 1970). The framboids range in diameter from about 6 to $20 \mu \mathrm{~m}$. Regardless of the total size of the framboidal spheroid, the individual spheres within the spheroid seem to be about $0.8 \mu \mathrm{~m}$ in size.

Sample P-4C (From well P4, 22.9 to 25.4 cm below tailings.)

In addition to pyrite framboids about $8 \mu \mathrm{~m}$ in diameter, this sample contained a mottled mass of iron oxide. Also, various shell fragments (snails?) showed only calcium during EDS and are probably composed of calcium carbonate. A grain with titanium and silica and in a silica matrix probably represents sphene trapped in quartz.

Sample P-5-A. (From well P5, 0 to 2.5 cm below tailings.)
This sample contained a relatively large ( 100 to $200 \mu \mathrm{~m}$ ) grain cluster of gypsum (calcium and sulfur on EDS). Barite grains in an iron-aluminum-silicon matrix were also observed.

Sample P-5-B (From well P5, 2.5 to 12.7 cm below tailings.)
Barite was observed in sample P-5-B, as well as a limited amount of framboidal pyrite particles about $8 \mu \mathrm{~m}$ in diameter.

## Sample P-5-C (From well P5, depth unknown.)

A grain of galena was found in quartz. Antimony and silver were detected by EDS on this grain, indicating the presence of a sulfosalt mineral. No pyrite framboids were found. Some gypsum, with a lead-rich core, was observed.

Sample P-6-A (From well P6, 0 to 10.1 cm below tailings.)
Pyrite framboids of about $8 \mu \mathrm{~m}$ in diameter were found in this sample. One of the framboids has an oxidation rind in which the relative amount of sulfur is less than in the central portion. Because the rind is thinner, about $2 \mu \mathrm{~m}$, than the spatial resolution of the SEM for semiquantitative analysis, it seems probable that the rind is composed entirely of iron (iron oxide, or goethite). Also found in this sample were grains of barite and an irontitanium oxide (ilmenite?).

Sample P-G-B (From well P6, 10.1 to 22.9 cm below tailings.)

This sample contains a cluster of three pyrite framboids, each about 16 to $18 \mu \mathrm{~m}$ in diameter, plus a number of dispersed, individual spherules, which may simply represent a larger framboid damaged during sample preparation.

## 1990 SAMPLES

## Sample B2A-1 (From well B2A, base of tailings.)

This sample appears to represent the bottom of the tailings, just above the organic layer. Barite was quite abundant. Also detected were K-feldspar, quartz, and iron oxide (goethite?). No sulfide grains, algae, or diatoms were seen in this interval.

Sample B2A-2 (From well B2A, 2.5 to 7.6 cm below tailings.)

Pyrite framboids from 2 to $6 \mu \mathrm{~m}$ in diameter were seen in this interval at the top of the organic layer. Radiolarian debris was abundant.

Sample B2A-3 (From well B2A, 30.5 to 40.6 cm below tailings.)

Volcanic ash was abundant in this interval. Excessive charging of the sample during SEM examination precluded taking any informative photographs.

Sample P3A-1 (From well P3A, 2.5 to 7.6 cm below tailings.)

Some pyrite framboids about $6 \mu \mathrm{~m}$ in diameter were observed along with abundant radiolarian debris and algal cysts (crysophytes).

Sample P3A-2 (From well P3A, 30.5 to 40.6 cm below tailings.)

Only a few pyrite framboids (about $4 \mu \mathrm{~m}$ in diameter) were found along with abundant algal cysts and radiolarian debris.

Sample P3A-3 (From well P3A, 48.3 to 58.4 cm below tailings.)

No pyrite framboids were found in this sample, which apparently consists largely of devitrified volcanic glass. An EDS spectrum of the material showed silicon, aluminum, potassium, and calcium, some of the major elements in dacitic-to-rhyolitic glass from volcanic ashfalls typical of the region.

Sample P3C-1 (From well P3C, base of tailings.)
This sample presumably contained oxidized tailings from above the organic layer. Fine-grained barite was very abundant, along with iron oxides. No sulfide minerals were found. No SEM photomicrographs were taken because of excessive charge buildup on the sample.

Sample P3C-2 (From well P3C, 0 to 7.6 cm below tailings.)
At the top of the organic-rich layer, abundant pyrite framboids, 10 to $20 \mu \mathrm{~m}$ in diameter, were observed. Some algal cysts were also found.

Sample P3C-3 (From well P3C, 7.6 to 15.2 cm below tailings.)

This sample had abundant algal cysts (chrysomonads, which are the resting state of algae), possible volcanic glass shards, well-formed pyrite framboids, and abundant diatom and radiolarian fossils.

Sample P3C-4 (From well P3C, 60.9 to 76.2 cm below tailings.)

A tan-to-brown clay-rich layer looked to be composed of partially devitrified volcanic glass. An EDS spectrum showed abundant silica, with detectable aluminum, potassium, calcium, and iron, as would be expected from rhyolitic to rhyodacitic ashfalls.

Sample P3C-5 (From well P3C, 76.2 to 94 cm below tailings.)

Volcanic glass shards and algal cysts were observed by SEM, in this brown-to-tan layer, but no pyrite framboids. Macroscopically, some green material was present, perhaps a live colony of moss or algae.

# APPENDIX D.-RESULTS OF CHEMICAL ANALYSES OF SOLID SAMPLES COLLECTED AT BASE AND BELOW TAILINGS 

(Analyses conducted by IGA1, Inc., Cheney, WA)
IGAL, Inc.
111 College Ave. Cheney, WA 99004 July 17, 1991
si (ppm)

| Sample No. | I | II | III | IV | V |
| :--- | ---: | ---: | ---: | ---: | ---: |
|  |  |  |  |  |  |
| P2A18 | 57 | 61 | 392 | 323 | 560 |
| B2A20 | 5 | 103 | 405 | 278 | 365 |
| P2A20 | 15 | 150 | 495 | 580 | 1210 |
| P2A22 | 78 | 395 | 680 | 435 | 805 |
| P3A19 | 125 | 520 | 428 | 1520 | 835 |
| P3A22 | 62 | 265 | 860 | 605 | 1030 |
| P3C24 | 15 | 75 | 218 | 125 | 362 |

Al (ppm)

| Sample No. | I | II | III | IV | V |
| :--- | ---: | ---: | ---: | ---: | ---: |
|  |  |  |  |  |  |
| P2A18 | 35 | 232 | 733 | 365 | 2450 |
| B2A20 | 15 | 270 | 1065 | 220 | 1075 |
| P2A20 | 3 | 45 | 260 | 535 | 1760 |
| P2A22 | $<1$ | 95 | 518 | 420 | 2350 |
| P3A19 | $<1$ | 36 | 180 | 1570 | 575 |
| P3A22 | $<1$ | 105 | 522 | 920 | 6320 |
| P3C24 | $<1$ | 12 | 50 | 5 | 80 |

Fe (ppm)

| Sample No. | I | II | III | IV | V |
| :--- | ---: | ---: | ---: | ---: | ---: |
|  |  |  |  |  |  |
| P2A18 | 50 | 428 | 1910 | 282 | 8450 |
| B2A20 | 15 | 370 | 1368 | 150 | 6420 |
| P2A20 | 7 | 5570 | 9710 | 4905 | 6750 |
| P2A22 | 3 | 2750 | 2015 | 860 | 4675 |
| P3A19 | 5 | 35 | 210 | 3300 | 1960 |
| P3A22 | 8 | 1080 | 1075 | 1510 | 4225 |
| P3C24 | 3 | 4750 | 1335 | 135 | 450 |

Mn (ppm)

| Sample No. | I | II | III | IV | V |
| :--- | ---: | ---: | ---: | ---: | ---: |
|  |  |  |  |  |  |
| P2A18 | 12 | 1 | 8 | $<1$ | 30 |
| B2A20 | 15 | 6 | 18 | 1 | 8 |
| P2A20 | 120 | 210 | 105 | 25 | 32 |
| P2A22 | 72 | 80 | $<1$ | 45 | 16 |
| P3A19 | 60 | 122 | 30 | 60 | 3 |
| P3A22 | 5 | 42 | 8 | 2 | $<1$ |
| P3C24 | 5 | 225 | 35 | $<1$ | $<1$ |

Mg (ppm)

| Sample No. | I | II | III | IV | V |
| :--- | ---: | ---: | ---: | ---: | ---: |
|  |  |  |  |  |  |
| P2A18 | 201 | 16 | 62 | 35 | 1890 |
| B2A20 | 162 | 20 | 33 | 21 | 542 |
| P2A20 | 1980 | 632 | 225 | 120 | 1250 |
| P2A22 | 1285 | 250 | 95 | 58 | 1025 |
| P3A19 | 860 | 1750 | 232 | 73 | 175 |
| P3A22 | 1015 | 1460 | 260 | 105 | 520 |
| P3C24 | 180 | 3350 | 220 | 35 | 65 |

Ca (ppm)

| Sample No. | I | II | III | IV | V |
| :--- | ---: | ---: | ---: | ---: | ---: |
|  |  |  |  |  |  |
| P2A18 | 506 | 37 | 530 | 83 | 145 |
| B2A20 | 490 | 110 | 492 | 70 | 67 |
| P2A20 | 14500 | 29450 | 5525 | 1610 | 1040 |
| P2A22 | 12250 | 8320 | 1915 | 5018 | 1850 |
| P3A19 | 16780 | 150850 | 27420 | 805 | 2885 |
| P3A22 | 19660 | 119950 | 16935 | 3522 | 2615 |
| P3C24 | 8840 | 324300 | 53230 | 42 | 1730 |

## Cu (ppm)

| Sample No. | I | II | III | IV | V |
| :--- | ---: | ---: | ---: | ---: | ---: |
|  |  |  |  |  |  |
| P2A18 | 10 | 52 | 12 | 18 | 405 |
| B2A20 | 1 | 40 | 5 | 7 | 170 |
| P2A20 | 1 | 4 | 1 | 3 | 48 |
| P2A22 | $<1$ | 3 | 1 | 6 | 45 |
| P3A19 | $<1$ | 4 | 1 | 4 | 34 |
| P3A22 | $<1$ | 4 | 1 | 6 | 46 |
| P3C24 | $<1$ | 3 | 1 | 2 | 8 |

Pb ( ppm )

| Sample No. | I | II | III | IV | V |
| :--- | ---: | ---: | ---: | ---: | ---: |
|  |  |  |  |  |  |
| P2A18 | 1 | 18 | 45 | 4 | 35 |
| B2A20 | $<1$ | 20 | 38 | 3 | 27 |
| P2A20 | $<1$ | $<1$ | $<1$ | $<1$ | 5 |
| P2A22 | $<1$ | $<1$ | $<1$ | $<1$ | 4 |
| P3A19 | $<1$ | $<1$ | $<1$ | $<1$ | 2 |
| P3A22 | $<1$ | $<1$ | $<1$ | $<1$ | $<1$ |
| P3C24 | $<1$ | $<1$ | $<1$ | $<1$ | $<1$ |

I Exhchangable
II Bond to carbonates
III Bond to iron and manganese oxides
IV Bond to organic matter
V Bond to sulfides


[^0]:    UNITED STATES DEPARTMENT OF THE INTERIOR Bruce Babbitt, Secretary

    ## BUREAU OF MINES

    Rhea Lydia Graham, Director

[^1]:    ${ }^{1}$ Mining engineer.
    ${ }^{2}$ Research civil engineer.
    Spokane Research Center, U.S. Bureau of Mines, Spokane, WA.

[^2]:    ${ }^{1}$ Wells P1 through P6 were sampled with a vacuum pump; wells B1-2 through B2-16 were sampled with the BAT sampler.
    ${ }^{2}$ The first part of the label is the sample location, and the second part following the hyphen is the sample depth in feet from ground level.
    ${ }^{3}$ BT indicates the completion media are at the base of the tailings or below the tailings.
    ${ }^{4}$ The fluctuation zone refers to that zone through or within which the water table fluctuates from its highest point to its lowest point in any given year.

[^3]:    ${ }^{1}$ All wells were sampled using the peristaltic method, except wells M5-53, BKG-20, and BKG-43, which were sampled with bladder pumps.

[^4]:    ${ }^{4}$ Information provided in "A Geophysical Investigation to Determine Groundwater Velocities at a Site in West-Central Washington," by W. R. Sill and K. J. Sjostrom. Final service agreement report to USBM, 1990, 13 pp .

[^5]:    ${ }^{4}$ The number following the hyphen is the sample depth in feet from ground level. The actual measurements were made using U.S. customary units.

[^6]:    ${ }^{5}$ See footnote 3.

[^7]:    Alpers, C. N., and G. H. Brimhall. Paleohydrologic Evolution and Geochemical Dynamics of Cumulative Supergene Metal Enrichment at La Escondida, Atacama Desert, Northern Chile. Econ. Geol., v. 84, 1989, pp. 229-255.

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[^8]:    Blowes, D. W., and J. L. Jambor. The Pore-Water Geochemistry and the Mineralogy of the Vadose Zone of Sulfide Tailings, Waite Amulet, Quebec, Canada. App. Geochem., v. 5, 1990, pp. 327-346.

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[^9]:    ECY 060-12 (Rev. 11/89)

[^10]:    ECY 050-12 (Rev. 11/89)

[^11]:    
    

