RI 9631

REPORT OF INVESTIGATIONS/1995

Treatment Of Fluvially Deposited Streamside Mine Waste—Material From Nine Mile Creek, Idaho

By Anthony J. Paulson, Robert Balderrama, Eric Zahl,
and Ryan L. Cox

UNITED STATES DEPARTMENT OF THE INTERIOR

UNITED STATES BUREAU OF MINES

U.S. Department of the Interior Mission Statement

As the Nation's principal conservation agency, the Department of the Interior has responsibility for most of our nationally-owned public lands and natural resources. This includes fostering sound use of our land and water resources; protecting our fish, wildlife, and biological diversity; preserving the environmental and cultural values of our national parks and historical places; and providing for the enjoyment of life through outdoor recreation. The Department assesses our energy and mineral resources and works to ensure that their development is in the best interests of all our people by encouraging stewardship and citizen participation in their care. The Department also has a major responsibility for American Indian reservation communities and for people who live in island territories under U.S. administration.

Report of Investigations 9631

Treatment Of Fluvially Deposited Streamside Mine Waste—Material From Nine Mile Creek, Idaho

By Anthony J. Paulson, Robert Balderrama, Eric Zahl,
and Ryan L. Cox

UNITED STATES DEPARTMENT OF THE INTERIOR
Bruce Babbitt, Secretary

BUREAU OF MINES
Rhea Lydia Graham, Director

International Standard Serial Number
ISSN 1066-5552

CONTENTS

Page

ILLUSTRATIONS

TABLES

TABLES—Continued

UNIT OF MEASURE ABBREVIATIONS USED IN THIS REPORT

Metric Units

cm	centimeter	min	minute
g	gram	mL	milliliter
h	hour	mm	millimeter
kg	kilogram	m*M*	millimolar
kPa	kilopascal	ms	millisiemens
kV	kilovolt	mV	millivolt
L	liter	nm	nanometer
L/kg	liter per kilogram	equil	equivalent
m	meter	ppm	part per million
M	molar	W	watt
mA	milliamphere	wt ave	weight average
mg	milligram	wt %	weight percent
mg/kg	milligram per kilogram	μm	micrometer
mg/L	milligram per liter	°C	degree Celsius

U.S. Customary Units

in	inch

TREATMENT OF FLUVIALLY DEPOSITED STREAMSIDE MINE WASTE—MATERIAL FROM NINE MILE CREEK, IDAHO

By Anthony J. Paulson,[1] Robert Balderrama,[2] Eric Zahl,[3] and Ryan L. Cox[4]

ABSTRACT

The size separation of flood plain material contaminated with mine waste was tested to determine if the interaction of water flow with geochemical processes could be changed sufficiently to reduce release rates of metals in a manner that would allow on-site disposal of all material as the sole remediation action. Size separation reduced Zn release by 60% over a 270-day period, partially by changing hydrogeochemical conditions and partially by the flushing action of the wet-separation process. Since Pb was controlled by anglesite solubility, reduced sulfate concentrations in the segregated material actually resulted in increased Pb release. The initial release of metals from the gravel fraction seemed to be controlled by adhered fines, even though the wet-separation process removed more of this finer material.

In ancillary separation tests, aggressive water treatment of the coarser fraction was required to limit initial metal release. This treatment involved thoroughly removing the finer fraction. Gravity separation of the finest fraction produced a concentrate high in Pb. In contrast, conventional flotation to remove sulfide minerals was ineffective because the material had been weathered and heavily oxidized on the flood plain.

---

[1] Hydrologist, formerly with the U.S. Bureau of Mines, Spokane Research Center, Spokane, WA.

[2] Metallurgist, formerly with the U.S. Bureau of Mines, Reno Research Center, Reno, NV.

[3] Civil engineer, Spokane Research Center, U.S. Dept. Of Energy, Spokane, WA.

[4] Student aide, formerly with the U.S. Bureau of Mines, Salt Lake City Research Center, Salt Lake City, UT.

INTRODUCTION

In the past, mine wastes were deposited with natural sediments along stream channels because of an absence of suitably engineered containment structures. These wastes were then washed downstream during periods of high flow. Such fluvially deposited mine wastes from past mining practices are continuing to degrade water quality in many mining districts both in the United States and abroad. The physical erosion and chemical weathering of these mine wastes and the migration of contaminants released into surface and ground water are the primary environmental concerns. For example, dissolution of zinc sulfate ($ZnSO_4$), which forms on the surface of fluvially deposited tailings as a result of evaporation in arid regions, has resulted in massive fish kills immediately after summer storms (Johnson and Schmidt, 1988). The listing of several mining sites, such as Bunker Hill, Kellogg, ID, on the National Priority List under the Comprehensive, Environmental Response, Compensation, and Liability Act (CERCLA, also known as Superfund) has focused attention on metal pollution from past and present mining practices in these watersheds.

The collection of tailings in settling ponds started in 1968 and has resulted in cleaner mining effluents. As a consequence, metal loads from presently operating mines and mills have decreased dramatically. In the Coeur d'Alene Basin, for instance, metal concentrations have decreased significantly since the passage of the Clean Water Act in 1972 (Horning and others, 1988; Collcott, 1989). However, a considerable amount of current metal loads in mining districts originates outside of presently operating mine and mill sites (Callcott, 1989; McCulley, Frick and Gilman, Inc., 1991, 1992). Release of zinc (Zn) from fluvially deposited tailings located within three large flood plains near Wallace and Kellogg, ID (Canyon Creek, Nine Mile Creek, and Smelterville Flats) contributes a large percentage of Zn loading to the Coeur d’Alene River. Controlling the release of heavy metals from these fluvially deposited tailings is required to improve water quality to acceptable standards.

The extent, nature, and mechanisms of metal releases from fluvially deposited mine waste have not been adequately addressed. The hydrologic, physical, and chemical characteristics of mixtures of mine waste and stream sediments are probably dramatically different from those of piles of pure mine waste. The nature of metal releases in more temperate regions has not been studied. In addition, the types of data needed to determine the most effective technology for controlling metal releases from fluvially deposited mine wastes have not been established. The study of a selected treatment for the containment of metals from fluvially deposited tailings will provide additional knowledge on the physical and chemical variables that govern the effectiveness of treatments in general. This knowledge should be transferable to other waste treatment technologies, as well as to wastes from geographic regions having different mineralogies.

Remediation technologies that have been utilized for other types of waste materials and/or sites were examined to evaluate their applicability to fluvially deposited mine waste. Metal release from sulfide minerals requires (1) an oxidant to oxidize the sulfide mineral and (2) water to activate the oxidation reaction and to transport oxidation products (sulfate and metals) from the mine waste into the surrounding ground or surface water. Control of molecular oxygen (O_2) diffusion into the mixed soils was not considered since the reservoir of oxygen in the already oxidized soils (i.e., Fe oxyhydroxides) can activate oxidation reactions in the absence of molecular oxygen (Rimstidt and others, 1994). A general premise of this research is that oxidation of sulfide minerals can only be slowed, not stopped. Below is a partial list of remediation options that were considered to have the potential to slow down oxidation or stabilize its products.

- Control of water movement within the mine waste-alluvium mixture to prevent the transport of oxidation products out of the mixture.
- Chemical stabilization of oxidation products both within and downstream of the soils mixture.
- Chemical stabilization, such as in situ neutralization, to retard the transport of oxidation products out of the tailings mixture.
- Interception of ground water that carries oxidation products from the mixture. The ground water could then be treated in-place by innovative technologies, such as constructed wetlands or engineered chemical treatments.
- Selective removal of oxidizing sulfide minerals.
- Pumping and treating ground water by conventional treatment processes.

For all options in which oxidation products are stabilized on site (i.e., hydrologic control, in situ stabilization, or groundwater interception), the possibility of catastrophic releases of metals must be evaluated. To the extent that metal releases are caused by erosion of tailings on the site, physical barriers can be designed.

The purpose of the interagency agreement (IAG) between the Environmental Protection Agency (EPA) and the U.S. Bureau of Mines (USBM) was to develop a treatment for fluvially deposited tailings that would be especially applicable to sites within the Coeur d’Alene Basin. In the initial phase of the project described in this Report of Investigations (RI), sites were examined for the significance of metal releases from fluvially deposited tailings. Within the practical considerations of the IAG, a site matched with an appropriate, highly rated remediation technology was selected with the consultation of Coeur d'Alene Restoration Project personnel and project constituencies. The nature of the waste material at a site chosen for initial remediation testing was characterized, and selected remediation options were evaluated.

SITE SELECTION

Sites containing significant amounts of fluvially deposited tailings in the Coeur d’Alene Basin have been described by Ioannou (1979), and additional sites have been identified by Federal agencies. Each site containing fluvially deposited tailings was visited to assess its hydrological setting. The extent and nature of metal migration into the surrounding surface and ground water were of primary interest. Metal release was inferred from surface water data for metals. Erosion of tailings by the force of flowing water is the primary mechanism causing physical migration. The tailings and other mine waste can also undergo chemical reactions that transform insoluble metals into a soluble form that can be transported by water into an aquifer or into adjacent streams.

Six sites were evaluated within the context of specific technologies. The Bureau of Land Management (BLM) nominated four sites that it controls: (1) the East Fork of Nine Mile Creek, (2) Nine Mile Creek at McCarthy, (3) the Woodland Park area on Canyon Creek , and (4) low-gradient areas in Highland Creek in the Pine Creek watershed. The U.S. Forest Service nominated (1) Tributary Creek below the Jack Waite Mine and (2) Moon Creek at the Silver Crescent millsite. No sites were nominated by private parties.

The geometry of the McCarthy site was found to present access problems for most types of on-site remediation techniques. Since the major sources of metals in Tributary Creek have been attributed to the adit and to seeps from the toes of tailings piles, rather than from fluvially deposited tailings (Gillette and Ralston, 1979), the Jack Waite mill and mine site were eliminated from consideration. Likewise, the USBM's recent investigation at the Silver Crescent millsite (Paulson, 1996) clearly indicates that the source of metal release is not from fluvially deposited tailings.

Because of the nature of the materials and their degree of connection with ground water, the three remaining sites were divided into two groups, depending on the connection between the waste and the aquifer. At Woodland Park, the ground water flowed through much of the mine waste (hydrologically connected), while at the East Fork of Nine Mile Creek and at Highland Creek, the mine wastes were perched above the water table. While sparse chemical data suggest that metals were released into the section of Highland Creek containing fluvially deposited tailings, the extent of metal releases from Highland Creek could not be confirmed because of the lack of flow data. The most promising research approach for Woodland Park appears to be some form of innovative in situ chemical or biological treatment to retard the oxidation of sulfide minerals or transport of the resultant oxidation products. However, such an extensive research and de- velopment program was beyond the scope of this IAG and would have been prematurely terminated with the initiation of remediation in the area in 1995. Therefore, an on-site treatment option for mine waste from the flood plain of the East Fork of Nine Mile Creek (the segment of the creek between the Success tailings and Dobson Pass Road) was selected for study. Most of the flood plain tailings in this stream segment probably originated from jig and flotation tailings located at three upstream mill sites. A small jig mill was also once present in the flood plain of this segment.

REMEDIATION SELECTION

The potential of a technology to reduce the amounts of dissolved metals released from sites containing fluvially deposited mine waste was the primary consideration for selecting a remediation technology. Size fractionation data and chemical analyses of a composite material collected from four sites in the flood plain of the East Fork of Nine Mile Creek are presented in figure 1 (the specific procedures are described in the sections on "Sampling" and "Analysis"). Sulfur (S), iron (Fe), and lead (Pb) were elevated in material smaller than 0.3 mm (less than 50 mesh). In contrast, Zn was depleted in the fine fraction. There are two probable causes for this depletion. The finer particles could have been flotation tailings, while the mid-sized particles could have been jig tailings. Because sphalerite (ZnS) is more efficiently removed during flotation milling, it was likely that, initially, fresh fine flotation tailings would have had lower Zn concentrations than coarser jig tailings. Alternatively, Zn concentrations may have been initially similar across the size spectrum. The higher specific area of irregular fine sphalerite may have caused its more rapid weathering. Because the oxidation products of sphalerite are soluble, Zn would have been washed away, causing the observed depletion in the finer fraction. The high Zn concentration in the larger fraction may be a result of low sampling numbers, commonly called the "nugget effect."

A process that removes the acid-generating, S-rich fines from the coarser material may decrease the net acid potential of the coarser fraction to low or negative (acid-neutralizing) values. If the sphalerite in the coarser fraction is removed from the acidic environment that is generated by the fine fraction, then the accelerated oxidation of sulfide minerals that occurs at low pH may be arrested. There are other physical properties that suggest that separation of fines from the coarser material may reduce Zn dissolution. Because of the presence of the coarser sands and gravels, oxygen diffusion through the mixed material is extensive. Oxygen diffusion through the material is critical because it enhances sulfide mineral dissolution. If the fines were separated and left at the site in a separate pile, the sum of Zn release from the three piles containing the fines, the sands, and the gravels may be much less than the Zn release from the mixed material. If the fines are placed in a separate pile with no additional treatment, the diffusion of oxygen will be inhibited because most of the pore spaces between particles will be occupied by water rather than air.

Because of the nature of the perched tailings material, selective removal of the mine tailings from the East Fork of Nine Mile Creek site was chosen as the option to test (figure 2). Size separation and/or removal of the fine fraction seemed to have a high probability of decreasing the rate of Zn release from the coarser fraction. The importance of

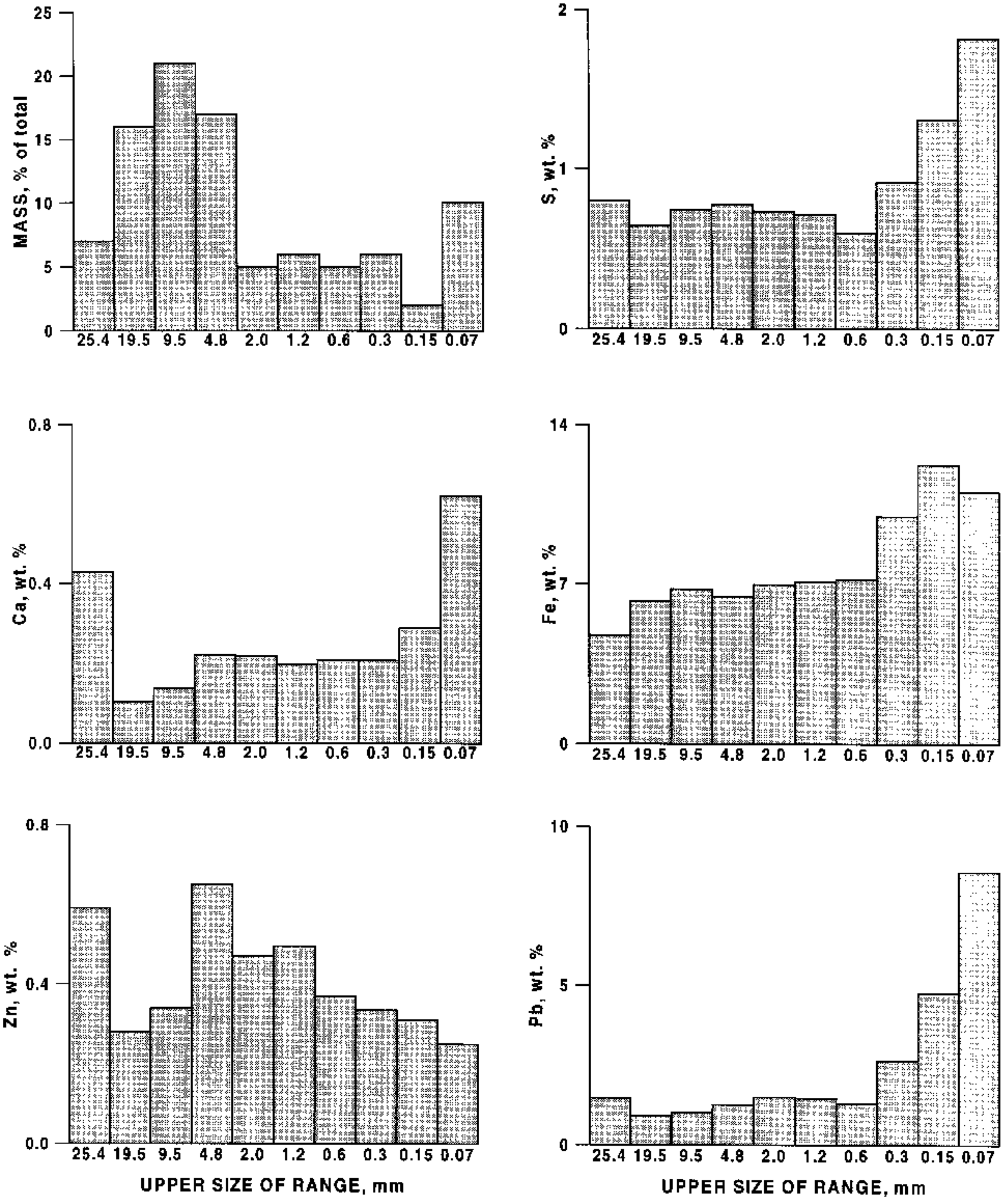

Figure 1.—Mass and elemental concentrations in 10 fractions of original composite material.

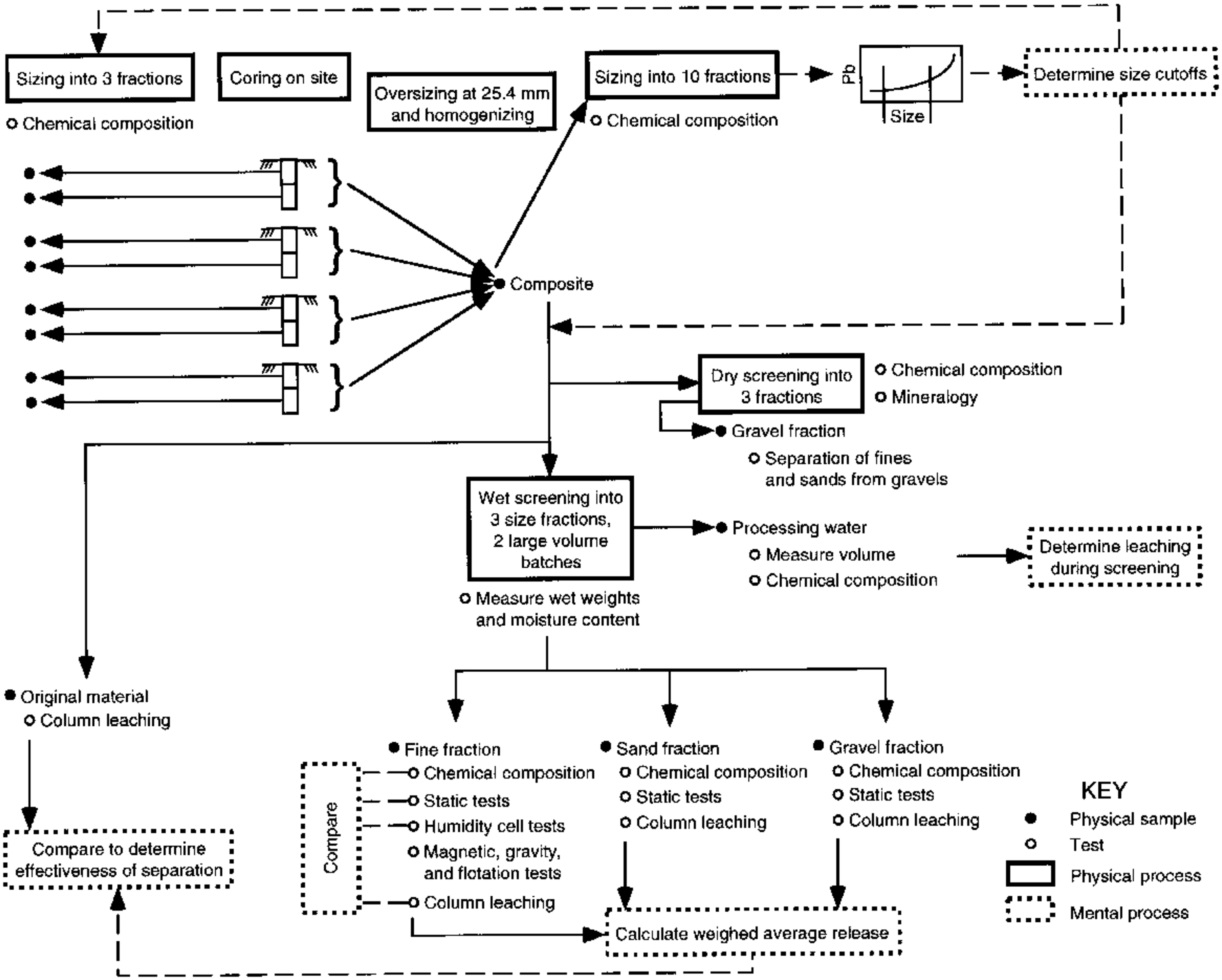

Figure 2.—Schematic of experiment.

segregating the highly reactive fine fraction has been identified as a controlling factor in experiments utilizing soil washing in which the less reactive, coarser material was left on site (EPA, 1989; Lauch and others, 1989; Masters and Rubin, 1991). The USBM has successfully treated metal-contaminated sediments at a nonmine site using mineral processing techniques designed for that specific site (Allen, 1994; Allen and Polls, 1993).

However, there are several factors that may make this approach unfavorable. The absence of fine particles in the pile containing the larger particles will make the pore spaces between the sands and gravels slightly larger and may result in a higher diffusion rate of oxygen. If these coarser fractions contain significant amounts of sulfide minerals, the release rate from these fractions may actually increase. Also, the pile containing the fine material will need to be engineered to control erosion because water from storms will not percolate through the fines very rapidly, which will lead to surface erosion of the fine fraction. If the initial chemical tests are encouraging, geotechnical engineering utilizing the gravels and sands could reduce the erosion of the fines in a full-scale operation. Preliminary slurry tests suggest that the use of water in the size fractionation processes (wet sieving and hydrocycloning) also results in dissolution of the oxidation products present on the original waste material. While this will lead to lower initial release rates once the material is placed back on the site, waste water from the separation process will probably have to be treated.

Previous literature (Stogran and Wagner, 1993) indicates that a variety of physical, biological, and chemical processes may be needed at mine-waste-contaminated sites to reduce metal concentrations to near-ambient concentrations. In selective removal processes, the metal release rate will de- crease as the bulk of the fractions containing easily releasable metals are removed by simple separation processes or are isolated from microenvironments that enhance release. As more and more material is removed (at higher and higher costs), decreases in Zn release will be less and less. The identification of the point of diminishing returns is a political decision. However, there are no scientific data on which to base a political decision at this time. The emphasis of this project was to determine the effects of each process on the Zn release *rate*, not Zn *concentrations* remaining in the material. Conditions of the physical separation methods were varied to optimize reduction in overall metal release.

Monitoring the effectiveness of decreasing Zn release is much more labor intensive and costly than simply measuring the remaining Zn concentrations. Therefore, serious thought must be given to the probability of detecting statistically different release rates relative to the control (i.e., no proc- essing). In any demonstration, a researcher is balancing control of the demonstration with establishing realistic environmental conditions. In laboratory static tests, such as slurry tests, the researcher has a large degree of control over environmental conditions, but may not be simulating a significant biogeochemical process at a site. At the other extreme, an on-site demonstration project of a fraction of the material (1 ton) more accurately simulates environmental conditions, but the researcher may not be able to control the conditions and statistically determine effectiveness. It is the opinion of the authors that monitoring the effectiveness of a demonstration at the site on the East Fork of Nine Mile Creek is not feasible. The magnitude of reduced loadings of Zn from a small reach in which an on-site demonstration would be performed would be completely masked by horizontal variations in release rate and interannual variations of high metal loads upstream. These conditions suggest that a demonstration having a significant amount of experimental control is necessary to assure that monitoring produces statistically valid results. Column leaching tests were chosen for the majority of tests because they offer sufficient experi- mental control while simulating many of the hydrological, chemical, and biological conditions found at the site over time. While column tests cannot be used to predict the absolute value of the release rate, this type of kinetic test can predict trends resulting from different remediation treatments.

Because of the time constraints on the proposed remediation project, humidity cell tests were also conducted to determine the kinetics of dissolution. Humidity cells accelerate the degree of weathering in column tests by a factor between 3 and 10. They can predict trends farther into the future than can column tests for a given test period. The data from the humidity cell tests provide additional assurances that decreased loads from the column tests are not temporary phenomena at the start of the experiment and will vanish with time. In this preliminary report, humidity cell tests for a duplicate sample of the fine fraction are compared to the results of the column tests.

Column leaching tests were used to simulate Zn releases under the following conditions:

1. The separation of fine particles (-0.3 mm), sands (2 to 0.3 mm), and gravels (+2 mm) and leaving all fractions on site.
2. The separation of fines and sands from the gravels and leaving only the gravels on site.
3. The separation and flotation of fines and removal of only the fine concentrate from the site.

This RI presents preliminary findings on the use of these mineral-processing techniques to reduce metal loads from material collected from the East Fork of Nine Mile Creek (figure 2). An attempt is made to relate the reactivity of the metals determined from column tests to the results of static tests. Such an overall approach to the physical separation of size classes could be incorporated into the proposed remediation plan in a manner that would reduce both dissolved and particulate metal loads. This technology will not only benefit the proposed remediation of the site, but will be extremely valuable nationwide by allowing the wise alloca- tion of resources for those stream segments where remediation funds are limited.

METHODS

This project was managed by USBM researchers at the Spokane Research Center (SRC) with assistance from USBM scientists at the Reno Research Center (RERC) and the Salt Lake City Research Center (SLRC). The collection of material from the site, preparation and analysis of the original composite material, separation of the large-volume wet-screened fractions, and the column leaching experiments were conducted by SRC personnel. The static and kinetic tests, and the separation experiments on the fine fraction were conducted by RERC. The static tests on the sand and gravel fractions were conducted by SLRC. The tests to separate the smaller material adhering to the gravel fraction were conducted jointly by SRC and SLRC.

Generally, different tasks were performed at each center. In some cases, standard procedures, such as determining elemental composition of solids, were performed at more than one center. Although different instruments and analytical methods were used at each center to determine each chemical constituent, quality control-quality assurance procedures give confidence that the results of analyses from the different types of tests used at the different centers can be compared. In cases where similar tasks were performed at different centers using dramatically different methods, these differences in procedure are noted and the implications discussed. For instance, the neutralization test for the fine fraction performed at RERC was conducted with an acid leachate, while the acidity tests for the gravel and sand fractions performed at SLRC were conducted with distilled water.

SAMPLING

A large amount (350 kg) of solid material was collected from four locations on BLM property between the Success Mine tailings pile and the intersection of the East Fork of Nine Mile Road and the Dobson Pass Road. Corer barrels (51 mm in diameter) were hammered into the waste material at each location to a depth of 0.5 m. The material around each corer (about 85 kg), from the surface to the bottom, was removed and placed in a drum. The core barrels were then removed, capped, and brought back to the laboratory. The core samples were analyzed to define the variability of solids characteristics at the site. Each core from the four sites was removed from the barrel and split into an upper section and a lower section.

The sample from the drum was split in half, and each half was screened for oversized material (+25 mm). The -25-mm material was homogenized in a Startac paddle mixer. The oversized material contained 5.4% of the mass of the sample and was not examined further in this project. The -25-mm material from the two halves was manually homogenized and placed back in the drum. This original composite material was the source of waste material for all laboratory experiments from this site. A subsample of the original composite material was dried and sized into 10 subfractions using conventional sieves. Based upon these results, size cutoffs of 2 mm (10 mesh) and 0.3 mm (50 mesh) were chosen for large-scale separation. The separation using these size cutoffs produced a gravel fraction [-25.4 +2 mm (-1 in +10 mesh)], a sand fraction [-2 +0.3 mm (-10 +50 mesh)], and a fine fraction [-0.3 mm (-50 mesh)].

The two sections from each of the four cores were individually dried and sized into three fractions using conventional sieves.

SEPARATION OF ORIGINAL COMPOSITE MATERIAL

The original composite material (-25.4 mm) was sized in two separate large-volume batches, each weighing approximately 100 kg. The -25.4-mm original composite material from each batch was wet screened through a 2-mm screen using the pressure from a peristaltic pump to rinse the smaller material off the larger gravels. The material passing the 2-mm screen (the sand and fine fractions) was then screened through a 0.3-mm screen to produce a sand fraction on the screen (-2 +0.3 mm) and a fine fraction (-0.3 mm) suspended in the wash water. The sand fraction was washed with clean tap water, and the wash water was added to the slurry containing the fines. The fine fraction from each batch was allowed to settle, and the water was siphoned off. The fine fraction from batch 1 was used for four flotation tests, while a combined sample of the fine fraction from both batches was used in a fifth flotation test as well as in gravity, magnetic, static, and kinetic tests. The three size fractions from each batch separation were measured for moisture content for evaluating mass balance and chemical composition. For each batch separation, all wash water was combined, weighed (approximately 100 kg), and sampled for elemental analysis after the solids had settled overnight. The amount of each element leached from the solids (milligram of element per kilogram of solid) was calculated from the concentration of the filtered processing water, the volume of processing water, and the dry weight of the starting material.

A portion of the original composite material was dried and sized into the three fractions in a vibrating percussion soil analyzer for mineralogical analyses. Another portion of the original composite material (-25.4 mm) was prepared for a test in which ways to minimize the retention of the fines and sands on the gravel fraction were investigated. This portion of the original composite material was not dried and had a 3% moisture content. To obtain the initial gravel fraction for this experiment, the original composite material was separated with a 2-mm screen attached to a Sweco vibrating screen without the use of water. The resulting 17.5 kg of semidry -25.4 +2-mm material was split into 16 aliquots ranging between 993 and 1,163 g.

ANALYSIS

Solids

Original Size Fractions

The elemental composition from (1) each of the 10 subfractions from the original composite material and (2) each of three fractions from the upper and lower sections from the four cores were determined. Each sample was dried, crushed, milled in a roll mill, pulverized, and dissolved in acids. A sample weighing 0.5 g was placed in a Savillex digestion vessel (part 568) and 6 mL of hydrochloric acid (HCl), 2 mL of nitric acid (HNO_3), and 2 mL of hydrofluoric acid (HF) were added. The vessel was heated for 2 min per sample in a microwave at 250 W and then cooled. Twenty milliliters of saturated boric acid was added, and the sample was diluted to a volume of 100 mL. The acid solution was analyzed by inductively coupled plasma (ICP) emission spectrometry in a manner similar to the analyses of chemical leachate liquids. Recovery of the Standard Reference Material MP1 (CANMET, Toronto, ON) were 91.5%, 98.6%, and 103% for Pb, Cu, and Zn, respectively.

Dried original composite material was sieved into gravel (-25 +2 mm), sand (-2 +0.3 mm), and fine (-0.3 mm) fractions and prepared for mineralogical analysis. Approximately 1 g of sample was mixed with epoxy resin and placed in a 25-mm Bakelite ring mold. The sample was then ground and polished to expose individual grains, and a thin conductive coating of gold was sputtered onto the sample to eliminate charge buildup in the scanning electron microscope (SEM). The composition, grain shape, and other characteristics of the sample were then examined in the SEM using back-scattered and secondary-electron imaging, energy x-ray dispersive analysis, and feature analysis.

For routine x-ray diffraction analyses, the samples were ground manually using a mortar and pestle to obtain a particle size of approximately 0.15 mm (100 mesh). The material was loaded into the manufacturer's standard holders, which contain 2-mm-thick aluminum plates with rectangular windows. A copper anode x-ray tube running at 40 kV and 30 mA was used to obtain the x-ray diffraction pattern. The International Center for Diffraction Data (ICDD) Powder Diffraction File was searched by computer to identify the possible minerals and compounds present in the sample. The resulting identifications were checked and verified by the analyst.

Energy-dispersive x-ray-fluorescence analyses were run on samples that had been ground to approximately 0.15 mm. The samples were pressed at 138,000 kPa to form pellets so that a thick, flat, smooth surface could be achieved to present to the x-ray beam. A dual rhodium-tungsten anode x-ray tube was used to excite the sample for spectra collection. A standardless fundamental parameters method was used to make a semiquantitative estimate of elements with atomic numbers greater than 10.

Wet-Screened Fractions from Separation of Original Composite Material

The subsamples of the sand and gravel fractions of the original composite material were analyzed for total metal content as described in the section on "Original Size Fractions." The fine fraction was analyzed both at SRC and RERC. A separate subsample was analyzed for total S and sulfate S. Total S was determined by ICP after acid dissolution. Sulfate S was determined by adding 1 g sodium carbonate (Na_2CO_3) to a 1-g sample. This mixture was then placed in a flask with 15 mL of concentrated hydrochloric acid and heated to boiling for 10 min. The carbon dioxide (CO_2) in solution from the Na_2CO_3 prevents the oxidation of hydrogen sulfide (H_2S), which is expelled. The solution was then analyzed for S by ICP. Sulfide S was calculated by difference and is the basis for the calculation of the acid potential in the acid-base accounting determinations.

Elements in Liquids

Static Tests (SLRC)

The major cations (calcium [Ca] and magnesium [Mg]) were analyzed by ICP (Jarell Ash 975) on wavelengths 317.9 and 279.5 nm, respectively. Aluminum (Al), manganese (Mn), and Fe concentrations were determined by ICP at 308.2, 257.6, and 259.9 nm, respectively. After every 16 samples, a standard was run and after every 8 samples, a quality control sample was run. If the results disagreed by more than 10%, the instrument was recalibrated and the samples were rerun.

K and Na were measured by flame atomic emission (Perkin Elmer 2100 or 5100) at 589 and 766.5 nm, respectively, with detection limits of 0.01 and 0.006 ppm, respectively. A quality control sample was run after every 20 samples in duplicate or triplicate. Spiked and blank samples were also run every 20 samples. Calibration verification was performed on one blank and one mid-range sample every 10 samples. If the control or the standard disagree by more than 10%, the last set of samples was rerun after recalibration.

Column Leaching Tests and Total Dissolution Solutions (SRC)

The major cations (sodium [Na], potassium [K], Ca, and Mg) were analyzed by ICP (Perkin Elmer Plasma II) on wavelengths 558.995, 589.593, 393.366, and 279.553 nm, respectively. Zn, Al, Mn, Fe, copper [Cu], cadmium [Cd], and Pb concentrations were determined by ICP at 213.860, 396.152, 257.610, 259.940, 324.754, 228.802, and 220.353 nm, respectively. Total S was determined at 180.731 nm. In all cases, a one-point calibration was performed, and a calibration blank containing 1% nitric acid was used. A calibration verification was performed after each calibration. A drift check was run after each group of 15 samples. Recalibration was performed and all samples in a group were reanalyzed any time the check samples for a group varied by more than 5% from the expected value. The relative standard deviation of the major element analyses was excellent, usually being below 0.1%.

Humidity Cell Tests and Total Dissolution Solutions (RERC)

Liquid solutions were analyzed for total metals and S concentrations on an ARL Q137 ICP (modified with an Interface Design analog to a digital converter) at the above wavelengths. One-point calibrations were performed in conjunction with a 2% nitric acid calibration blank. Total S concentrations were converted to sulfate concentrations using the 1:3 stoichiometry.

Anions in Liquids

Anion analyses were performed with a Dionex ion chromatograph (IC) using an ES4A column and a detector based on conductivity suppression. Sulfate calibration was performed with 3, 9, 30, 50, 60, and 100 ppm standard solutions. After every 10 samples, a standard was run. The previous set of 10 samples was rerun if the results of the standard differed by more than 5%.

STATIC TESTS

Two types of static tests were performed: (1) neutralization potential of the fine fraction and (2) acid generated by the sand and gravel fractions. The amount of acid generated from solids was also used as the criterion to judge the success of the test, as described in the section entitled "Separation of Fines and Sands from Gravels.

Static Tests with Fines

The neutralization potential was determined by treating a sample with excess standardized hydrochloric acid at 25 to 30 °C for 24 h (Sobek and others, 1978). A fizz test was employed to provide a guide for the initial amount of acid to be added to the test. Acid was added as required during the acid treatment to maintain sufficient acidity to generate the neutralization reaction. After treatment, the unconsumed acid was titrated with a standardized base to pH 8.3 to allow calculation of the acid consumed (as calcium carbonate [$CaCO_3$] equivalents).

Static Tests with Gravels and Sands

Five splits of the sand fraction, each approximately 20 g, were added to separate beakers. To each of three samples, 2.5 mL of cold, deionized, distilled water per gram of sample was added and put on an orbital shaker at 150 rpm for 20 min, 2 h, and over the weekend. After the designated time, each slurry was filtered through a Whatman glass fiber filter, and the filtrate was titrated using an automatic titrator (Mettler DK11 and DV103). The effluent was analyzed for metals by ICP and sulfate by IC as described above. Water heated to just below boiling (~85 °C at the elevation of Salt Lake City, UT) was added to two samples at a liquid-to-solids ratio of 2.5 L/kg. After being shaken for 20 min and 2 h, the slurries were cooled and processed in the same manner as those samples to which cold water was added.

The equation used to determine the acidity of the bottle roll effluent (N_A = normal) is as follows:

$$N_{A} = (N_B \times V_B)/\text{sample volume}, \qquad (1)$$

where N_B = normality of base used, V_B = volume (in milliliters) of base used, and amount of sample volume titrated is in milliliters.

The acidity (milligrams $CaCO_3$ per kilogram of solids) was calculated from N_A and the liquid-to-solids ratio in the static bottle roll tests (2.5 L/kg of sample) was as follows:

$$\text{mg } CaCO_3\text{/kg of sample} = 50{,}040 \text{ mg } CaCO_3\text{/equil} \times N_A \times 2.5 \text{ L/kg of sample.}$$

Acidity represents cations present in the leachate that are hydrolyzed when the pH is increased to 8.3 (i.e., H^+, Al^{3+}, Fe^{3+}, Fe^{2+}, Mn^{2+}, and Zn^{2+}).

A 2-h, cold-water static test was also used to characterize the release of metals from the wet-screened gravel fraction of the original composite material in the manner described above (for rationale, see the section on “Static Tests”). In addition, cold-water static tests were used to test the success of the methods for separating the smaller material from the gravels. In these tests, approximately 170 g of gravels processed by wet and dry methods were mixed with 425 mL of cold, deionized, distilled water in high-density polyethylene (HDPE) bottles and placed on a roller for 2 h before being processed as described for the static tests on the sand fraction.

KINETIC TESTS

Column Leaching Tests

Three subsamples, each containing 7 kg of the original composite material (-25.4 mm), were loaded into individual 102-mm-diam columns supported by a Buchner-like funnel containing filter paper. Three 7-kg subsamples of the wet-screened gravel (-25.4 +2 mm) were loaded into three similar 102-mm-diam columns. Three 5.5-kg subsamples of the sand (-2 +0.3 mm) were also loaded into columns. Because of the limited amount of fine material, only one column containing 7 kg of the fine material (-0.3 mm) was prepared. In addition, a half column was prepared by loading 3.5 kg of fine material into the 102-mm-diam column. However, this column clogged, and water added to the column collected above the fines during many leaching cycles. Although the results from this column are reported, they will not be used in the mass balance comparisons that follow.

One-hundred-milliliter aliquots of artificial rain water were added to each column in a manner than would provide a wet and a dry period each 4 months while still maintaining the annual rainfall of 94 cm found throughout much of the Coeur d'Alene Basin. The first wet-dry cycle consisted of 21 leach- ings, with leachings 1 through 14 being the wet period in which leachant was generally added every 2 or 3 days. During a simulated rain-on-snow event (leachings 9 through 11), twice the volume of leachant was added every other day. Leachings 15 through 19 simulated a dry period with a simulated summer thunderstorm (leachings 16, 17, and 18) occurring in the middle of the dry period. Leachings

22 through 42 constituted the second wet-dry cycle with rain-on-snow events simulated by leachings 28 through 30 and a summer thunderstorm simulated by leachings 35, 36, and 37. The leachate from each addition was allowed to flow down through the column of material by gravity and was collected in an open 1-L, acid-cleaned, HDPE bottle. These columns were designed to simulate the chemistry of leachate from an unconfined surface pile of waste material flowing into an aquifer. Since any ferrous Fe in the leachate would be oxidized in the open bottles, these column tests best simulate leachate flowing into an oxygenated aquifer.

The leachate that drained from each aliquot addition was processed before the next aliquot was added or within 4 days, whichever came first. The collection bottle was not cleaned between leachate collection from subsequent aliquot additions. For each leachate, an aliquot was taken, and pH was measured using a Ross combination electrode attached to an Orion EA 940 meter that had been calibrated with pH 4 and pH 7 buffers. The remaining sample was filtered through an acid-cleaned, 0.4-µm, 47-mm polycarbonate Nuclepore filter held in an acid-cleaned Nalgene polysulfone filter holder. One fraction for ICP analysis was transferred to an acid-cleaned, 60-mL HDPE bottle to which Fisher Trace-Metal Grade nitric acid was added to achieve 0.1 *M*. An additional aliquot was transferred to a 30-mL HDPE bottle and submitted for IC analysis.

Humidity Cell Tests

Two humidity cells were loaded with 300 g of the sample fines (-0.3 mm), separated during large-volume wet screening of the original composite material. This sample size was chosen to obtain a bed depth of 40 mm in each cell, which allowed the sample to be flooded during leaching without overflowing the air lines. The cell and the sample were weighed at the start of the test, at the end of each leaching step, after the dry-air portion of each cycle, and after the wet-air portion of each cycle. The first cycle consisted of 1 day of leaching followed by 3 days of dry air, with the goal of removing soluble sulfate minerals from the samples. The entire apparatus was contained in a constant-temperature chamber.

All subsequent cycles were 7 days long using a pattern of 1 day of leaching, 3 days of purging with dry air, and 3 days of purging with wet air. The leaching cycle was conducted by weighing the required quantity of leachant for each cell into individual wash bottles that could be emptied by squeezing. The leachant was introduced into each cell through the gas dispersion tube. The effluent was collected in a wide-mouth Erlenmeyer flask vented to the atmosphere. The volume and element concentrations of each effluent were determined. Electrical conductivity (EC) and oxidation-reduction potential (ORP) were determined by standard methods (Skougstad and others, 1979). The acid generated during the tests was monitored using three separate techniques: pH measurement, titration, and sulfate concentration.

SEPARATION TESTS

Two types of separation experiments were performed. In the first set, different wet and dry mineral-processing techniques were used to maximize the amount of fine material removed from the gravel fraction. In the second set of tests, gravity, magnetic, and flotation separation methods were tested to maximize the removal of metals from the fine fraction.

Separation of Fines and Sands from Gravels

This experiment was designed to determine the treatment that minimized the initial release of metals from the gravel fraction after fine and sand fractions had been removed. The relationship between the amount of metal released from the treated gravels and the amount of fines and sands remaining on the gravels was also examined. A subsample of the original composite material (-25.4 mm) was initially dry screened to produce 16 aliquots weighing between 993 and 1,164 g. One aliquot (GS1) did not undergo any additional processing after it was split (table 1). Since a significant amount of dust was generated during splitting of the dry-screened gravel, another aliquot (GS2) was placed on a 1-mm screen within a vibrating, percussion, grain-size analyzer (Ro-Tap) for 15 min.

In two experiments, aliquots GS5 and GS6 were not initially screened prior to mineral processing. Aliquot GS5 was tumbled (autogenous milling) for 15 min. Aliquot GS6 was milled with eight No. 55-size balls (diameter = 2.5 cm) for 50 min. After each treatment, the gravel was poured onto a 1-mm screen, and any dust in the interior of the milling apparatus was brushed onto screen. The screen apparatus was then placed in the Ro-Tap analyzer for 15 min. The -1-mm material collected at the end of these experiments included both the amount of dust adhering loosely to the gravels and the amount generated during processing.

Three experiments utilized the Sweco vibrating 1-mm screen. The gravels were washed with pressurized tap water, which was collected in the underflow along with the -1-mm material washed off the gravel surfaces. The gravel aliquots used as starting material had already been dry screened to remove any loose dust. In the first wet experiment, aliquot GS3 was simply wet screened. Analogous to the experiment of dry screening after tumbling (aliquot GS5), aliquot GS7 was tumbled for 15 min and then wet screened. Analogous to the dry screening after milling (aliquot GS6), aliquot GS8 was

Table 1.–Procedures used to test separation of fines and sands from gravels

Experiment number	Treatment	Procedure			
		Initial Ro-Tap	SWECO	Final Ro-Tap	Wet-screened material
		DRY TREATMENTS			
GS1	Split only[1]				
GS2	Ro-Tap	X-F			
GS5	Tumble, 15 min			F	
GS6	Mill, 60 min			F	
		WET TREATMENTS WITH TAP WATER			
GS3	Wet sieve	X	X-F		
GS7	Tumble, 15 min; wet sieve	X	X-F		
GS8	Mill, 50 min; wet sieve	X	X-F		
		WET TREATMENTS WITH DISTILLED WATER			
GS16	Impeller, 1 min	X			F
GS15	Impeller, 5 min	X			F
GS13	Bottle roll, 120 min	X			F

X Procedure used as treatment.
F Method to determine fines after treatment.
X-F Procedure used as treatment and also method of determining fines after treatment.
[1] Control sample, no separation.

milled with balls for 50 min and then wet screened. In each experiment, the pH of the underflow was measured, and a sample was filtered through a 47-mm, 0.4-µm pore size, Nuclepore polycarbonate filter and collected for cation and anion analyses. The amount of fines generated during the treatment was determined by filtering the remaining underflow onto paper filters and reweighing both filters after drying.

In two experiments, two aliquots (GS16 and GS15) were placed in 2 L of distilled water in separate buckets and mixed continuously with an impeller mixer for 1 min and for 5 min, respectively. The liquid from each bucket was decanted separately, and some of the decant water was used to transfer the respective material out of the buckets. The wet solids from each experiment were then screened through a 1-mm screen. It appeared that the film of water on the surfaces of the gravels was as turbid as the decant water. All decant water from each separate experiment was combined, and the pH was measured. Cations, anions, and the amount of fines recovered were determined in a manner similar to experiments with aliquots GS7 and GS8.

In the last experiment, 166 g of aliquot GS13 was placed in a 1-L bottle with 414 mL of water. The bottle was rolled for 2 h and the liquid decanted. The solids were then rinsed with a small amount of distilled water. The decant was filtered for metal and anion analyses, and the mass of fines on three Nuclepore filters was determined by weighing after drying. This first bottle roll was considered the treatment.

In this set of experiments, the initial release of metals from the treated gravels was emphasized. It is assumed that the initial metal release was generated from soluble metal salts that had precipitated on the surfaces of the gravels or from sands and fines physically adhering to the gravels, rather than from reactions with the rock matrix itself. Static bottle roll tests were used to indicate the success of the treatment in removing the soluble salts. The treated dry gravels (aliquots GS1, GS2, GS5, and GS6) or the treated wet gravels (aliquots GS3, GS7, GS8, GS15, and GS16) were then each split into five subfractions. One of these five subfractions was then rolled in a bottle with 2.5 L of cold, distilled water per kilogram of solid for 2 h. All the wet material from the bottle roll treatment (aliquot GS13) was subjected to a second bottle roll test. The decant was filtered and analyzed for neutralization potential, anions, and metals. The solids recovered during the static bottle roll tests were also measured in most experiments.

Separation of Metals in Fine Fraction

Gravity Separation Test

A 250-g subsample of the fine fraction produced from both batches of the large-scale, wet-screened original composite material was separated on a Vanner gravity separator with the table calibrated with a tilt between 1.0° and 2.5°.

Magnetic Separation Test

A 104.6-g subsample of the fine fraction from both batches of the large-scale, wet-separation was placed in a 600-mL beaker with 500 mL of water processed through a reverse osmosis cartridge. Anionic surfactant 7 was added to the slurry and stirred for 5 min. The slurry was then fed to a Davis wet magnetic separator in stages.

Flotation Tests

Four flotation tests were conducted on representative portions of the fine fraction from the wet screening. A combination of xanthates, promoters, and frothers was added in stages. Flotation times varied from 20 to 30 min. These tests were conducted without grinding, and 5 min of attrition was necessary to break the agglomeration of particles before the material was conditioned with flotation reagents. One test was conducted at an unaltered pH of 4 (flotation test [FS] 1). In the three other tests, the pH was adjusted to 9 using Na_2CO_3 (FS2) and sodium hydroxide (NaOH) (FS3 and FS4).

In experiments FS4 and FS5, a three-step flotation scheme resulted in a rougher concentrate, two scavenger concentrates, and tailings. A mixture of fine material produced from the large-scale, wet screening of both batches of original composite material was used in FS5.

GEOCHEMICAL MODELING

The solubilities of several mineral phases were examined using the geochemical speciation and solubility model PHREEQE (Parkhurst and others, 1980). The solubilities of silica (SiO_2) and anglesite ($PbSO_4$) in the column leachate from all the fractions and the solubility of ferric Fe minerals in the leachate from the fines were examined. The leachates from one of the replicate columns containing the four different size fractions were subjected to geochemical modeling for the first wet-dry cycle. The processing wash water from the separation experiments with the gravels were examined for Zn and Pb solubility, while the static bottle roll tests were analyzed only to evaluate anglesite solubility. The thermodynamic constants for the major elements from the PHREEQE database were accepted. The stability and solubility constants for Cu, Zn, Cd, and Pb from Paulson (1996) were amended to the database.

The ORP of leachates from the column leaching and static bottle roll tests was not measured, and it was assumed that ORP was dependent upon pH according to the O_2:H_2O equilibrium. The ORP of leachate from the fines was assumed to be the same as the ORP of the leachate from the humidity cells containing the same fine fraction. If the model for a column leachate did not converge, Fe was removed from the model and the model was rerun. Because alkalinity was not measured, alkalinity for the processing wash water in which tap water had been used was estimated by balancing the charge. The liquids from the static bottle roll tests were examined for anglesite solubility by setting the pH to 4.

RESULTS

ORIGINAL COMPOSITE MATERIAL

The chemical analyses of 10 subfractions from the original composite material, sized by dry screening, suggested changes in mineral and chemical characteristics at 2 and 0.3 mm (figure 1). Such changes in chemical characteristics suggest possible changes in metal release. Therefore, the four coarsest of these 10 subfractions become the gravel fraction. Likewise, the three finest subfractions become the fine fraction, and the three middle-sized subfractions became the sand fraction.

The concentrations of many of the more reactive major elements (i.e., Ca, Fe, S) in the fine fraction were 50% to 100% higher than the concentrations found in the sand and gravel fractions (figure 1 and table 2). Elements associated with gangue minerals (i.e., Na, K, and Al) and Mn showed less tendency to be concentrated in the fine fraction (table 2). In contrast, Pb concentrations (9 wt %) in the smallest subfraction (-0.07 mm) were almost 10 times the Pb concentrations of the gravel and sand subfractions (figure 1). When the three finest subfractions were averaged, Pb concentrations in the fine fraction (5 to 6 wt %) used in the static and kinetic experiments were five times the Pb concentrations of the sand and gravel fractions (~1 wt %).

Cu concentrations in the fine fraction were also higher than concentrations in the sand and gravel fractions. Zn and Cd exhibited a pattern different from those of Cu and Pb. Zn concentrations in the sand fraction averaged about 0.55 wt %. Zn concentrations below 0.6 mm decreased with decreasing size to a value of about 0.3 wt % for particles less than 0.07 mm. Zn was also enriched in the coarsest fraction. It is unclear whether the Zn exhibited two maximums in concentration or was affected by the small number of individual rocks sampled in the coarsest fraction. Cd concentrations in the sand and gravel fractions were between 0.002 and 0.003 wt % while Cd concentrations in the fine fraction were less than the detection limit of the analytical method (0.001 wt %). The original composite material consisted of 61% gravel (-25.4 +2 mm), 15% sand (2 -0.3 mm), and 24% fines (-0.3 mm).

The gangue minerals of the three fractions were mostly quartz, with decreasing amounts of orthoclase feldspar, chlorite, and muscovite-like mica. X-ray diffraction patterns for galena (PbS), sphalerite, and possibly magnetite (Fe_3O_4) were identified in the gravel fraction, and patterns for anglesite, galena, sphalerite, and possibly hematite (Fe_2O_3) and massicot (PbO) were identified in the sand fraction. In the sand fraction, SEM analysis detected galena as discreet grains around the perimeter of large gangue minerals. Galena was also found as veinlets in fractured quartz grains. No pyrite was observed in the sand samples studied, but the cubic grain structure of hematite suggests it was present as a pyrite oxidation product.

Table 2.—Elemental analyses of gravel, sand, and fine fractions of original composite material, and weighted average of bulk composite sample, weight percent

	Na	K	Ca	Mg	Al	Fe	Mn	Cu	Zn	Cd	Pb	S
WEIGHTED AVERAGE OF ORIGINAL COMPOSITE MATERIAL (-25.4 mm)												
Dry—from 10 fractions	0.47	2.4	0.24	0.31	ND	7.3	0.33	0.031	0.41	0.0020	2.11	0.86
Dry—from 3 fractions	ND	2.5	0.25	0.34	5.2	7.5	0.42	0.013	0.36	0.0018	1.44	0.68
Wet screened—from 3 fractions	ND	2.1	0.25	0.34	5.4	8.4	0.39	0.017	0.38	ND	1.97	0.83
GRAVELS (-25.4 +0.2 mm)												
Dry—weighted average from 4 fractions	0.37	2.4	0.19	0.30	ND	6.3	0.32	0.02	0.44	0.003	1.09	0.7
Dry	ND	2.7	0.18	0.35	5.0	6.4	0.44	0.01	0.36	0.002	0.67	0.5
Wet screened (batch 1)	ND	2.6	0.18	0.32	5.4	6.9	0.36	0.01	0.35	0.002	0.97	0.7
SANDS (-2 +0.3 mm)												
Dry—weighted average from 3 fractions	0.70	2.8	0.21	0.26	ND	7.1	0.34	0.05	0.45	0.002	1.41	0.7
Dry	ND	2.3	0.32	0.28	5.0	8.2	0.35	0.01	0.61	0.003	1.26	0.8
Wet screened (batch 1)	ND	3.1	0.33	0.32	5.4	7.7	0.32	0.01	0.52	0.003	1.29	0.7
FINES (-0.3 mm)												
Dry—weighted average from 3 fractions	0.59	2.0	0.45	0.41	ND	10.8	0.36	0.04	0.29	<0.001	6.2	1.5
Dry	ND	1.7	0.49	0.38	5.4	12.8	0.39	0.03	0.36	<0.001	5.4	1.5
Wet screened (batch 1, SRC)	ND	2.0	0.34	0.39	5.4	12.8	0.42	0.04	0.33	<0.001	5.0	1.2
Wet screened (batch 1, RERC)	0.80	ND	0.31	0.40	5.1	11.5	0.35	0.03	0.29	ND	5.1	1.1
Wet screened (batch 1 and 2, SRC)	0.71	ND	0.31	0.40	4.9	10.5	0.34	0.03	0.28	ND	5.0	[1]1.2

ND Not determined.

[1] $S^{=}$ = 0.22 wt%.

Sphalerite was observed as large-sized grains. The trace components of the fine fraction detected by x-ray defraction included magnetite, hematite, massicot, and galena. Galena was observed by SEM as individual grains associated with limonite and the pyrite with limonite and/or hematite. Sphalerite was observed as individual particles. Zn was also associated with an unidentified Fe-Al oxide.

CORE SAMPLES FROM SPECIFIC LOCATIONS

The elemental composition of samples taken from individual sites was examined to determine variability of metal concentrations in the three size fractions among sites and with depth. Such variability must be considered when devising a system to treat material having a mixed composition. Exact sample location no longer has any significance because the area has been excavated. The samples were renumbered for this RI, with sample 1 being from the most upgradient position within the reach. In three upgradient locations, only minor differences were found between the fractionation of mass in the upper and lower halves of the cores. There seemed to be a gradation toward finer material with distance downstream. The percent- age of gravel decreased from 68% at the location most upstream to 43% at the location farthest downstream. In contrast, the percentage of sands increased from 25% at the most upgradient location to 52% at the most downgradient location.

In general, the elements associated with the gangue material (Na, K, and Al) did not vary greatly among sites, with depth, or as a function of size fraction (not shown). Elements associated with sulfide minerals showed much greater variations. In samples 1 and 3, Fe and S increased with decreasing size and did not vary with depth (figure 3). Both S and Fe were low in sample 4. Sample 2 exhibited little variation in S with size, but there was a two-fold increase with depth, with S concentrations of 1.6 wt % in the lower section of sample 2. Fe in the lower section of sample 2 followed the general trend of higher concentrations in finer material. The highest Zn concentrations were found in the lower section of sample 2, but no differences were seen among the different size fractions. Upon revisiting the site prior to excavation, we found that the core barrel at this location had bored through a large piece of wood half way down the core. Perhaps this piece of wood had acted as a barrier to downward water movement and may have precluded any oxidation products from being washed away. In most of the other samples, a maximum in Zn was observed in the sand-sized material (-2 +0.3 mm). Pb concentrations in the -0.3-mm material were dramatically greater than in the coarser material of samples 1 and 3. Pb concentrations in sample 4 were low in general.

The variability of the mineral and chemical characteristics of the material being processed can have an effect on the overall performance of the treatment process. Whatever the reasons for these metal distributions, it seems likely that the Zn and S concentrations in the lower section of sample 2 skewed the composition of the original composite material used in the following tests.

STATIC TESTS

The gravel and sand fractions were subjected to a 2-h leaching test with cold distilled water. The leachate was tested for both metals and sulfate, as well as for the acidity of the leachate (table 3). More metals were leached from the sand fraction than from the gravel fraction, except for Al and Pb. The sand fraction was also subjected to four other leaching treatments using cold and hot distilled water for varying contact times. In general, increasing the contact time increased the amount of constituents leached. However, less Mn, Cu, Zn, Pb, and $SO_4^{=}$ were released when contact with cold water was increased from 2 h to 2 days. When results of the cold water leachings are compared to the hot water leachings, no consistent differences were observed for the major cations (K, Ca, and Mg), Al, and Mn. Only small differences were observed for Cu, Zn, and $SO_4^{=}$. The hot water leachings at both contact times leached considerably more Pb, Fe, and Si than the cold water leachings. Because the release of Si may indicate an attack on lattice minerals, hot water leaching was not chosen for further use. Because the 2-day cold water leaching seemed to leach less constituents of interest (Zn, Cu, Pb, and $SO_4^{=}$) and more Si than did the 2-h cold treatment, the 2-h cold water leaching was chosen as the test to determine the efficiency of the separation of fines and sands from gravels.

The release of acidity was examined in all three fractions using different methods. The gravel and sand fractions were subjected to a distilled water leaching test, after which the leachate was titrated with base to pH 8.3 to provide an estimate of the acidity released from their surfaces. The fine fraction was subjected to acid treatment, and the leachate was then titrated. The amount of acid originally added to the test solution was subtracted from the amount of base titrated into the leachate at the end of the test to determine the amount of acid added or consumed by the fines (neutralization potential or NP). The acid treatment of the fines is considered a harsher treatment than the distilled water treatment used for the gravels and sands and is thought to dissolve more acid-consuming minerals in the rock matrix.

During these short treatments, all three fractions released acid rather than consuming acid through neutralization by basic minerals. The sand and gravel fractions released considerable amounts of acidity (table 3), probably through the dissolution of Fe and Al hydroxy sulfates (Nordstrom, 1982) present on mineral surfaces. For the aged fines studied, the harsher acid treatment during the determination of NP reflects both the acid produced from surface precipitates and the base generated by dissolution of basic minerals in the rock matrix. Therefore, the dissolution of the basic minerals dramatically lowers the acidity produced by the fines (observed as a negative NP) when compared to the method used for the sands and gravels, which

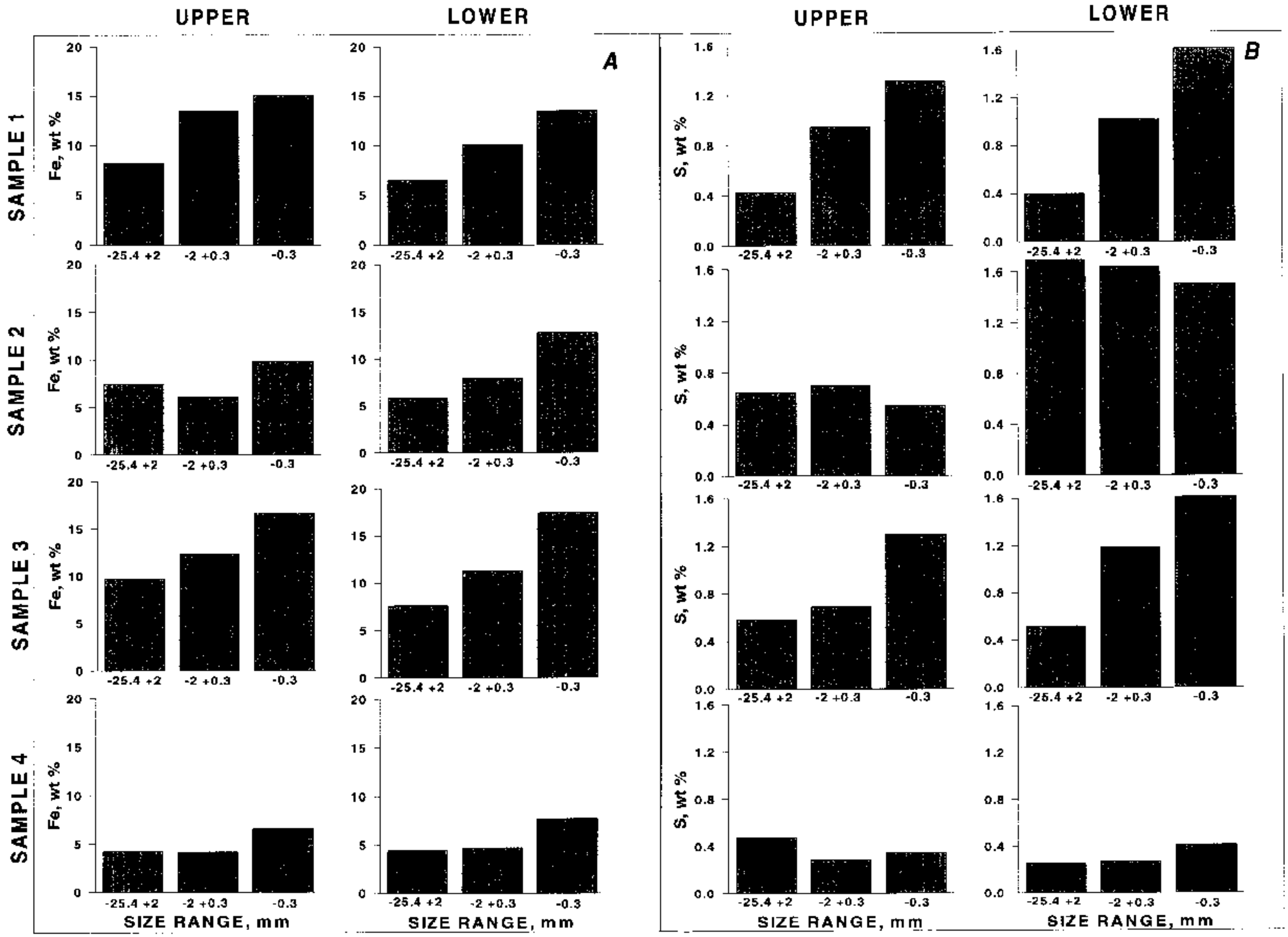

Figure 3.—Size fractionation of elements in upper and lower sections of four cores. *A*, Fe; *B*, S.

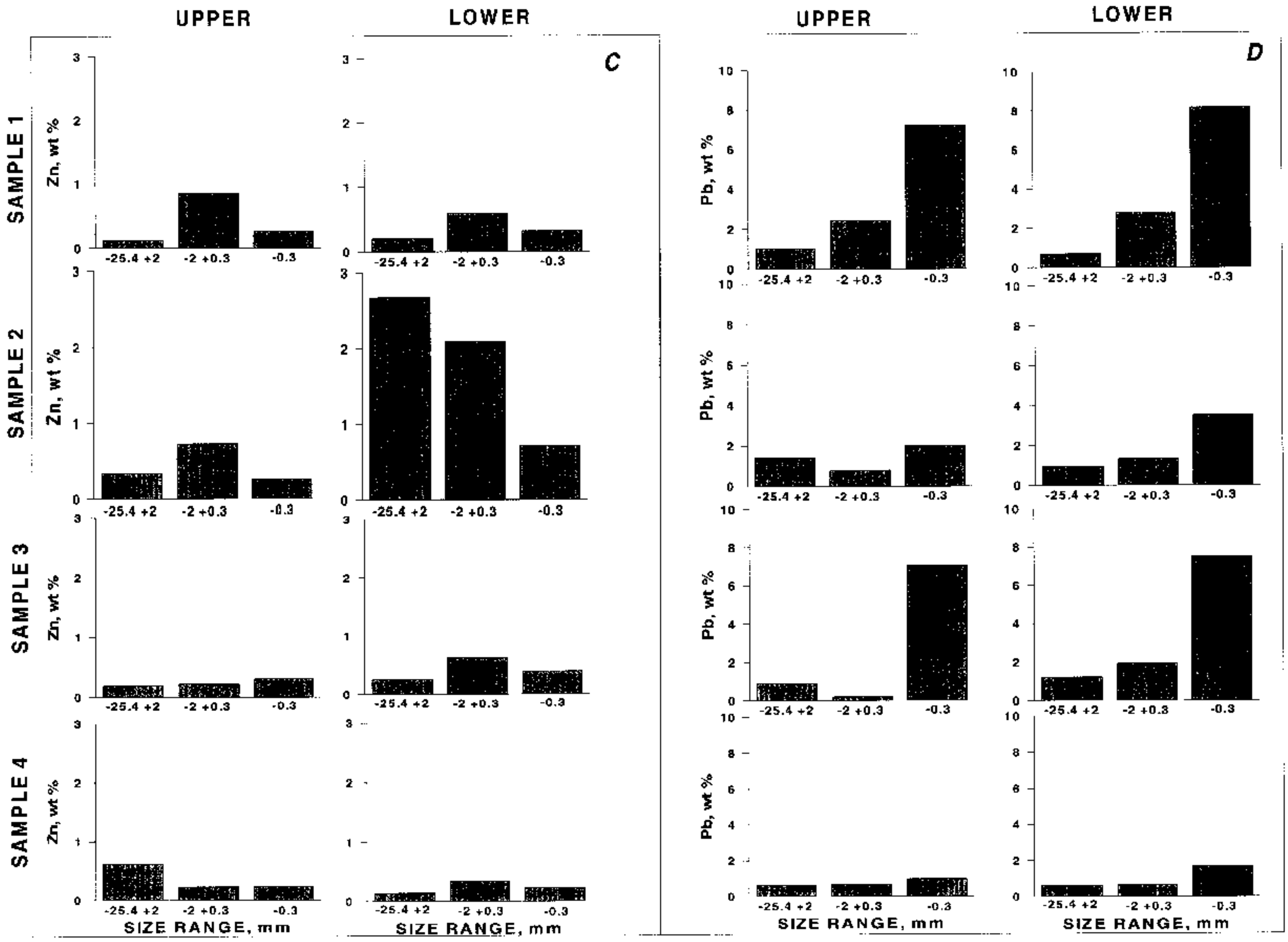

Figure 3 (continued).—Size fractionation of elements in upper and lower sections of four cores. *C*, Zn; *D*, Pb.

Table 3.—Results of static tests for gravel and sand fractions, milligrams of element per kilogram of solid

Treatment	Element											SO_4	Acidity,[1-2] mg $CaCO_3$/kg
	Na	K	Ca	Mg	Al	Fe	Mn	Cu	Zn	Pb	Si		
GRAVELS (-25.4 +2 mm)													
Cold, 2 h	2.2	2.2	10	2.5	1.6	0.75	7.5	0.22	30	23	12.5	131	240
SANDS (-2 +0.3 mm)													
Cold, 20 min	ND	24	29	3.5	<0.9	0.3	12	0.6	43	12.3	<2.5	175	163
Cold, 2 h	ND	21	30	4.7	1.1	2.1	15	0.5	47	18.7	4.3	209	195
Cold, 2 day	ND	35	23	7.3	<0.9	6.3	11	0.2	25	17.0	35	179	300
Hot, 20 min	ND	16	23	2.8	<0.9	0.7	11	0.3	39	24.5	13	185	253
Hot, 2 h	ND	29	30	4.3	<0.9	4.5	15	1.0	44	28	43	235	280

[1] 20 min cold treatment on gravels yielded acidity of 205 mg $CaCO_3$/kg.

[2] 20 min hot treatment on gravels yielded acidity of 290 mg $CaCO_3$/kg.

ND Not determined.

does not include rock matrix dissolution. When the acid potentially available (AP) from the oxidation of sulfide S in the fines is included (tables 2 and 4), the net neutralization potential (NNP) of the fine fraction is even more negative. These measurements suggest that all three fractions contain easily dissolvable, acid-generating, secondary minerals that have persisted, even after being subjected to the original wet-screening separation process.

Table 4.—Results of static tests for fine fraction, milligrams of $CaCo_3$ per kilogram

$S^=$, wt%	AP	NP	NP/AP	NNP
0.22	6.88	−6.66	0.97	−13.53
0.22	6.88	−6.81	0.99	−13.69
0.22	6.88	−6.55	0.95	−13.42

AP Acid potential.
NP Neutralization potential.
NNP Net neutralization potenital (NP - AP).

KINETIC TESTS

Column Leaching Tests

Triplicate 7-kg samples of the original composite material and the gravel fraction, and triplicate 5.5-kg samples of the sand fraction were packed into nine columns. Because of sample limitation, only one full-height column and one half-height column containing the fine fraction were packed (tables 5 through 15). Columns were leached for 259 days with artificial rain water through 42 leachings that included two wet-dry cycles, each simulating a wet period (with a rain-on-snow event) and a dry period interrupted by a summer thunderstorm. The half-height column of fines (designated F1) clogged, resulting in ponding of leachant. Therefore, this column is disregarded in all future discussions.

Based on the mass contribution of each of the three fractions, weighted-average leachate concentrations were calculated for each element. In the absence of any change in the interaction between hydrology and geochemistry, these weighted-average values are the concentrations of leachate that would be expected if one volume of waste material (unit height times surface area) was segregated. Three piles of unit height would be generated so that their areas would be proportional to their mass contributions in the original composite material. By comparing weighted-average values to the concentrations of columns containing original composite material, the effect on metal release rate from only the segregation process could be ascertained. The weighted-average values would simulate a treatment process in which all solid material was left on site.

The average water balances for the three sets of triplicate columns and for the fines column are shown in figure 4. Retention of water by the test material and evaporation resulted in water recoveries less than the volume added. Over 350 mL was retained by the columns containing the semidry original composite material before any water was recovered. Occasionally during the wet cycles, there was carryover from previous leaching cycles, resulting in water recovery greater than the amount added. For the three fractions segregated by wet screening, 0.06, 0.1, and 0.55 L were initially drained from the gravel, sand, and fine columns, respectively, after the fractions had been packed into the columns.

After the columns were initially drained, the pH of the segregated columns was about 4 (figure 5*A*). The pH of the leachate from the sand columns remained between 3.8 and 4.0 throughout most of the first wet-dry cycle and the second wet cycle except for the first leaching in the dry period (leaching 16) in which column S1 had a pH of 2.89 (table 11). During the second dry period, the average pH in the sand columns decreased to 3.4. The leachate from the gravel column decreased to about pH 3.5 and remained at that level throughout the entire experiment. In contrast, the pH of the leachate from the column containing fines decreased to about 2.7 during the first wet period and increased after each dry cycle. When water was recovered from the columns containing the original composite material (fourth leaching), the pH of the leachate was about 3.3 and remained fairly constant. After 50 days, the pH of the leachates generally followed the order—

Fines < original composite material < gravels < sands.

Table 5. - Results of original material column, T1, elemental concentrations in milligrams per liter

Leaching	Leaching time, days	Period in cycle	Leachate recovered, L	pH	Na	K	Ca	Mg	Al	Mn	Fe	Cu	Zn	Cd	Pb	Si	S	Cl
4	20	Wet	0.0524	3.08	16.3	16	380	86	247	296	14.4	14.9	1620	11.5	1.7	75	1760	NA
5	24	Wet	0.0817	3.18	11.6	14	229	48	141	156	3.3	8.2	1010	7.20	2.4	64	1040	4.0
6	27	Wet	0.0811	3.10	9.5	14	194	44	106	139	2.6	6.7	823	6.04	0.5	59	878	<0.5
7	32	Wet	0.0879	3.09	8.5	16	156	29	80	117	1.3	6.6	751	5.16	0.7	57	789	8.8
8	35	Wet	0.0938	3.24	NA	NA	NA	NA	NA	NA	NA	5.9	710	5.06	2.2	NA	686	<0.5
9	38	W-RS	0.1773	3.36	NA	NA	NA	NA	NA	NA	NA	5.6	611	4.31	1.8	NA	686	<0.5
10	40	W-RS	0.1792	3.28	NA	NA	NA	NA	NA	NA	NA	5.1	572	3.84	2.7	NA	514	<0.5
11	42	W-RS	0.1966	3.21	5.2	19	102	22	58	64	0.6	5.0	521	3.4	2.5	50	536	<0.5
12	45	Wet	0.0957	3.24	4.1	12	88	18	46	57	0.8	4.7	445	3.1	2.4	47	446	<0.5
13	47	Wet	0.0983	3.31	4.0	9	86	15	50	56	0.4	4.4	450	3.1	1.9	49	265	<0.5
14	49	Wet	0.0910	3.17	2.7	16	81	14	44	46	0.6	4.0	405	2.8	1.3	48	416	<0.5
15	56	Dry	0.0726	3.25	3.7	17	87	13	48	50	0.5	4.4	429	2.9	1.6	53	466	<0.5
16	84	Dry-TS	0.0425	3.15	3.8	17	118	26	75	87	0.8	6.5	732	5.0	2.1	63	687	<0.5
17	87	Dry-TS	0.0697	3.22	3.7	15	131	29	92	87	1.3	8.0	926	6.0	2.1	66	809	<0.5
18	91	Dry-TS	0.0635	3.25	6.1	16	143	33	94	97	1.0	7.9	1010	6.3	2.6	69	892	6.0
19	125	Dry	0.0402	3.29	5.8	16	150	35	119	114	1.0	8.3	1120	7.2	2.4	70	988	NA
20	130	Wet	0.0842	3.16	5.2	18	128	32	111	95	0.9	8.3	1070	7.0	2.6	66	927	5.2
21	132	Wet	0.0856	3.28	4.6	18	107	27	104	73	0.9	7.7	934	6.1	2.0	63	764	NA
22	136	Wet	0.0862	3.22	4.6	15	98	26	93	65	1.9	6.7	877	5.8	1.7	63	718	5.0
23	139	Wet	0.0869	3.29	4.3	14	91	25	81	62	3.4	7.3	816	5.3	1.9	67	676	3.6
24	143	Wet	0.0881	3.32	3.8	16	78	23	112	59	4.2	6.3	722	4.7	2.2	59	594	3.7
25	146	Wet	0.0893	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
26	151	Wet	0.0713	3.14	1.9	14	71	20	79	54	1.7	6.4	713	4.7	2.8	65	592	<1.0
27	154	Wet	0.0705	3.37	2.0	13	71	20	73	47	1.2	6.6	704	4.4	2.3	65	592	4.3
28	157	W-RS	0.1748	3.22	1.6	12	61	21	72	15	1.0	5.4	602	3.9	2.1	57	520	4.5
29	159	W-RS	0.1871	3.31	1.5	11	50	13	47	33	0.9	5.8	506	3.1	1.6	56	420	31
30	161	W-RS	0.1902	3.39	1.4	10	37	10	36	24	0.9	4.9	372	2.3	1.4	50	314	<1.0
31	164	Wet	0.0939	3.37	1.3	12	33	10	35	24	1.4	3.8	326	2.3	2.9	52	290	<1.0
32	166	Wet	0.0806	3.51	1.2	10	31	8.0	32	21	2.1	3.8	306	1.9	3.3	52	254	<1.0
33	168	Wet	0.0863	3.28	1.2	11	29	8.7	31	6	1.3	4.0	315	1.9	2.4	54	260	<1.0
34	175	Dry	0.0791	NA	1.4	11	32	11	36	25	1.7	4.0	337	2.2	3.0	59	292	<1.0
35	203	Dry-TS	0.0534	3.38	2.0	13	49	16	46	35	1.6	2.1	396	2.5	2.1	61	356	NA
36	206	Dry-TS	0.0892	3.18	2.1	12	46	17	45	33	2.2	4.7	433	2.8	3.1	61	385	NA
37	210	Dry-TS	0.0878	3.19	4.3	13	49	19	53	34	2.0	4.6	436	2.8	2.5	60	395	NA
38	245	Dry	0.0414	3.22	5.3	17	73	26	71	52	2.6	5.4	565	3.6	2.5	62	518	NA
39	250	Wet	0.0830	3.35	4.5	15	44	22	62	44	2.5	5.5	491	3.1	2.2	55	431	NA
40	252	Wet	0.0924	3.32		21	60	37	68	51	1.4	5.2	541	3.5	2.8	57	502	NA
41	257	Wet	0.0845	3.25	4.0	16	56	20	58	49	1.4	5.6	523	3.4	3.2	55	472	NA
42	259	Wet	0.0930	3.23	2.9	11	46	20	56	41	0.8	4.9	457	3.0	3.4	53	410	NA

RS- Rain on snow.
TS- Thunderstorm.
NA- Not analyzed.

Table 6. - Results of original material column, T2, elemental concentrations in milligrams per liter

Leaching	Leaching time, days	Period in cycle	Leachate recovered, L	pH	Na	K	Ca	Mg	Al	Mn	Fe	Cu	Zn	Cd	Pb	Si	S	Cl
5	24	Wet	0.0842	3.40	13	14	271	65	189	206	0.8	9.2	1340	9.76	1.7	61	1390	<0.5
6	27	Wet	0.0811	3.35	9.7	15	199	47	112	150	0.6	6.6	957	6.88	1.7	57	990	NA
7	32	Wet	0.0626	3.24	10.6	19	190	35	102	141	0.6	7.3	911	6.23	0.9	62	920	NA
8	35	Wet	0.0580	3.36	NA	NA	NA	NA	NA	NA	NA	6.6	845	5.93	2.6	NA	NA	<0.5
9	38	W-RS	0.1516	3.44	NA	NA	NA	NA	NA	NA	NA	0.4	426	2.91	1.2	NA	197	<0.5
10	40	W-RS	0.1726	3.40	NA	NA	NA	NA	NA	NA	NA	5.0	559	3.85	3.0	NA	483	<0.5
11	42	W-RS	0.1781	3.34	4.6	14	85	18	47	54	1.1	4.5	443	3.1	2.4	44	435	<0.5
12	45	Wet	0.0741	3.37	4.1	11	89	19	52	59	0.3	5.1	481	3.8	1.7	49	464	NA
13	47	Wet	0.0766	3.40	3.8	9	85	15	47	58	<0.1	5.1	465	3.2	2.3	49	228	<0.5
14	49	Wet	0.0892	3.29	2.7	15	82	14	49	48	0.3	4.3	415	3.0	1.3	52	433	<0.5
15	56	Dry	0.0712	3.35	3.6	19	87	14	52	49	0.3	5.0	458	3.1	1.7	56	469	<0.5
16	84	Dry-TS	0.0235	3.26	3.9	16	105	24	87	79	0.3	7.7	800	5.3	2.2	66	729	NA
17	87	Dry-TS	0.0782	3.35	3.2	16	112	27	93	76	0.7	8.0	880	5.7	1.9	67	766	NA
18	91	Dry-TS	0.0414	3.34	6.0	21	138	33	119	95	1.0	8.8	1050	6.8	3.2	72	907	<0.5
19	125	Dry	0.0028	3.34	6.1	20	146	40	151	122	0.9	10.6	1300	8.6	3.1	74	1130	NA
20	130	Wet	0.0908	3.23	4.1	19	114	34	124	88	0.7	8.8	1070	7.0	2.7	69	925	3.6
21	132	Wet	0.0944	3.36	4.4	22	101	31	126	74	0.8	8.6	974	6.3	2.5	67	827	NA
22	136	Wet	0.1053	3.31	3.9	16	90	33	108	72	0.9	7.5	915	5.9	2.8	68	774	4.0
23	139	Wet	0.1162	3.32	4.1	18	82	27	96	61	1.1	8.3	829	5.5	2.4	68	699	<1.0
24	143	Wet	0.0867	3.36	3.5	14	70	25	134	61	1.2	6.9	753	4.6	1.9	63	622	3.5
25	146	Wet	0.0909	3.35	3.9	18	65	23	86	54	2.5	6.7	673	4.5	2.7	63	593	4.1
26	151	Wet	0.0773	3.18	1.8	13	61	21	84	52	0.9	6.6	684	4.2	1.2	68	570	4.0
27	154	Wet	0.0695	NA	2.0	7	59	24	92	62	1.2	6.1	647	4.2	1.5	40	576	5.1
28	157	W-RS	0.1611	3.22	1.5	10	45	19	69	13	0.9	5.2	508	3.3	1.8	61	448	3.7
29	159	W-RS	0.1546	3.29	1.3	11	32	10	39	24	0.4	5.1	371	2.3	1.5	51	320	<1.0
30	161	W-RS	0.1932	3.41	1.2	10	25	8.3	32	18	0.4	4.2	286	1.8	2.1	44	247	<1.0
31	164	Wet	0.0930	3.38	1.3	10	28	10	39	24	0.6	4.3	314	2.0	3.0	53	277	<1.0
32	166	Wet	0.0767	3.48	1.3	11	28	8.7	38	22	1.1	4.6	327	2.2	1.9	55	280	<1.0
33	168	Wet	0.0871	3.23	1.0	10	27	8.8	35	19	0.6	4.6	314	2.0	3.2	58	270	<1.0
34	175	Dry	0.0674	3.25	1.4	12	30	12	44	26	0.6	4.5	347	2.4	2.7	65	313	<1.0
35	203	Dry-TS	0.0000	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
36	206	Dry-TS	0.0223	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
37	210	Dry-TS	0.0814	3.24	4.6	12	40	20	64	34	3.0	5.6	469	3.0	2.5	59	409	NA
38	245	Dry	0.0391	3.21	4.4	15	47	26	80	47	2.6	5.6	563	3.3	2.3	56	491	NA
39	250	Wet	0.0816	3.35	5.2	17	62	26	66	60	2.8	6.0	625	3.8	1.8	59	552	NA
40	252	Wet	0.0900	3.31		15	40	22	64	43	1.8	4.6	448	2.9	3.1	53	406	NA
41	257	Wet	0.0862	3.28	2.9	13	38	18	53	41	2.2	5.1	424	2.7	2.4	52	397	NA
42	259	Wet	0.0943	3.27	2.2	14	33	18	52	35	1.1	4.4	368	2.5	2.9	48	341	NA

RS- Rain on snow.
TS- Thunderstorm.
NA- Not analyzed.

Table 7. - Results of original material column, T3, elemental concentrations in milligrams per liter

Leaching	Leaching time, days	Period in cycle	Leachate recovered, L	pH	Na	K	Ca	Mg	Al	Mn	Fe	Cu	Zn	Cd	Pb	Si	S	Cl
4	20	Wet	0.0539	3.33	13.6	13	326	75	187	257	0.9	11.1	1570	11.1	0.9	61	1480	NA
5	24	Wet	0.0786	3.36	13.5	15	277	61	177	199	0.6	8.8	1350	9.67	1.2	65	1350	<0.5
6	27	Wet	0.0825	3.29	10.7	14	216	53	130	171	0.7	8.1	1100	8.01	1.0	58	1090	NA
7	32	Wet	0.0631	3.27	10.9	19	193	39	110	153	0.6	8.5	989	6.89	0.8	61	1003	NA
8	35	Wet	0.0642	3.32	NA	NA	NA	NA	NA	NA	NA	7.4	838	6.10	3.0	NA	NA	<0.5
9	38	W-RS	0.1497	3.36	NA	NA	NA	NA	NA	NA	NA	1.6	634	4.54	2.7	NA	294	<0.5
10	40	W-RS	0.1698	3.37	NA	NA	NA	NA	NA	NA	NA	5.7	640	4.46	2.6	NA	509	<0.5
11	42	W-RS	0.1701	3.27	4.6	18	91	20	50	57	0.4	5.1	474	3.32	2.4	50	469	<0.5
12	45	Wet	0.0702	3.35	3.8	12	83	17	46	55	0.3	5.1	444	3.5	2.2	49	424	NA
13	47	Wet	0.0722	3.38	3.4	8	76	13	40	51	0.1	5.0	415	3.0	2.2	49	133	<0.5
14	49	Wet	0.0922	3.26	2.4	18	72	12	40	41	0.5	4.3	366	2.6	1.7	52	379	<0.5
15	56	Dry	0.0788	3.32	2.8	18	70	11	41	37	0.3	4.6	380	2.6	1.6	54	406	<0.5
16	84	Dry-TS	0.0702	3.15	2.8	15	76	18	63	55	0.4	6.4	599	4.1	2.8	59	534	NA
17	87	Dry-TS	0.0878	3.31	2.3	14	83	21	70	56	0.6	7.0	696	4.8	2.5	64	588	NA
18	91	Dry-TS	0.0504	3.33	4.3	17	96	25	86	67	0.9	7.7	806	5.2	2.3	68	707	<0.5
19	125	Dry	0.0319	3.36	4.1	16	93	28	91	87	0.7	7.6	928	5.0	3.4	68	791	NA
20	130	Wet	0.0934	3.19	4.5	18	87	32	95	80	0.7	7.1	898	5.6	2.8	67	766	<1.0
21	132	Wet	0.1010	3.36	4.0	19	78	27	104	63	0.8	7.7	816	5.2	2.1	64	690	<1.0
22	136	Wet	0.1111	3.30	3.6	13	71	27	85	60	0.8	6.7	766	4.9	2.5	64	625	4.0
23	139	Wet	0.1227	3.32	4.0	16	64	22	76	53	1.0	7.1	694	4.4	3.5	65	585	4.7
24	143	Wet	0.0927	3.36	3.2	14	53	19	95	48	1.0	6.2	609	4.0	1.7	61	496	<1.0
25	146	Wet	0.0964	3.36	3.3	15	44	16	55	36	0.9	5.3	482	3.2	2.2	56	402	<1.0
26	151	Wet	0.0850	3.20	1.4	12	41	15	53	35	1.1	5.1	482	3.0	2.5	60	395	<1.0
27	154	Wet	0.0579	3.23	1.6	12	40	14	51	30	1.0	5.4	469	3.0	2.3	60	393	3.8
28	157	W-RS	0.1562	NA	1.3	11	34	16	50	NA	0.7	4.7	406	2.6	1.3	58	351	<1.0
29	159	W-RS	0.1649	3.31	1.3	11	28	10	34	22	0.8	5.1	347	2.0	2.6	56	292	3.6
30	161	W-RS	0.1863	3.42	1.1	8	20	7.4	25	16	0.7	4.0	248	1.4	2.1	45	213	<1.0
31	164	Wet	0.0990	3.41	1.3	10	23	9.2	32	22	1.2	4.0	274	1.8	2.6	54	245	<1.0
32	166	Wet	0.0806	3.48	1.1	12	21	8.1	28	17	1.4	3.7	262	1.7	2.3	52	226	<1.0
33	168	Wet	0.0913	3.28	1.0	11	20	7.6	26	17	0.8	3.7	252	1.6	3.4	54	220	<1.0
34	175	Dry	0.0846	3.30	1.3	10	22	11	32	22	0.7	3.9	275	1.8	3.7	59	248	<1.0
35	203	Dry-TS	0.1163	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
36	206	Dry-TS	0.0872	3.47	1.2	12	31	15	45	30	1.3	4.9	379	2.2	3.3	68	340	NA
37	210	Dry-TS	0.0881	3.27	4.1	13	30	17	49	29	1.2	4.6	367	2.3	3.3	59	315	NA
38	245	Dry	0.0913	3.24	4.0	13	35	22	60	40	1.0	4.9	455	2.7	2.4	53	394	NA
39	250	Wet	0.0812	3.32	4.6	15	36	22	55	46	1.3	5.2	470	2.7	2.9	58	425	NA
40	252	Wet	0.0939	3.31	4.4	14	36	23	64	49	0.7	5.0	459	2.9	2.6	57	419	NA
41	257	Wet	0.0908	3.26	3.6	13	36	21	58	48	0.7	5.4	468	3.0	3.5	57	432	NA
42	259	Wet	0.0987	3.26	2.9	13	33	21	57	43	0.4	4.7	414	2.8	3.3	54	389	NA

RS- Rain on snow.
TS- Thunderstorm.
NA- Not analyzed.

Table 8. - Results of gravel column, G1, elemental concentrations in milligrams per liter

Leaching	Leaching time, days	Period in cycle	Leachate recovered, L	pH	Na	K	Ca	Mg	Al	Mn	Fe	Cu	Zn	Cd	Pb	Si	S	Cl
0	1	Draining	0.0113	NA	NA	NA	117	34	31	77	0.6	2.7	330	2.53	2.5	37	394	NA
1	10	Wet	0.0578	3.49	8.2	10.4	122	26	29	64	3.2	3.0	345	2.42	2.4	34	418	4.0
2	13	Wet	0.0932	3.63	5.9	7.9	87	20	25	51	0.2	2.6	294	2.17	2.1	29	NA	2.4
3	17	Wet	0.0816	4.03	6.7	7.3	95	19	27	61	0.1	3.3	340	2.28	1.0	33	327	1.9
4	20	Wet	0.0947	3.60	5.9	5.5	86	20	22	54	0.5	3.5	321	2.18	2.5	36	316	1.9
5	24	Wet	0.0780	3.41	5.1	9.3	59	14	20	35	0.2	2.3	237	1.66	1.0	31	247	<0.5
6	27	Wet	0.1034	3.42	3.3	6.4	47	12	14	29	0.2	2.0	179	1.35	1.3	27	180	<0.5
7	32	Wet	0.0737	3.50	3.9	10.2	50	11	16	30	0.1	2.8	211	1.6	2.5	32	212	13
8	35	Wet	0.0774	3.52	NA	NA	NA	NA	NA	NA	NA	2.0	183	1.17	2.0	NA	186	5.4
9	38	W-RS	0.1754	3.79	NA	NA	NA	NA	NA	NA	NA	6.4	162	1.11	3.1	NA	154	<0.5
10	40	W-RS	0.1761	3.51	NA	NA	NA	NA	NA	NA	NA	1.4	112	0.74	3.5	NA	89	<0.5
11	42	W-RS	0.2036	3.56	2.1	6.6	19	4.8	5.4	11	NA	1.3	85	0.6	3.6	17	88	17
12	45	Wet	0.0658	3.62	1.7	4.3	23	5.8	6.6	13	0.1	1.5	103	0.7	3.0	21	101	NA
13	47	Wet	0.0795	3.59	2.0	1.2	25	5.9	7.9	16	0.0	1.6	122	0.8	3.3	25	73	<0.5
14	49	Wet	0.1157	3.55	1.1	6.3	23	5.1	6.4	13	0.2	1.4	107	0.7	3.1	25	102	<0.5
15	56	Dry	0.0458	3.66	1.5	8.4	30	6.2	8.4	16	0.1	1.6	128	0.9	2.3	30	137	<0.5
16	84	Dry-TS	0.0378	3.50	2.2	9.0	36	12	14	28	0.1	2.4	222	1.5	3.2	39	198	NA
17	87	Dry-TS	0.0636	3.50	1.6	9.1	45	21	16	28	3.1	2.7	251	1.7	3.4	40	219	NA
18	91	Dry-TS	0.0795	3.43	3.3	8.3	44	15	16	32	0.3	3.0	263	1.7	3.1	40	222	<0.5
19	125	Dry	0.0334	3.44	3.2	8.3	45	17	21	42	0.3	3.7	299	2.0	3.5	37	266	NA
20	130	Wet	0.0967	3.49	2.3	8.1	34	16	18	33	0.1	2.7	262	1.7	3.1	34	221	<1.0
21	132	Wet	0.1013	3.63	2.3	9.3	31	14	21	27	0.1	1.1	243	1.6	3.0	32	210	<1.0
22	136	Wet	0.0935	3.56	2.1	8.1	31	15	18	28	0.2	2.6	246	1.6	3.0	34	210	<1.0
23	139	Wet	0.0857	3.57	2.3	5.9	29	12	17	26	0.2	2.8	230	1.5	2.5	35	197	<1.0
24	143	Wet	0.0672	3.61	1.9	7.0	24	11	21	24	0.2	2.4	197	1.2	2.6	30	167	<1.0
25	146	Wet	0.1033	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	<1.0
26	151	Wet	0.0703	3.46	1.1	6.5	22	10	13	20	0.2	2.2	181	1.2	3.4	33	152	<1.0
27	154	Wet	0.0600	3.50	1.0	5.8	19	8.3	12	16	0.1	2.3	168	1.0	2.8	32	140	<1.0
28	157	W-RS	0.1739	3.52	0.8	4.2	10	5.4	6.9	0.2	0.1	1.3	85	0.5	2.8	17	77	<1.0
29	159	W-RS	0.1817	3.56	0.9	2.3	10	3.9	5.2	8.2	0.1	1.5	83	0.4	3.3	17	75	<1.0
30	161	W-RS	0.2010	3.66	0.9	2.9	8	3.7	5.0	7.4	0.1	1.3	75	0.4	3.3	16	68	<1.0
31	164	Wet	0.0910	3.65	1.0	2.8	11	5.1	7.3	12	0.1	1.6	94	0.6	3.9	24	85	<1.0
32	166	Wet	0.0499	3.69	0.9	4.3	11	5.4	6.9	10	0.1	1.2	101	0.7	3.3	25	87	<1.0
33	168	Wet	0.1259	3.52	1.9	4.7	11	5.6	7.2	3.6	0.2	1.5	104	0.7	4.4	27	92	<1.0
34	175	Dry	0.0854	NA	1.0	5.0	13	8.0	9.4	15	0.1	1.6	125	0.9	3.4	32	115	<1.0
35	203	Dry-TS	0.0431	3.56	0.9	5.7	21	12	14	22	0.3	4.2	204	1.3	4.2	33	173	NA
36	206	Dry-TS	0.0912	3.52	1.3	4.3	17	9.3	12	18	0.5	2.2	192	1.3	3.2	34	160	NA
37	210	Dry-TS	0.0886	3.46	2.1	6.6	21	12	16	21	0.1	2.5	191	1.4	3.5	36	167	NA
38	245	Dry	0.0462	3.41	3.1	11.5	30	21	26	38	0.3	3.3	308	1.9	2.9	37	257	NA
39	250	Wet	0.0733	3.53	2.1	6.2	22	14	16	29	0.2	2.6	224	1.4	2.7	32	193	NA
40	252	Wet	0.0939	3.53	1.2	7.9	20	14	17	28	<0.1	2.3	209	1.4	2.3	31	191	NA
41	257	Wet	0.0845	3.50	1.0	5.4	19	11	15	26	0.1	2.4	199	1.3	4.2	29	176	NA
42	259	Wet	0.1103	3.49	0.4	4.7	16	12	16	23	0.0	2.2	179	1.2	3.4	27	158	NA

RS- Rain on snow.
TS- Thunderstorm.
NA- Not analyzed.

Table 9. - Results of gravel column, G2, elemental concentrations in milligrams per liter

Leaching	Leaching time, days	Period in cycle	Leachate recovered, L	pH	Na	K	Ca	Mg	Al	Mn	Fe	Cu	Zn	Cd	Pb	Si	S	Cl
0	1	Draining	0.0370	3.55	NA	NA	113	35	31	81	0.3	2.6	380	2.66	2.7	38	408	NA
1	10	Wet	0.0533	3.51	8.4	11.7	118	30	33	73	0.2	3.3	409	2.74	2.7	36	460	4.3
2	13	Wet	0.0946	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
3	17	Wet	0.0854	3.73	6.7	7.4	90	19	27	61	0.2	3.4	349	2.54	3.0	32	341	1.8
4	20	Wet	0.0000	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
5	24	Wet	0.0803	3.42	4.5	8.0	60	14	18	35	<0.1	2.3	242	1.56	2.4	31	226	4.1
6	27	Wet	0.0986	3.38	3.4	8.8	50	13	17	32	0.4	2.0	216	1.52	0.7	29	212	<0.5
7	32	Wet	0.1004	3.37	4.1	10.2	53	12	18	33	0.1	2.5	246	1.56	2.1	34	231	19
8	35	Wet	0.1202	3.47	NA	NA	NA	NA	NA	NA	NA	2.2	218	1.50	3.4	NA	206	<0.5
9	38	W-RS	0.2136	3.72	NA	NA	NA	NA	NA	NA	NA	1.6	204	1.39	2.2	NA	267	<0.5
10	40	W-RS	0.2258	3.43	NA	NA	NA	NA	NA	NA	NA	1.3	107	0.73	2.9	NA	90	<0.5
11	42	W-RS	0.2362	3.45	2.0	6.4	20	5.1	5.8	12	0.2	1.2	98	0.6	3.3	17	94	<0.5
12	45	Wet	0.1000	3.52	1.8	5.7	24	6.1	7.4	14	0.1	1.5	118	0.7	3.2	23	111	<0.5
13	47	Wet	0.1164	3.48	1.8	1.5	24	5.1	6.9	15	0.0	1.6	129	0.8	2.3	24	65	<0.5
14	49	Wet	0.1188	3.47	1.0	7.5	23	5.3	6.7	14	0.9	1.6	115	0.7	2.8	26	114	<0.5
15	56	Dry	0.0853	3.58	1.4	9.9	24	4.7	7.4	13	0.1	1.4	113	0.7	2.2	25	115	<0.5
16	84	Dry-TS	0.0437	3.09	1.8	8.5	31	9.5	13	25	1.1	2.4	203	1.3	3.4	36	176	NA
17	87	Dry-TS	0.0797	3.36	1.3	8.5	39	14	15	26	6.5	3.3	240	1.6	2.7	38	205	10.8
18	91	Dry-TS	0.1100	3.42	2.8	10.0	42	14	16	30	0.2	2.8	267	1.6	2.8	40	224	6.4
19	125	Dry	0.0507	3.45	3.3	11.7	47	18	24	45	0.3	4.4	368	2.3	3.2	40	311	NA
20	130	Wet	0.0981	3.51	2.3	9.8	34	15	17	32	0.1	2.7	283	1.8	3.1	34	225	<1.0
21	132	Wet	0.1092	3.63	2.2	12.2	29	12	18	24	0.2	2.4	249	1.6	3.6	33	195	<1.0
22	136	Wet	0.0843	3.58	2.1	6.4	30	13	16	26	0.2	2.2	249	1.7	2.9	34	199	<1.0
23	139	Wet	0.0594	3.59	2.4	7.1	27	11	15	24	0.2	2.4	237	1.6	3.2	34	195	<1.0
24	143	Wet	0.0711	3.62	2.0	8.6	22	10	19	22	0.1	2.1	203	1.3	2.9	30	158	<1.0
25	146	Wet	0.1140	3.66	1.9	8.9	19	8.6	12	17	0.1	1.8	173	1.2	3.0	29	141	<1.0
26	151	Wet	0.0700	3.49	1.0	6.3	19	8.7	12	18	0.2	1.7	182	1.2	3.5	32	146	<1.0
27	154	Wet	0.0645	3.55	1.0	6.7	17	7.3	11	15	0.1	1.9	165	1.1	3.5	31	135	<1.0
28	157	W-RS	0.2003	3.55	0.8	2.3	10	4.7	6.0	9.2	0.1	1.1	93	0.6	2.6	18	81	<1.0
29	159	W-RS	0.2082	3.58	0.8	2.7	9	3.6	4.6	7.6	0.1	1.2	84	0.6	3.1	17	74	<1.0
30	161	W-RS	0.2002	3.68	0.7	2.3	8	3.1	4.3	6.6	0.1	1.0	74	0.5	2.9	16	62	<1.0
31	164	Wet	0.0950	3.68	1.0	2.8	10	4.8	6.8	11	<0.1	1.3	100	0.6	3.1	24	85	<1.0
32	166	Wet	0.0498	3.71	0.8	5.0	10	5.0	6.3	3.2	0.1	1.1	108	0.7	3.3	24	90	<1.0
33	168	Wet	0.1287	3.56	1.2	3.9	11	4.6	6.6	10	0.2	1.3	110	0.7	4.6	27	93	<1.0
34	175	Dry	0.0912	3.47	1.1	5.4	13	7.6	9.4	15	0.2	1.4	139	1.0	3.5	35	119	<1.0
35	203	Dry-TS	0.0336	3.58	0.8	4.8	18	9.4	12	17	0.2	3.0	197	1.3	3.0	34	154	NA
36	206	Dry-TS	0.0950	3.56	1.5	4.3	19	11	13	19	0.2	2.2	182	1.1	3.2	33	161	NA
37	210	Dry-TS	0.0953	3.51	2.3	4.8	19	10	15	19	0.1	2.2	185	1.4	3.2	35	155	NA
38	245	Dry	0.0500	3.39	3.2	9.0	29	19	25	36	0.3	3.3	345	2.1	3.2	45	276	NA
39	250	Wet	0.0761	3.55	2.4	7.8	21	13	16	29	0.2	2.6	259	1.6	3.1	32	208	NA
40	252	Wet	0.0987	3.55	0.8	7.1	19	12	16	26	<0.1	2.1	217	1.5	4.3	30	177	NA
41	257	Wet	0.0771	3.51	0.8	5.6	17	12	16	25	<0.1	2.3	216	1.6	4.0	28	184	NA
42	259	Wet	0.1192	3.52	0.4	4.2	15	10	13	21	<0.1	1.9	183	1.3	2.6	26	154	NA

RS- Rain on snow.
TS- Thunderstorm.
NA- Not analyzed.

Table 10. - Results of gravel column, G3, elemental concentrations in milligrams per liter

Leaching	Leaching time, days	Period in cycle	Leachate recovered, L	pH	Na	K	Ca	Mg	Al	Mn	Fe	Cu	Zn	Cd	Pb	Si	S	Cl
0	1	Draining	0.0365	3.33	NA	NA	115	33	41	80	0.5	3.0	350	2.90	2.7	39	420	
1	10	Wet	0.0570	3.47	8.7	10.2	135	30	44	78	0.4	3.6	409	3.26	1.9	39	509	3.0
2	13	Wet	0.0910	3.55	7.1	11.5	112	26	43	71	0.4	3.9	407	3.01	NA	34	455	4.9
3	17	Wet	0.0826	3.62	8.6	8.9	131	29	48	85	0.4	5.1	496	3.44	2.2	42	509	3.1
4	20	Wet	0.0983	3.49	7.5	9.1	114	24	42	73	0.3	4.9	458	3.04	1.9	44	471	3.7
5	24	Wet	0.0854	3.45	4.7	7.7	74	18	34	47	0.2	3.2	310	2.27	1.9	37	322	4.6
6	27	Wet	0.0959	3.37	3.9	7.0	59	15	27	39	0.3	2.7	264	1.99	1.4	35	266	<0.5
7	32	Wet	0.0968	3.42	4.3	12.0	63	13	27	40	1.3	3.5	304	2.02	0.8	40	300	22
8	35	Wet	0.1169	3.54	NA	NA	NA	NA	NA	NA	NA	2.7	259	1.65	2.7	NA	266	<0.5
9	38	W-RS	0.2178	3.75	NA	NA	NA	NA	NA	NA	NA	3.9	231	1.59	2.7	NA	100	<0.5
10	40	W-RS	0.2212	3.48	NA	NA	NA	NA	NA	NA	NA	1.7	153	1.02	3.6	NA	117	<0.5
11	42	W-RS	0.2330	3.49	1.9	7.1	22	5.7	9.2	13	0.1	1.5	119	0.8	3.3	20	114	<0.5
12	45	Wet	0.0983	3.47	1.7	5.0	25	6.5	10.6	16	0.1	1.9	138	1.0	3.2	25	132	NA
13	47	Wet	0.1164	3.49	1.9	2.0	26	5.7	9.5	18	0.8	1.9	136	0.9	3.2	27	52	<0.5
14	49	Wet	0.1011	3.42	1.2	7.3	25	6.0	10.7	16	0.4	2.0	136	0.9	2.7	29	133	<0.5
15	56	Dry	0.0547	3.57	1.9	10.4	33	6.6	14	19	0.1	2.2	164	1.0	2.5	35	173	<0.5
16	84	Dry-TS	0.0430	3.45	1.6	7.9	38	10	17	27	0.4	2.4	209	1.4	2.8	34	196	NA
17	87	Dry-TS	0.0783	3.43	1.3	8.8	50	16	26	34	0.3	3.5	328	1.9	2.4	44	284	6.4
18	91	Dry-TS	0.1023	3.46	3.2	12.5	60	22	34	49	0.3	4.4	422	2.7	3.5	50	371	5.2
19	125	Dry	0.0546	3.53	2.7	8.4	45	17	28	42	0.2	3.3	348	2.1	2.8	33	301	NA
20	130	Wet	0.0937	3.51	2.2	10.0	42	20	31	43	0.1	3.2	369	2.3	2.4	38	325	<1.0
21	132	Wet	0.1033	3.61	2.6	11.9	34	18	39	39	0.1	2.5	380	2.3	3.0	37	319	<1.0
22	136	Wet	0.0923	3.56	2.1	8.3	33	18	29	35	0.2	3.0	334	2.2	2.8	38	277	<1.0
23	139	Wet	0.0807	3.56	2.5	5.8	30	14	28	32	0.2	3.5	313	2.2	3.5	39	255	<1.0
24	143	Wet	0.0682	3.57	2.1	8.6	28	14	39	31	0.1	3.4	295	1.8	2.3	36	239	<1.0
25	146	Wet	0.1166	3.61	1.7	8.9	22	12	19	26	0.2	2.7	233	1.5	2.4	34	199	<1.0
26	151	Wet	0.0711	3.59	1.1	5.5	20	12	23	26	0.1	2.9	264	1.6	3.1	35	214	<1.0
27	154	Wet	0.0938	3.54	1.1	3.5	18	8.5	17	18	0.1	2.5	202	1.2	2.1	33	168	<1.0
28	157	W-RS	0.2201	3.52	0.9	3.0	11	6.3	11	13	0.1	1.5	124	0.8	3.2	22	109	<1.0
29	159	W-RS	0.2117	3.56	0.8	2.8	10	4.6	7.9	9.9	0.1	1.7	109	0.6	3.2	20	90	<1.0
30	161	W-RS	0.2018	3.64	0.8	2.6	8	4.0	7.3	8.6	0.1	1.4	95	0.6	3.2	19	83	<1.0
31	164	Wet	0.0926	3.66	1.1	3.4	12	6.1	12	14	0.1	1.7	129	0.9	3.2	28	112	<1.0
32	166	Wet	0.0544	3.71	0.8	3.6	10	5.4	9.2	3.7	0.3	1.4	116	0.7	3.9	25	100	<1.0
33	168	Wet	0.1292	3.56	0.9	5.0	12	5.6	10.5	13	0.1	1.8	135	0.9	2.8	30	114	<1.0
34	175	Dry	0.0914	3.55	1.1	5.9	15	9.2	14	18	0.1	1.9	159	1.1	3.1	37	144	<1.0
35	203	Dry-TS	0.0308	3.57	1.0	5.0	35	13	20	26	0.2	3.3	262	1.6	3.3	43	219	NA
36	206	Dry-TS	0.0921	3.55	0.7	6.4	31	17	31	35	0.2	3.8	346	2.1	3.3	50	303	NA
37	210	Dry-TS	0.0921	3.48	2.5	8.5	26	17	34	34	0.2	3.8	332	2.1	2.9	44	274	NA
38	245	Dry	0.0411	3.42	3.2	11.1	45	28	47	54	0.5	4.5	496	3.1	2.9	45	418	NA
39	250	Wet	0.0740	3.54	2.5	6.8	31	20	35	46	0.2	4.0	410	2.4	2.8	43	341	NA
40	252	Wet	0.0959	3.55	1.3	9.1	30	18	36	39	0.2	3.0	395	2.4	3.5	40	320	NA
41	257	Wet	0.0735	3.52	0.5	4.0	19	15	28	32	<0.1	3.2	288	1.9	3.8	34	247	NA
42	259	Wet	0.1199	3.51	0.3	4.2	16	12	22	26	<0.1	2.6	237	1.5	4.0	31	197	NA

RS- Rain on snow.
TS- Thunderstorm.
NA- Not analyzed.

Table 11. - Results of sand column, S1, elemental concentrations in milligrams per liter

Leaching	Leaching time, days	Period in cycle	Leachate recovered, L	pH	Na	K	Ca	Mg	Al	Mn	Fe	Cu	Zn	Cd	Pb	Si	S	Cl
0	1	Draining	0.0877	4.05	NA	NA	43	13	0.8	5.8	<0.1	0.4	31	0.26	5.3	10	73	9.4
1	10	Wet	0.0556	4.02	5.0	7.3	68	17	1.7	11	<0.1	0.6	67	0.47	3.7	19	125	3.3
2	13	Wet	0.0827	4.04	4.6	5.1	74	19	2.5	13	0.1	0.6	83	0.69	1.5	20	141	2.8
3	17	Wet	0.0919	4.03	6.7	2.5	109	23	4.1	21	0.2	0.9	143	1.01	2.7	27	202	3.1
4	20	Wet	0.0917	3.93	7.4	4.1	136	30	4.7	24	0.1	1.2	184	1.28	3.0	33	247	2.7
5	24	Wet	0.0900	3.95	5.4	8.0	109	25	5.0	19	<0.1	0.8	167	1.15	2.9	30	215	3.1
6	27	Wet	0.0864	3.89	5.6	4.9	116	28	5.0	22	0.5	0.9	165	1.19	0.9	31	233	3.2
7	32	Wet	0.0932	3.92	6.2	6.8	126	27	4.6	24	<0.1	1.5	188	1.30	2.1	32	255	6.3
8	35	Wet	0.0931	3.93	NA	NA	NA	NA	NA	NA	<0.1	0.8	209	1.29	2.5	NA	269	5.2
9	38	W-RS	0.1936	3.96	NA	NA	NA	NA	NA	NA	<0.1	0.3	89	0.52	2.3	NA	471	<0.5
10	40	W-RS	0.1977	3.95	NA	NA	NA	NA	NA	NA	<0.1	1.0	195	1.42	3.3	NA	217	<0.5
11	42	W-RS	0.1981	3.85	2.6	9.4	82	18	3.8	14	<0.1	0.9	165	1.1	3.3	31	186	<0.5
12	45	Wet	0.0967	3.96	2.1	4.9	68	14	3.2	12	1.0	0.8	141	1.0	2.0	28	154	<0.5
13	47	Wet	0.0950	3.94	1.9	2.2	69	11	2.3	12	<0.1	0.9	145	0.9	2.9	29	77	<0.5
14	49	Wet	0.0948	3.82	1.3	8.6	67	10	2.8	11	0.5	0.7	130	0.9	1.7	31	157	<0.5
15	56	Dry	0.0717	3.83	1.8	9.0	74	10	3.3	11	0.4	0.7	148	1.0	2.3	32	171	<0.5
16	84	Dry-TS	0.0448	2.89	1.8	8.5	91	14	5.6	20	0.7	1.0	240	1.7	3.1	38	229	NA
17	87	Dry-TS	0.0872	3.59	1.4	6.6	105	16	7.3	21	5.0	1.5	305	2.0	2.9	42	266	<0.5
18	91	Dry-TS	0.0850	3.76	3.2	10.2	132	20	10.9	27	2.3	1.8	379	2.5	3.3	47	342	<0.5
19	125	Dry	0.0558	3.79	2.8	10.9	152	23	16	33	0.1	2.2	519	3.4	2.6	48	440	NA
20	130	Wet	0.0967	3.76	3.1	10.7	146	26	17	35	<0.1	2.3	544	3.4	2.8	48	458	<1.0
21	132	Wet	0.0930	3.86	3.8	13.9	174	24	22	37	0.3	0.1	694	4.4	2.8	52	541	<1.0
22	136	Wet	0.0914	3.75	3.4	11.9	158	26	21	35	0.2	2.4	626	4.2	2.5	51	489	<1.0
23	139	Wet	0.0898	3.76	3.5	12.1	150	23	34	35	2.7	2.6	641	4.1	1.5	52	504	<1.0
24	143	Wet	0.0881	3.77	3.2	11.5	135	20	28	32	0.1	2.5	608	3.7	1.8	50	457	<1.0
25	146	Wet	0.1012	3.80	2.7	11.4	114	18	16	27	0.2	2.3	529	3.5	2.5	49	403	17
26	151	Wet	0.0888	3.72	1.6	7.4	104	13	15	21	0.1	2.2	534	3.3	2.0	53	395	<1.0
27	154	Wet	0.0787	3.69	1.7	7.4	88	13	15	21	<0.1	2.2	493	3.4	1.4	52	365	<1.0
28	157	W-RS	0.1890	3.69	1.2	7.8	72	10	14	15	0.1	2.0	431	2.9	2.1	49	316	<1.0
29	159	W-RS	0.1905	3.72	1.2	7.0	55	6.8	10.0	11	0.1	2.4	365	2.2	2.4	46	251	<1.0
30	161	W-RS	0.1965	3.80	1.1	9.4	41	5.9	9.1	10	0.1	1.9	296	1.9	1.1	43	211	<1.0
31	164	Wet	0.0957	3.81	1.1	6.1	36	4.9	8.2	9.2	0.1	1.7	262	1.8	2.1	42	187	<1.0
32	166	Wet	0.0803	3.84	0.9	6.4	34	4.7	7.8	2.5	0.1	1.7	268	1.7	2.2	42	182	<1.0
33	168	Wet	0.0958	3.72	1.3	7.8	36	4.0	5.2	7.1	0.1	0.4	276	1.7	3.1	45	186	<1.0
34	175	Dry	0.0849	NA	1.1	7.0	37	6.0	10.8	10	0.1	2.0	302	2.0	2.2	49	212	<1.0
35	203	Dry-TS	0.0447	3.68	1.2	7.4	51	7.2	18	15	0.1	2.8	474	3.0	2.8	51	317	<1.0
36	206	Dry-TS	0.0928	3.64	1.6	6.6	55	8.9	21	15	0.2	3.0	512	3.2	3.2	57	345	<1.0
37	210	Dry-TS	0.0936	3.56	4.4	11.6	69	11	32	19	0.2	4.0	588	3.7	2.7	59	395	<1.0
38	245	Dry	0.0516	3.52	4.2	12.0	78	14	42	27	0.3	3.2	757	4.4	3.3	55	519	<1.0
39	250	Wet	0.0894	3.57	4.2	10.7	78	13	39	30	0.2	3.6	795	4.4	3.1	58	540	<1.0
40	252	Wet	0.0959	3.56	3.3	13.0	78	16	48	33	0.1	3.5	830	4.9	4.3	57	582	NA
41	257	Wet	0.0915	3.51	3.1	9.7	79	16	49	31	0.2	3.1	815	4.8	3.1	56	582	NA
42	259	Wet	0.0994	3.50	3.0	10.2	73	15	47	28	0.2	2.5	786	4.6	2.7	56	547	NA

RS- Rain on snow.
TS- Thunderstorm.
NA- Not analyzed.

Table 12. - Results of sand column, S2, elemental concentrations in milligrams per liter

Leaching	Leaching time, days	Period in cycle	Leachate recovered, L	pH	Na	K	Ca	Mg	Al	Mn	Fe	Cu	Zn	Cd	Pb	Si	S	Cl
0	1	Draining	0.1191	4.10	NA	NA	46	13	1.4	7.0	<0.1	0.5	36	0.3	4.5	11	80	3.4
1	10	Wet	0.0594	4.05	5.0	5.3	88	16	1.7	15	<0.1	0.5	65	0.44	2.4	19	149	3.4
2	13	Wet	0.0916	4.10	4.5	5.0	87	16	2.4	16	0.2	0.4	75	0.53	0.5	19	155	2.6
3	17	Wet	0.0879	4.08	6.8	1.9	145	24	4.3	25	0.1	0.9	147	1.06	3.4	27	234	2.6
4	20	Wet	0.0904	3.98	6.1	5.2	156	27	4.2	27	0.2	0.8	184	1.24	3.1	29	264	2.4
5	24	Wet	0.0840	4.00	5.6	4.0	141	25	5.0	25	0.4	0.5	170	1.19	1.5	28	259	<0.5
6	27	Wet	0.0931	3.91	5.6	4.0	156	29	4.7	28	0.2	0.5	188	1.32	1.3	30	275	3.6
7	32	Wet	0.0892	3.95	5.8	6.6	160	28	4.5	31	0.2	0.5	230	1.6	2.1	32	296	8.3
8	35	Wet	0.0917	3.94	NA	NA	NA	NA	NA	NA	NA	0.4	223	1.60	2.8	NA	303	3.4
9	38	W-RS	0.1898	3.98	NA	NA	NA	NA	NA	NA	NA	0.9	152	1.04	2.5	NA	617	<0.5
10	40	W-RS	0.1983	4.00	NA	NA	NA	NA	NA	NA	NA	0.5	243	1.57	3.4	NA	237	<0.5
11	42	W-RS	0.1923	3.89	2.5	8.7	95	16	3.1	15	0.1	0.5	175	1.2	1.9	30	193	<0.5
12	45	Wet	0.1005	4.09	1.8	5.4	78	13	2.4	12	0.1	0.5	159	1.0	2.5	28	175	<0.5
13	47	Wet	0.1033	4.03	2.0	1.6	78	10	1.3	13	<0.1	0.4	156	1.0	2.5	29	77	<0.5
14	49	Wet	0.0851	3.86	1.3	7.2	80	9.3	2.2	11	0.1	0.3	146	0.9	2.0	30	169	<0.5
15	56	Dry	0.0778	3.90	1.9	9.3	80	9.1	3.1	10	0.0	0.7	160	1.0	2.0	33	181	<0.5
16	84	Dry-TS	0.0424	3.30	1.6	6.7	115	13	4.1	22	0.9	0.4	293	1.9	3.1	39	273	NA
17	87	Dry-TS	0.0786	3.81	1.4	7.1	134	16	5.5	26	0.7	0.6	382	2.4	2.5	42	321	<0.5
18	91	Dry-TS	0.0678	3.81	3.5	10.1	183	20	8.4	34	0.4	0.9	504	3.1	3.5	46	442	<0.5
19	125	Dry	0.0529	3.84	3.1	9.1	197	23	13	40	0.4	0.6	683	3.9	3.0	47	559	NA
20	130	Wet	0.0961	3.76	3.4	11.5	201	26	14	45	0.4	0.9	697	4.1	3.1	50	576	<1.0
21	132	Wet	0.0958	3.88	4.3	12.6	222	25	21	42	0.4	1.5	809	4.5	2.8	52	643	<1.0
22	136	Wet	0.0972	3.80	3.5	7.1	201	27	17	43	0.4	0.8	768	4.3	3.2	49	577	<1.0
23	139	Wet	0.0987	3.80	3.4	11.9	192	23	23	44	0.3	0.6	764	4.2	3.0	50	576	<1.0
24	143	Wet	0.0852	3.80	3.4	11.8	165	19	20	35	0.3	0.4	726	3.8	2.3	49	520	<1.0
25	146	Wet	0.0960	3.82	2.9	12.4	129	16	10.2	27	0.5	0.3	588	3.4	2.7	46	424	<1.0
26	151	Wet	0.0797	3.77	1.5	7.8	113	11	9.0	19	2.4	0.2	548	2.9	2.0	48	383	<1.0
27	154	Wet	0.0748	3.70	1.4	7.6	96	11	8.6	20	0.3	0.1	504	2.7	1.4	47	372	<1.0
28	157	W-RS	0.1850	3.71	1.2	6.3	84	10	8.3	16	0.3	0.3	474	2.7	1.0	48	340	<1.0
29	159	W-RS	0.1922	3.81	1.2	7.4	64	6.7	6.2	11	0.3	0.6	412	2.6	2.4	47	279	<1.0
30	161	W-RS	0.1946	3.93	1.1	8.6	45	5.8	5.6	10	0.2	0.6	321	2.4	2.8	44	219	<1.0
31	164	Wet	0.0930	3.91	1.1	7.6	38	4.3	4.7	8.2	0.1	0.5	270	2.0	2.3	41	178	<1.0
32	166	Wet	0.0747	3.93	1.0	6.4	35	4.2	4.5	2.3	0.1	0.2	268	1.8	1.9	42	172	<1.0
33	168	Wet	0.0937	3.80	1.5	8.2	35	4.9	9.1	2.6	<0.1	2.0	292	1.8	3.0	46	201	<1.0
34	175	Dry	0.0808	3.64	1.2	7.8	41	6.0	7.4	10	0.1	0.2	323	2.2	2.5	50	220	<1.0
35	203	Dry-TS	0.0465	3.74	1.1	6.0	57	6.7	13	13	0.4	2.5	432	2.0	2.5	49	282	NA
36	206	Dry-TS	0.0877	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
37	210	Dry-TS	0.0893	3.61	4.5	10.2	77	10	25	19	0.3	0.9	596	3.2	2.9	59	398	NA
38	245	Dry	0.0506	3.55	3.9	11.8	86	13	33	25	0.6	0.4	715	2.5	3.0	50	491	NA
39	250	Wet	0.0847	3.62	4.7	9.2	99	14	35	33	0.8	0.6	849	3.0	3.9	56	573	NA
40	252	Wet	0.0932	3.61	3.5	10.6	99	16	45	35	0.7	0.9	882	3.9	2.8	57	619	NA
41	257	Wet	0.0898	3.60	2.8	10.3	95	15	42	31	0.7	0.6	812	3.5	2.2	54	577	NA
42	259	Wet	0.0995	3.56	3.0	8.2	94	15	40	30	0.6	0.4	818	3.3	3.3	54	572	NA

RS- Rain on snow.
TS- Thunderstorm.
NA- Not analyzed.

Table 13. - Results of sand column, S3, elemental concentrations in milligrams per liter

Leaching	Leaching time, days	Period in cycle	Leachate recovered, L	pH	Na	K	Ca	Mg	Al	Mn	Fe	Cu	Zn	Cd	Pb	Si	S	Cl
0	1	Draining	0.0944	3.99	NA	NA	46	13	1.4	6.4	0.1	0.6	34	0.28	5.6	11	76	10.5
1	10	Wet	0.0545	3.98	5.2	5.8	80	17	2.0	12	0.0	0.6	72	0.49	3.5	19	143	3.1
2	13	Wet	0.0852	4.09	5.0	5.8	82	16	2.8	14	0.1	0.5	83	0.55	1.7	21	148	3.0
3	17	Wet	0.0917	4.05	6.7	3.5	131	26	4.5	22	<0.1	1.0	156	1.11	2.0	27	229	2.7
4	20	Wet	0.0897	3.95	6.4	3.9	141	29	5.3	25	0.1	1.0	195	1.34	2.7	30	258	2.7
5	24	Wet	0.0897	3.99	5.5	7.1	127	29	7.5	24	0.1	1.0	188	1.34	3.0	30	255	<0.5
6	27	Wet	0.0899	3.91	5.4	5.5	132	29	5.4	24	0.1	0.9	188	1.31	1.1	30	261	4.2
7	32	Wet	0.0816	3.99	5.7	5.8	149	28	5.5	30	0.1	0.9	224	1.4	2.0	33	291	8.6
8	35	Wet	0.0792	3.94	NA	NA	NA	NA	NA	NA	NA	0.8	232	1.64	4.1	NA	303	<0.5
9	38	W-RS	0.1980	3.97	NA	NA	NA	NA	NA	NA	NA	1.6	125	0.89	2.6	NA	123	<0.5
10	40	W-RS	0.1934	3.99	NA	NA	NA	NA	NA	NA	NA	1.0	257	1.58	3.4	NA	214	<0.5
11	42	W-RS	0.1909	3.88	2.0	7.4	78	16	3.9	13	0.1	0.8	175	1.2	2.5	29	180	<0.5
12	45	Wet	0.1046	4.00	2.0	6.7	75	14	3.3	12	0.1	0.8	171	1.2	3.0	31	175	<0.5
13	47	Wet	0.0948	4.03	1.8	NA	69	10	1.8	11	<0.1	0.7	156	1.1	1.7	28	72	<0.5
14	49	Wet	0.1164	3.87	1.3	8.7	72	10	2.8	10	0.8	0.7	149	0.9	2.1	31	169	<0.5
15	56	Dry	0.0857	3.92	1.8	9.1	87	9.2	2.4	12	0.1	0.3	159	1.0	1.9	31	182	<0.5
16	84	Dry-TS	0.0563	3.84	1.8	7.4	102	14	4.0	21	<0.1	0.7	256	1.8	2.9	37	245	<0.5
17	87	Dry-TS	0.0822	3.93	1.4	6.5	113	16	5.8	22	0.2	0.9	328	2.2	2.4	41	280	<0.5
18	91	Dry-TS	0.0833	3.87	3.5	9.6	154	20	8.5	30	0.2	1.1	449	2.8	3.1	48	383	<0.5
19	125	Dry	0.0513	3.88	3.1	10.8	163	21	12	33	0.1	1.2	575	3.6	2.7	48	474	NA
20	130	Wet	0.0912	3.70	3.3	10.2	161	24	14	38	2.5	1.3	593	3.8	2.9	49	483	<1.0
21	132	Wet	0.0983	3.82	4.1	14.2	171	24	24	35	0.1	2.9	650	4.1	2.8	54	528	<1.0
22	136	Wet	0.0946	3.79	3.5	10.2	178	27	21	39	0.4	1.7	756	4.7	3.5	53	579	<1.0
23	139	Wet	0.0909	3.79	3.5	11.8	164	24	31	39	0.5	1.6	761	4.6	2.4	53	542	<1.0
24	143	Wet	0.0848	3.80	4.1	13.4	159	21	32	33	0.4	1.6	762	4.6	2.1	55	539	<1.0
25	146	Wet	0.0928	3.81	3.0	12.2	121	17	17	28	0.4	1.4	605	4.1	2.2	49	454	<1.0
26	151	Wet	0.0855	3.76	1.6	8.9	110	13	16	21	0.4	1.3	607	3.8	2.6	53	429	<1.0
27	154	Wet	0.0846	3.70	1.5	7.2	94	13	17	24	0.3	1.4	564	3.6	1.6	52	413	<1.0
28	157	W-RS	0.1877	3.71	1.3	6.4	75	10	15	16	0.3	1.6	470	3.1	2.3	51	347	3.9
29	159	W-RS	0.1922	3.75	1.2	7.9	57	6.9	11	11	0.2	2.1	390	2.5	1.7	47	267	<1.0
30	161	W-RS	0.1940	3.84	1.1	7.6	41	6.0	9.7	10	0.1	1.8	302	2.1	1.4	42	219	<1.0
31	164	Wet	0.0917	3.84	1.2	6.7	39	5.1	9.5	9.4	0.1	1.7	294	2.1	2.1	44	207	<1.0
32	166	Wet	0.0800	3.85	1.0	6.9	36	5.0	8.5	2.6	0.2	1.3	290	1.8	1.5	43	199	<1.0
33	168	Wet	0.0913	3.74	1.2	8.7	37	4.4	9.2	7.8	0.2	1.5	296	1.9	3.0	47	203	<1.0
34	175	Dry	0.0725	3.67	1.2	8.3	43	6.8	13	11	0.3	1.3	347	2.4	2.7	53	241	<1.0
35	203	Dry-TS	0.0388	3.71	1.3	8.3	56	7.8	17	14	0.6	3.2	465	2.7	3.2	53	316	NA
36	206	Dry-TS	0.0912	3.66	1.6	8.5	69	8.4	17	17	0.4	0.7	516	2.5	2.9	59	362	NA
37	210	Dry-TS	0.0000	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
38	245	Dry	0.0419	3.51	5.3	14.6	100	16	52	32	0.7	1.1	916	4.0	3.1	60	634	NA
39	250	Wet	0.0814	3.58	4.6	10.8	86	14	43	30	0.9	0.8	832	3.7	3.3	57	573	NA
40	252	Wet	0.0913	3.56	3.4	12	84	16	56	35	0.9	1.0	870	4.5	2.6	58	606	NA
41	257	Wet	0.0895	3.52	3.3	10.4	86	18	61	34	0.9	1.2	940	5.0	2.8	59	679	NA
42	259	Wet	0.0967	3.49	3.2	11.3	79	17	56	31	0.7	1.2	898	5.0	2.8	57	647	NA

RS- Rain on snow.
TS- Thunderstorm.
NA- Not analyzed.

Table 14. - Results of fine column, F1, elemental concentrations in milligrams per liter

Leaching	Leaching time, days	Period in cycle	Leachate recovered, L	pH	Na	K	Ca	Mg	Al	Mn	Fe	Cu	Zn	Cd	Pb	Si	S	Cl
0	1	Draining	0.2496	3.45	NA	NA	45	13	2.3	17	0.1	0.8	49	0.41	4.2	13	89	45
1	10	Wet	0.0809	3.97	4.8	6.5	56	15	3.1	45	<0.1	0.9	73	0.53	2.4	19	143	3.2
2	13	Wet	0.0929	3.98	4.4	5.9	51	14	4.1	48	<0.1	0.9	67	0.54	1.2	20	133	2.6
3	17	Wet	0.0930	3.95	5.3	4.5	62	15	5.5	72	0.1	1.3	84	0.61	2.8	23	159	3.0
4	20	Wet	0.0921	3.80	5.1	0.2	65	18	6.8	77	4.2	1.5	88	0.62	4.1	28	179	2.5
5	24	Wet	0.0926	3.76	3.9	6.2	50	13	8.0	55	1.6	1.0	74	0.56	2.4	26	138	4.4
6	27	Wet	0.0899	3.60	3.6	5.4	48	14	8.8	59	15	1.0	72	0.53	2.8	25	152	<0.5
7	32	Wet	0.0897	3.50	4.3	6.8	47	13	6.6	53	14	1.0	61	0.4	2.2	27	142	15
8	35	Wet	0.0915	3.58	NA	NA	NA	NA	NA	NA	NA	0.6	56	0.29	2.6	NA	160	5.2
9	38	W-RS	0.1884	3.64	NA	NA	NA	NA	NA	NA	NA	0.5	51	0.38	3.0	NA	163	<0.5
10	40	W-RS	0.1897	3.72	NA	NA	NA	NA	NA	NA	NA	0.2	49	0.33	1.4	NA	140	<0.5
11	42	W-RS	0.1929	3.61	2.7	6.3	33	9.7	2.3	35	68	0.2	43	0.3	3.4	20	133	1.0
12	45	Wet	0.0870	3.50	2.3	4.3	31	9.0	3.4	34	23	0.3	47	0.3	3.7	21	108	<0.5
13	47	Wet	0.0942	3.54	2.3	0.0	31	8.2	1.8	32	65	0.1	42	0.3	1.8	21	87	<0.5
14	49	Wet	0.0944	2.78	1.5	6.2	28	6.6	2.1	27	8.4	0.1	36	0.2	2.3	20	114	<0.5
15	56	Dry	0.0785	3.12	2.5	7.7	36	7.7	4.8	31	1.4	0.3	48	0.3	3.3	25	117	<0.5
16	84	Dry-TS	0.0768	3.23	1.1	1.4	5.5	1.5	1.6	5.7	0.1	0.3	20	0.1	10.4	3	21	NA
17	87	Dry-TS	0.0557	3.04	1.8	2.5	47	14	8.4	48	16	0.2	71	0.5	2.6	34	161	<0.5
18	91	Dry-TS	0.1144	2.80	3.9	7.4	60	18	10.0	66	57	0.2	89	0.4	3.1	41	256	<0.5
19	125	Dry	0.0956	3.48	1.8	0.7	15	4.3	3.3	17	0.5	0.2	31	0.1	5.7	9	56	NA
20	130	Wet	0.0433	2.90	3.6	6.5	56	22	9.0	76	159	0.0	84	0.5	3.4	39	284	<1.0
21	132	Wet	0.0792	3.64	4.2	6.6	60	20	6.7	70	314	<0.1	89	0.4	2.4	39	322	4.5
22	136	Wet	0.0747	3.19	3.8	5.0	60	22	5.2	74	306	0.1	90	0.4	1.7	38	348	5.2
23	139	Wet	0.0701	3.13	4.0	7.8	61	21	7.0	84	357	0.1	94	0.2	1.5	40	361	<1.0
24	143	Wet	0.0342	3.01	7.2	6.8	62	21	7.9	78	285	<0.1	90	0.2	1.2	37	358	<1.0
25	146	Wet	0.0875	2.90	3.7	7.1	58	21	4.5	80	285	0.1	85	0.3	1.3	38	331	<1.0
26	151	Wet	0.0459	2.89	2.2	6.2	58	18	4.4	71	247	0.1	81	0.2	1.3	39	354	<1.0
27	154	Wet	0.0534	2.76	2.0	6.1	57	20	4.6	84	247	0.1	77	0.1	0.3	40	367	3.9
28	157	W-RS	0.0373	2.81	1.9	5.1	56	20	4.4	73	314	<0.1	77	0.1	0.6	38	369	<1.0
29	159	W-RS	0.0315	2.86	2.0	5.7	56	18	4.1	69	305	0.1	78	0.3	0.9	38	356	6.0
30	161	W-RS	0.0537	2.74	2.1	6.7	56	21	4.5	84	186	0.1	78	0.3	1.5	39	360	<1.0
31	164	Wet	0.0627	2.79	2.2	5.8	56	19	4.7	82	211	0.1	77	0.3	1.0	38	362	<1.0
32	166	Wet	0.0218	2.96	2.4	6.8	41	13	3.0	16	215	<0.1	55	0.2	0.1	27	261	<1.0
33	168	Wet	0.1288	2.91	1.0	6.2	54	17	3.6	70	333	<0.1	77	0.3	0.6	39	363	<1.0
34	175	Dry	0.2049	2.61	1.9	6.4	51	20	3.5	78	206	<0.1	69	0.1	1.1	39	353	<1.0
35	203	Dry-TS	0.3078	2.77	1.3	4.3	43	14	2.1	51	169	1.2	61	0.1	1.2	35	305	NA
36	206	Dry-TS	0.0653	2.68	1.1	6.5	36	11	5.4	35	2.1	0.6	63	0.4	3.8	33	131	NA
37	210	Dry-TS	0.0808	2.63	4.3	9.0	40	13	7.1	38	5.1	0.6	67	0.4	4.1	36	145	NA
38	245	Dry	0.0601	2.82	3.7	9.0	43	12	7.5	46	48	0.1	84	1.7	3.7	38	196	NA
39	250	Wet	0.0582	2.92	3.5	7.8	33	10	5.3	39	89	0.2	60	1.0	2.4	33	190	NA
40	252	Wet	0.1004	2.97	2.2	6.4	29	8.8	4.3	37	160	<0.1	51	0.6	2.4	31	207	NA
41	257	Wet	0.0544	2.96	1.7	6.4	25	7.6	3.8	30	140	<0.1	44	0.4	3.6	27	189	NA
42	259	Wet	0.1497	2.88	1.5	5.1	23	7.1	3.1	27	126	<0.1	42	0.4	2.6	27	179	NA

RS- Rain on snow.
TS- Thunderstorm.
NA- Not analyzed.

Table 15. - Results of fine column, F2, elemental concentrations in milligrams per liter

Leaching	Leaching time, days	Period in cycle	Leachate recovered, L	pH	Na	K	Ca	Mg	Al	Mn	Fe	Cu	Zn	Cd	Pb	Si	S	Cl
0	1	Draining	0.5540	3.83	NA	NA	50	14	2.6	24	<0.1	0.8	54	0.46	4.7	16	106	6.0
1	10	Wet	0.1079	3.91	4.5	5.0	52	16	3.1	50	0.1	0.8	67	0.43	2.5	19	139	3.3
2	13	Wet	0.0996	3.72	3.8	5.4	49	15	3.8	57	2.3	0.7	64	0.45	2.0	19	134	NA
3	17	Wet	0.0953	3.70	5.8	2.1	73	19	6.2	92	5.6	1.1	92	0.68	3.7	25	197	3.2
4	20	Wet	0.0471	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
5	24	Wet	0.0960	3.56	5.0	4.4	66	19	10.5	78	18	0.9	91	0.73	3.2	29	203	<0.5
6	27	Wet	0.0873	3.46	5.6	3.9	67	21	8.6	85	51	0.7	81	0.6	1.7	29	221	5.0
7	32	Wet	0.0957	3.35	6.1	8.7	70	21	8.4	92	46	0.6	87	0.6	1.8	32	228	23
8	35	Wet	0.0952	3.36	NA	NA	NA	NA	NA	NA	NA	0.4	85	0.64	2.7	NA	254	6.3
9	38	W-RS	0.1404	3.39	NA	NA	NA	NA	NA	NA	NA	1.9	61	0.44	1.6	NA	221	<0.5
10	40	W-RS	0.1287	3.33	NA	NA	NA	NA	NA	NA	NA	0.4	93	0.61	2.4	NA	260	<0.5
11	42	W-RS	0.2108	3.12	5.4	9.6	71	23	10.9	91	96	0.4	92	0.7	2.2	32	281	<0.5
12	45	Wet	0.1106	3.14	4.2	6.6	65	21	9.1	83	86	0.3	77	0.5	2.6	30	250	<0.5
13	47	Wet	0.0955	3.09	4.3	2.7	67	18	7.6	91	87	0.3	81	0.5	2.4	31	NA	<0.5
14	49	Wet	0.0941	2.74	3.6	9.2	66	17	8.8	80	40	0.2	72	0.4	1.6	33	259	<0.5
15	56	Dry	0.0768	2.79	4.2	8.0	74	18	10.2	76	36	0.4	78	0.5	1.6	35	265	<0.5
16	84	Dry-TS	0.0961	2.75	2.9	6.4	76	24	18.3	113	58	0.4	90	0.5	2.3	40	314	NA
17	87	Dry-TS	0.0963	3.08	2.3	7.1	72	23	6.3	93	514	<0.1	79	0.4	1.5	35	464	NA
18	91	Dry-TS	0.0907	2.64	4.0	5.4	84	25	14.5	104	166	0.1	85	0.4	2.1	43	404	<0.5
19	125	Dry	0.1087	3.04	3.7	7.4	68	23	16.5	99	111	0.1	83	0.5	3.3	46	294	NA
20	130	Wet	0.1010	2.99	3.9	7.6	72	22	6.5	77	247	<0.1	66	0.3	2.8	41	316	<1.0
21	132	Wet	0.1005	3.00	3.9	9.1	52	17	3.5	64	279	<0.1	62	0.3	1.7	35	309	<1.0
22	136	Wet	0.1004	2.66	3.9	6.9	52	19	2.6	65	169	0.1	63	0.2	1.9	34	308	<1.0
23	139	Wet	0.1003	2.88	3.7	8.9	52	18	3.6	70	255	0.1	65	0.2	0.3	36	298	3.4
24	143	Wet	0.0964	2.97	4.9	10.5	60	19	4.9	74	130	<0.1	72	0.1	1.3	38	319	<1.0
25	146	Wet	0.0959	2.89	3.6	8.1	51	18	2.0	70	237	<0.1	60	0.3	1.4	34	278	<1.0
26	151	Wet	0.0842	2.85	1.9	6.9	51	16	2.7	60	162	0.1	63	0.1	0.8	38	286	<1.0
27	154	Wet	0.0914	NA	1.7	12.5	55	17	5.4	33	81	<0.1	71	0.5	2.0	40	266	5.0
28	157	W-RS	0.1772	2.83	1.8	6.1	49	17	3.0	59	246	<0.1	60	0.2	1.2	37	298	<1.0
29	159	W-RS	0.1499	2.94	1.7	5.4	45	14	1.9	51	241	0.1	56	0.2	1.2	34	281	4.0
30	161	W-RS	0.2230	2.88	1.7	7.0	41	14	1.8	53	146	<0.1	50	0.3	1.8	32	245	<1.0
31	164	Wet	0.1094	2.93	1.6	4.3	37	12	1.7	49	138	<0.1	47	0.2	0.9	30	227	<1.0
32	166	Wet	0.0757	2.99	1.5	6.9	38	12	1.5	14	175	<0.1	49	0.2	0.9	32	234	<1.0
33	168	Wet	0.1069	3.05	1.1	6.3	37	11	1.5	42	204	<0.1	47	0.2	1.5	32	233	<1.0
34	175	Dry	0.0916	2.75	1.7	7.4	44	16	5.2	58	43	<0.1	61	0.5	2.6	41	205	<1.0
35	203	Dry-TS	0.0593	3.38	0.8	3.3	25	8.1	3.0	23	3.5	2.9	43	0.3	2.9	21	88	NA
36	206	Dry-TS	0.0893	3.16	1.4	5.7	44	14	2.1	51	185	<0.1	59	0.1	0.5	36	316	NA
37	210	Dry-TS	0.0926	2.99	4.0	6.7	47	15	2.7	55	171	0.2	55	0.0	0.4	35	305	NA
38	245	Dry	0.0667	3.45	2.6	4.9	17	4.7	2.0	14	0.8	0.4	28	0.2	4.3	11	51	NA
39	250	Wet	0.0940	3.45	3.2	8.2	32	10	5.2	33	1.6	0.9	57	0.3	5.0	24	105	NA
40	252	Wet	0.0976	3.46	2.5	8.9	33	10	6.1	35	2.7	0.8	61	0.3	3.8	28	115	NA
41	257	Wet	0.0975	3.42	2.3	7.6	35	12	7.8	39	3.2	0.9	65	0.5	4.1	29	127	NA
42	259	Wet	0.0983	3.30	2.3	9.1	37	13	8.1	40	1.8	1.0	67	0.5	3.8	31	132	NA

RS- Rain on snow.
TS- Thunderstorm.
NA- Not analyzed.

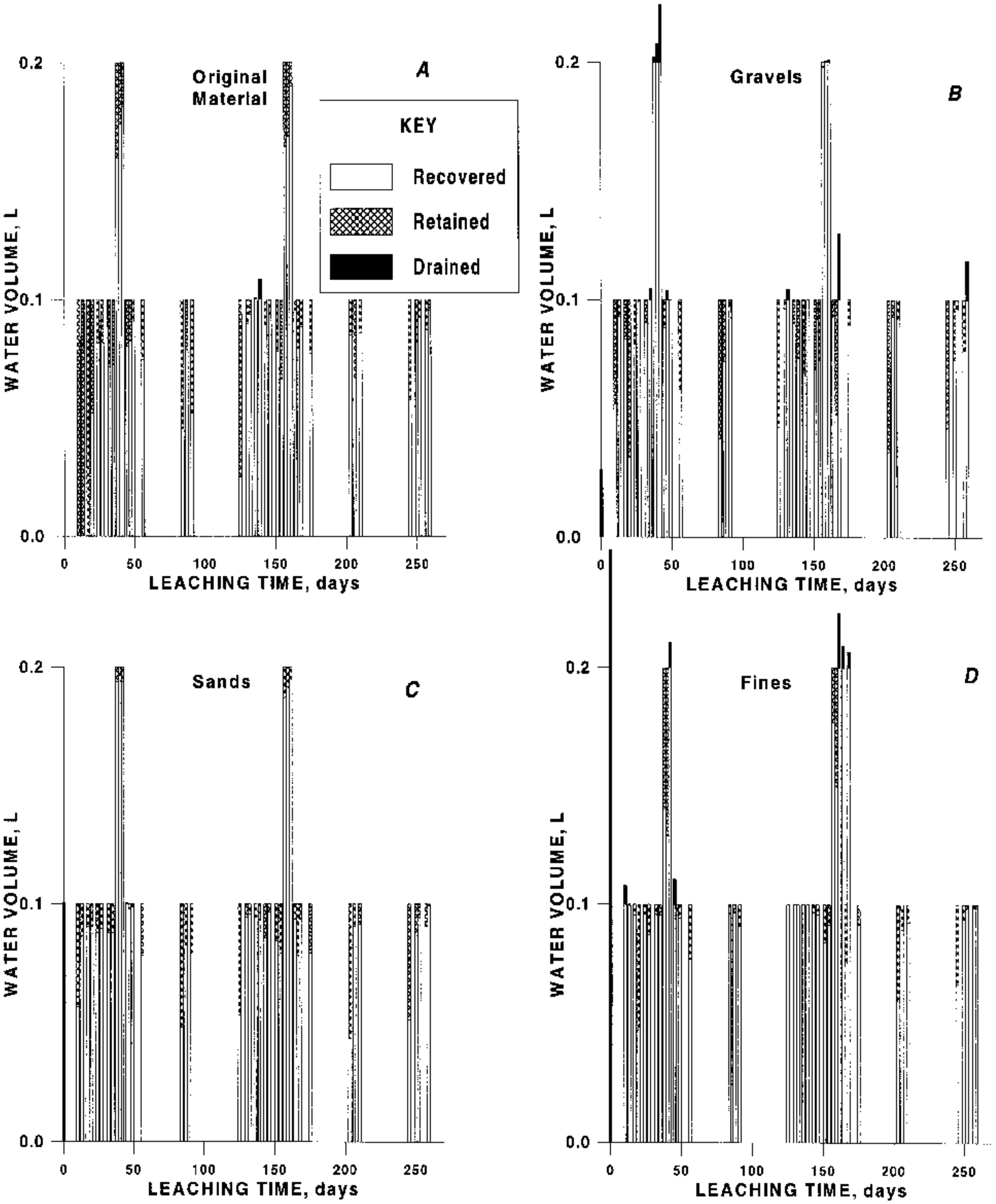

Figure 4.—Average water balances of columns containing original composite material, gravels, and sands, and water balance of full-height fine column. Water added to columns was recovered as leachate or retained by columns. Water recovered in excess of volume added (drained) originated from wet-screening separation or from previous leachings. Initially, 0.55 L drained from fine column.

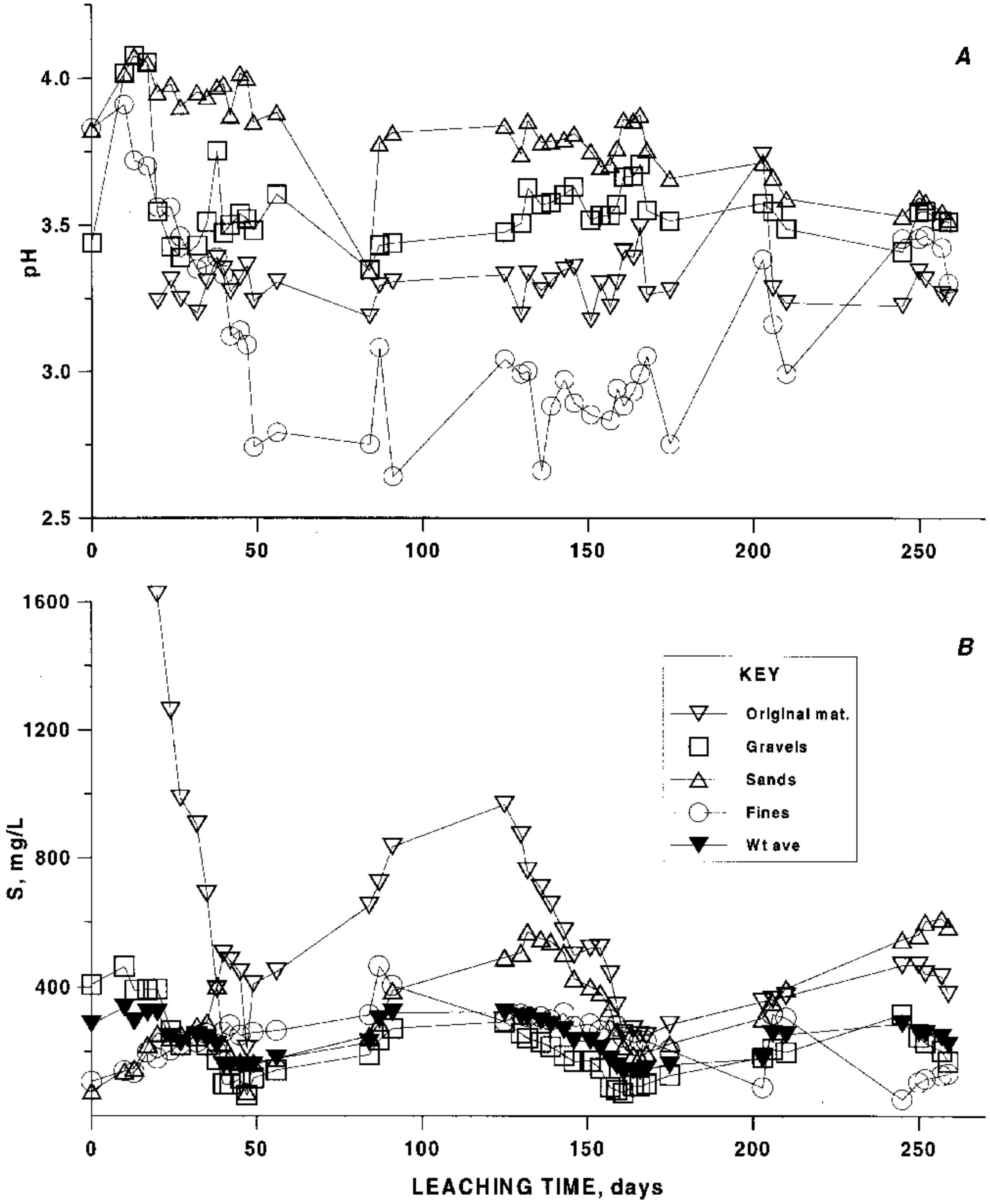

Figure 5.—Average leachate from triplicate columns containing original composite material, gravel fraction, and sand fraction, and from single column containing fine fraction. ***A*****, pH;** ***B*****, S. Weighted-average S concentrations were calculated from concentrations of three fractions and their respective contributions to mass of original composite material (61%, 15%, and 25%).**

Sulfate was the dominant anion in the column leachates. An initial comparison of the ICP analysis of S and the IC analysis of sulfate indicated that S was primarily in the sulfate form, within analytical errors. Therefore, the molar quantities of S and sulfate are assumed by be equivalent, and S from the ICP analysis is reported. Since pH's were generally below 4, no bicarbonate was expected. In addition, chloride concentrations were generally less than 10 mg/L and dropped below the detection limit of 1 mg/L by the seventh leaching (tables 6, 7, and 8).

The initial S in the leachates from columns containing the original composite material decreased from 1,300 to about 300 mg/L during the first wet cycle (figure 5*B*). This decrease was probably a result of the flushing of secondary sulfate precipitates present in this waste material, which had not recently been in contact with water. S then increased to 1,000 mg/L after the first dry cycle, which is indicative of flushing of oxidation products from sulfide minerals during the dry cycle (Doepker, 1991). The decrease during the wet cycle and the increase after the dry cycle were repeated in the second cycle, although to a lesser extent. S concentrations of the leachates of the three types of segregated material were much lower (100 to 200 mg/L). The leachates of the segregated columns showed the same pattern as the columns containing original composite material, with the sand column exhibiting the greatest increase after the dry cycle. The weighted-average concentrations of the segregated columns were much less than those from the columns containing the original composite material.

Zn^{2+} was the dominant cation in the leachates from the original composite material, gravels, and sands. Agreements in the trends and absolute values of Zn concentrations in the triplicate columns containing original composite material, the gravel fraction, and the sand fraction were very good (figure 6). The erratic behavior of the half-height column of fines (F1) because of ponding is shown in figure 6, justifying its elimination from subsequent consideration. As with S, the highest Zn concentrations were found in the columns containing original composite material (figure 7*A*). The first leachate from the columns containing original composite material averaged 1,600 mg/L and decreased to 400 mg/L as secondary pre- cipitates were flushed from the column. As with S, there were significant increases after both dry periods and decreases during both wet periods.

Initial Zn concentrations in the leachate from the gravel columns were significantly higher than those from the sand and fine columns. Visual examination revealed that the wet screening was not totally effective, and that fine and sand particles were still attached to the surfaces of the gravels. With the removal of the free fines and sands between the gravels, the column containing the gravels essentially became a thin-film reactor, with the fines and sands being the reactive components. At the end of the first wet cycle, the leachate from the gravels had decreased to 100 mg/L. The decrease during the second wet cycle in the gravel columns was similar to the decrease in the first cycle, and the increase after the second dry cycle was similar to the increase after the first dry cycle. The leachate in the sand columns increased from near zero to about 300 mg/L at the beginning of the first wet cycle and then decreased to about 100 mg/L during the first simulated rain-on-snow event. In contrast to the gravel columns, Zn concentrations in the leachates from the sand columns increased to 600 mg/L after the first dry cycle and reached concentrations of 900 mg/L after the second dry cycle. Zn concentrations in the leachate from the fines were much lower and ranged between 40 and 80 mg/L. The behavior of Cd in the leachate of all columns paralleled that of Zn (figure 7*B*). As with Zn, the weighted-average Cd con- centrations of the segregated columns were less than those of columns containing the original composite material.

The concentrations of Ca, Mg, and Mn in the columns containing the original composite material were initially higher than the respective concentrations from the segregated columns that had contact with tap water (figure 8). As with Zn, the Ca in the sand columns was higher than in any other column type. In contrast, Mg concentrations were the highest in the columns containing the original composite material. After the initial flushing of Mn from the original composite material, the fines column exhibited the highest Mn concentrations, possibly because of the lower pH. Na and K releases for all columns were low (figure 9) with K releases being greater than Na releases. During the second wet cycle, the major cations exhibited different trends. Na releases in the second cycle were less than in the first cycle for all columns. K releases from the columns containing the original composite material, the sand fraction, and the fine fraction were equal during the two cycles whereas they decreased in the gravel columns.

Si concentrations in the columns containing original composite material were higher than in the segregated columns and did not show the initial flushing seen in most of the other elements (figure 10*A*). Si in the columns containing original composite material reached a maximum of 70 mg/L. After the first three leachings of the segregated columns, all the columns were saturated or supersaturated with respect to silica. The saturation index [log(ion activity product/K_{sp})] of silica was higher for the original composite material than the segregated columns.

Al concentrations in the leachate from the segregated columns were much lower than concentrations from columns containing the original composite material (figure 10*B*). Sig- nificant amounts of Fe were found only in leachate from the fines (figure 10*C*).

Cu was flushed from the columns containing the original composite material and the gravel fraction during both wet cycles (figure 11*A*). Cu concentrations in the leachate from the segregated fractions were low. The behavior of Pb was anomalous in that the segregation of the columns increased the concentrations of Pb in the leachate (figure 11*B*). The gravel column generally produced the highest leachate Pb con- centrations. The leachate from all columns was near saturation or slightly undersaturated with respect to anglesite, and there did not seem to be any difference in the saturation index among the columns.

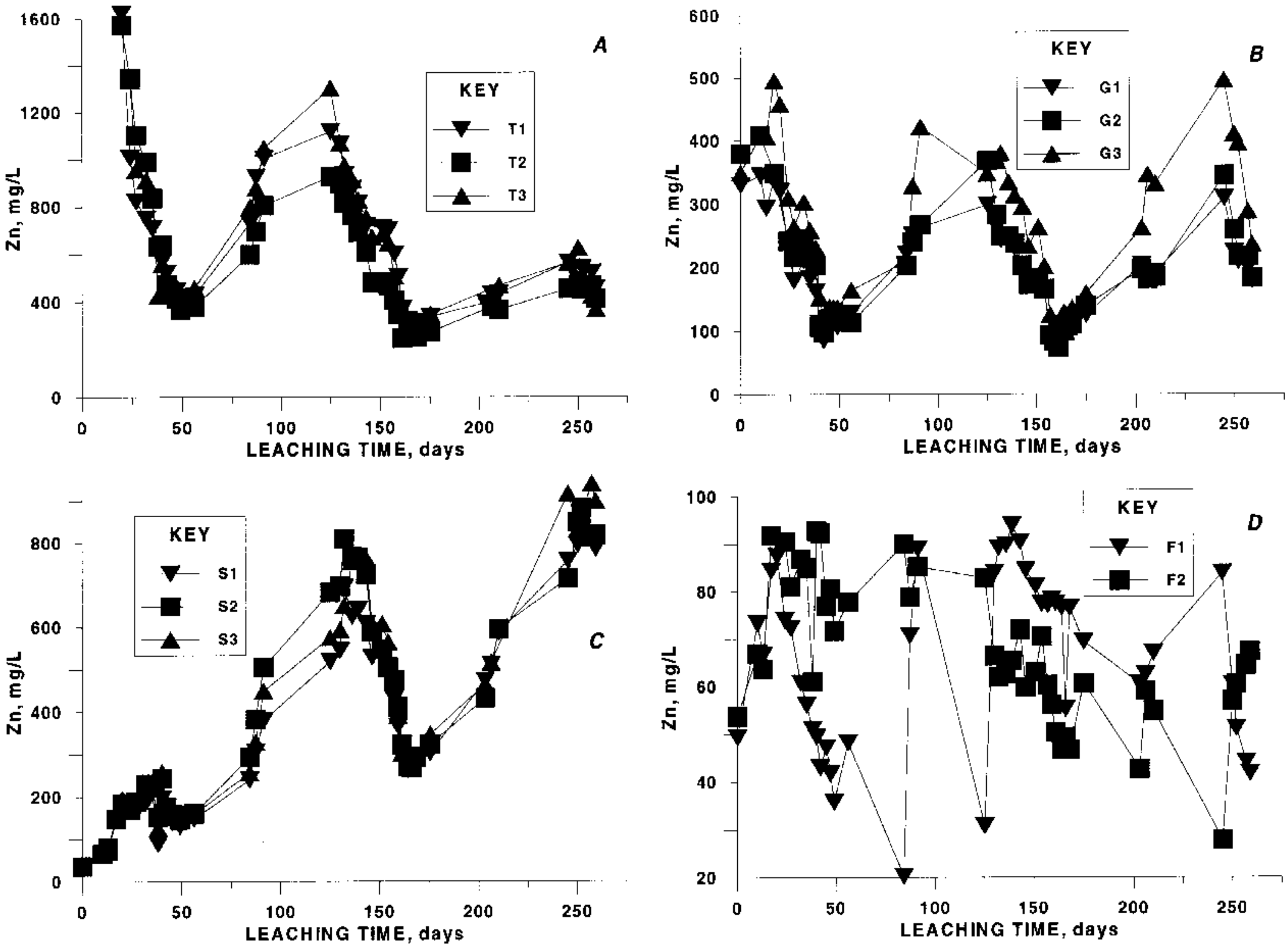

Figure 6.—Results of leachate analyses of Zn for replicate columns. *A*, Triplicate columns containing original material; *B*, triplicate columns containing gravel fraction; *C*, triplicate containing sand fraction; *D*, half-height (F1) and full-height (F2) columns containing the fine fraction. Because of ponding of leachant over the column, F1 was disregarded.

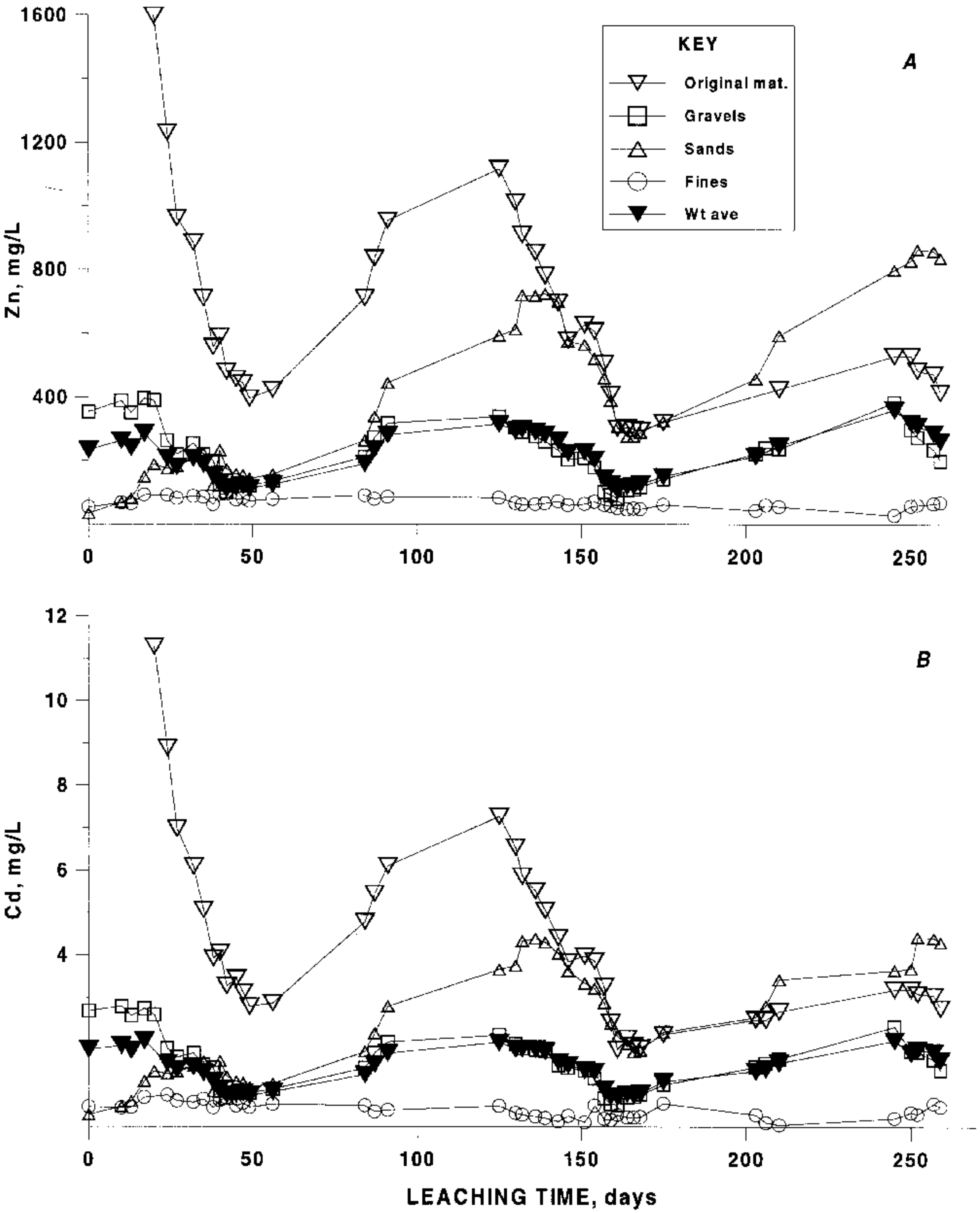

Figure 7.—Average leachate measurements of (*A*) Zn and (*B*) Cd from triplicate columns containing original composite material, gravel fraction, and sand fraction, and from single column containing fine fraction. Weighted-average concentrations were calculated from concentrations of three fractions and their respective contributions to mass of original composite material (61%, 15%, and 25%).

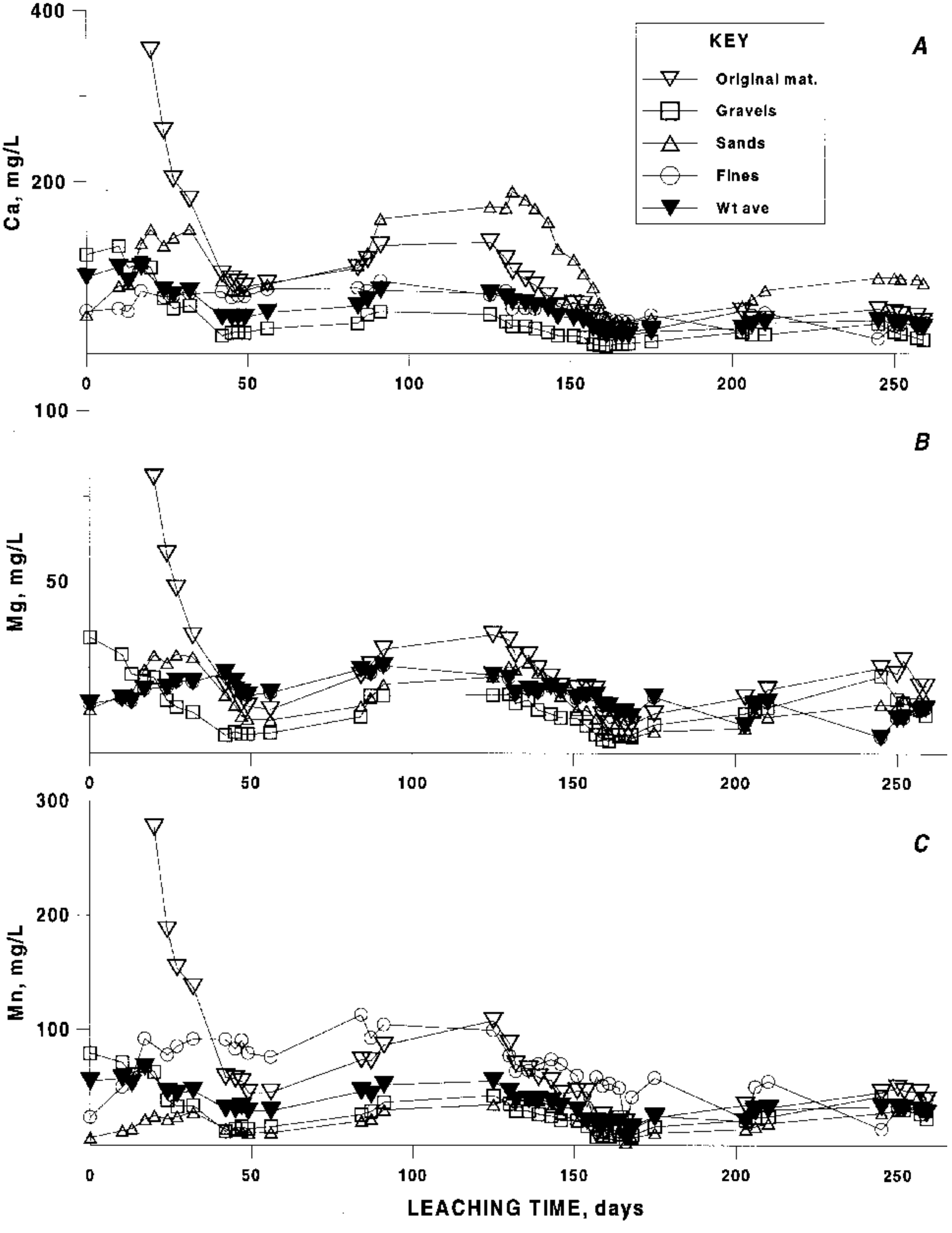

Figure 8.—Average leachate measurements of (*A*) Ca, (*B*) Mg, and (*C*) Mn from triplicate columns containing original composite material, gravel fraction, and sand fraction, and from single column containing fine fraction. Weighted-average concentrations were calculated from concentrations of three fractions and their respective contributions to mass of original composite material (61%, 15% and 25%).

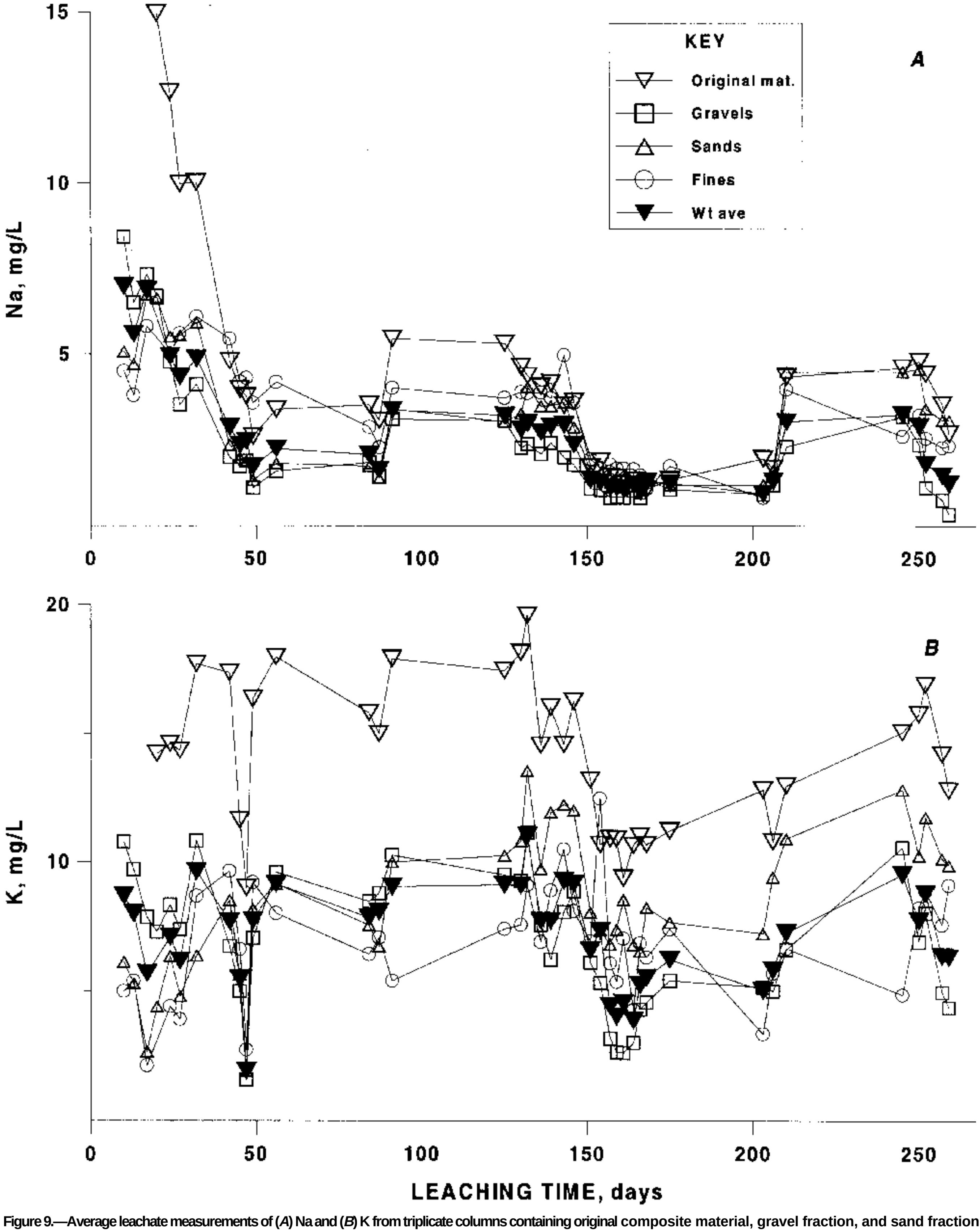

Figure 9.—Average leachate measurements of (*A*) Na and (*B*) K from triplicate columns containing original composite material, gravel fraction, and sand fraction, and from single column containing fine fraction. Weighted-average concentrations were calculated from concentrations of three fractions and their respective contributions to mass of original composite material (61%, 15%, and 25%).

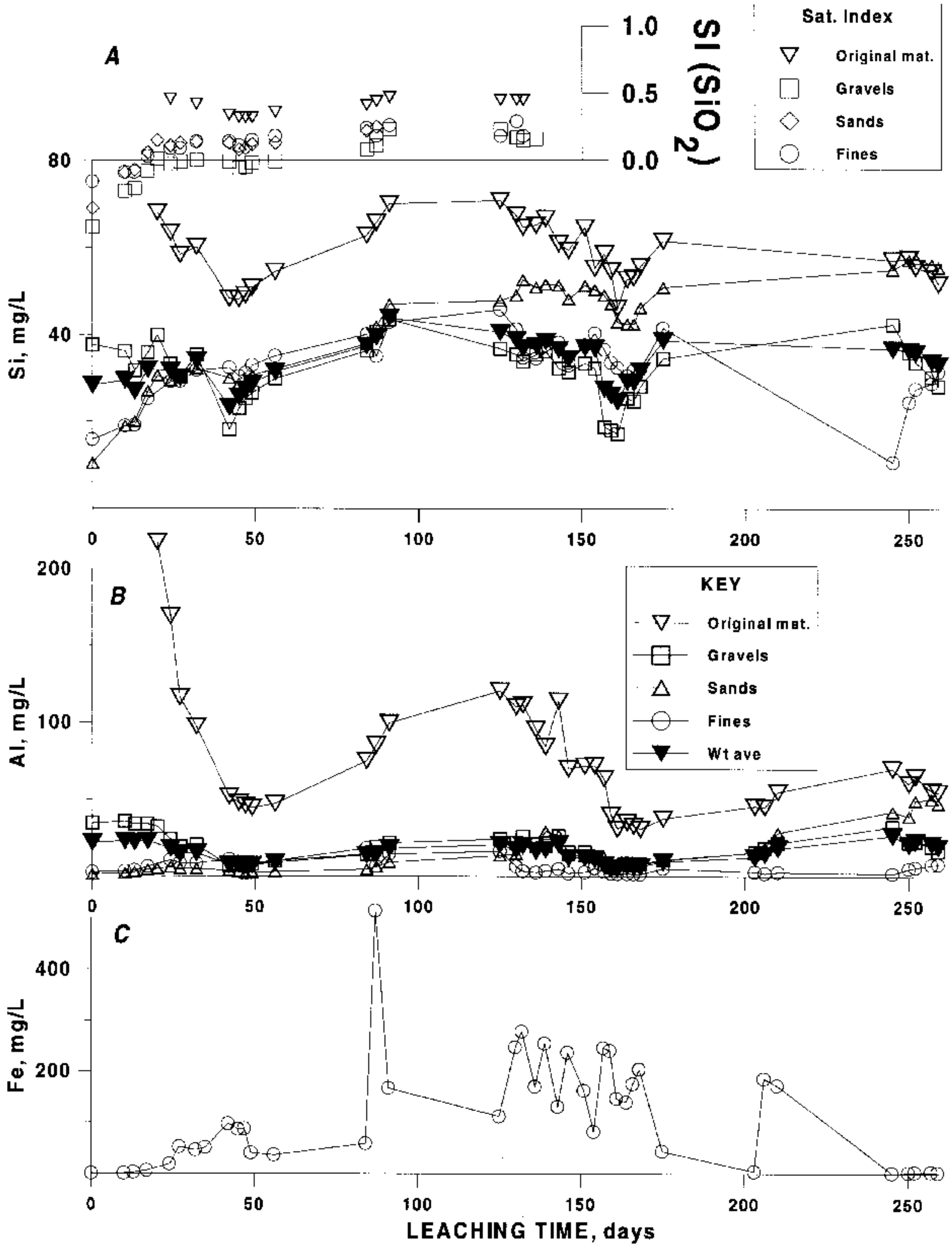

Figure 10.—Average leachate measurements of Si, Al, and Fe from triplicate columns containing original composite material, gravel fraction, and sand fraction, and from single column containing the fine fraction. Weighted-average concentrations were calculated from concentrations of three fractions and their respective contributions to mass of original composite material (61%, 15% and 25%). *A*, Si with saturation index of amorphous silica during first wet-dry cycle; *B*, Al; *C*, Fe in fines column only.

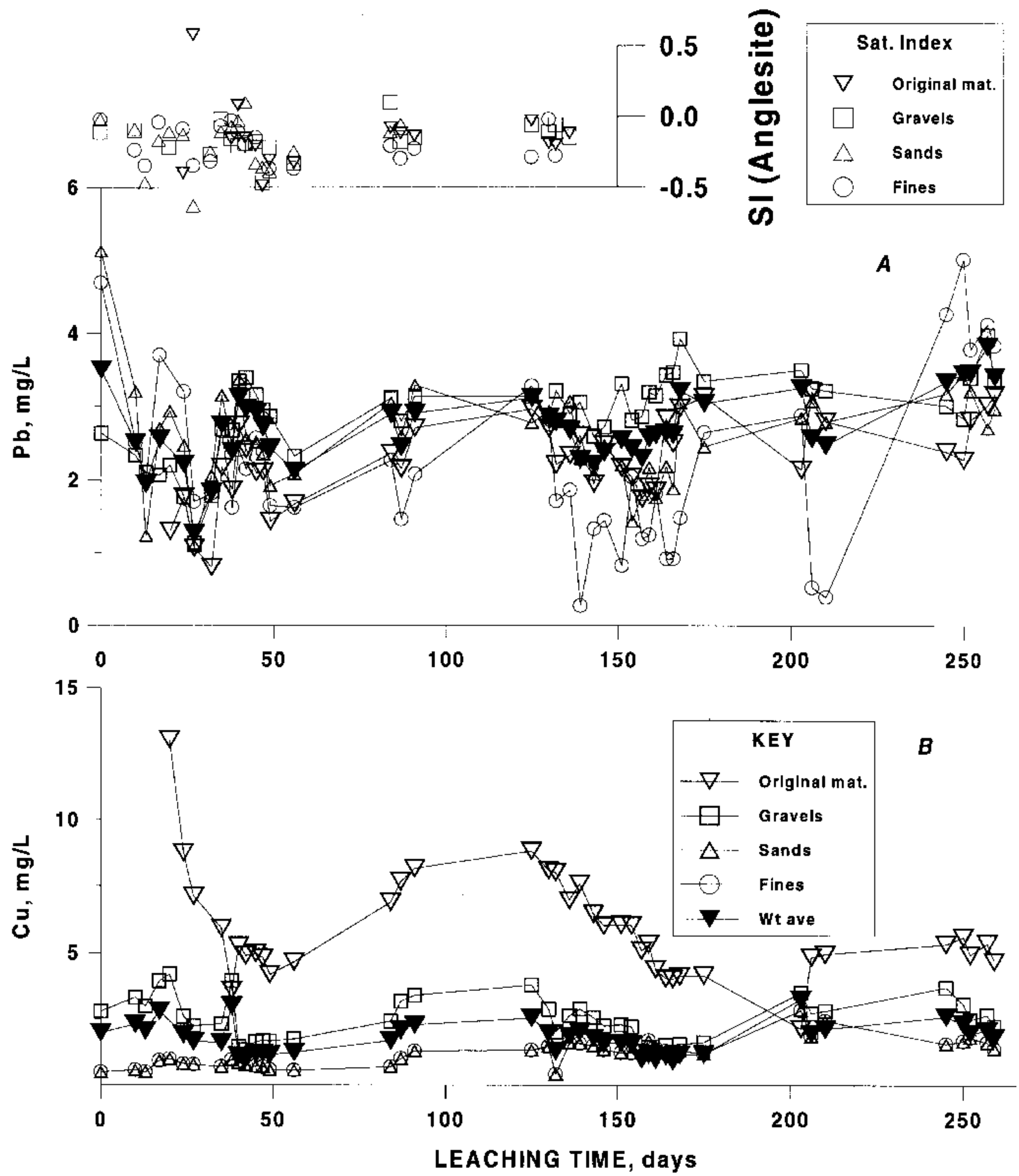

Figure 11.—Average leachate measurements of Pb and Cu from triplicate columns containing original composite material, gravel fraction, and sand fraction, and from single column containing fine fraction. Weighted-average concentrations were calculated from concentrations of three fractions and their respective contributions to mass of original composite material (61%, 15%, and 25%). *A*, Pb with saturation index of anglesite during first wet-dry cycle; *B*, Cu.

Humidity Cell Tests

Kinetic humidity cell tests were performed on duplicate 300-g samples of the fine fraction of the original composite material. Over a period of 281 days, 40 7-day cycles were conducted. Each cycle consisted of 3 days of dry air circulation, 3 days of wet air circulation, and leaching with about 150 mL of water during the last day. Of the 150 mL, approximately 100 mL was recovered, while 50 mL was retained by the solids (tables 16 and 17). Most of the retained 50 mL was lost by evaporation during circulation of dry air. The pH for both cells ranged between 3.3 and 3.5 (figure 12*A*). This value was similar to the pH of the leachate from the fine column during the first wet cycle. However, the pH of the leachate from the humidity cells throughout much of the later part of the tests was higher than the pH during the later part of the column leaching tests. The ORP of the humidity cell leachate ranged between 450 and 500 mV for cell 1 and was slightly lower for cell 2 (~450 mV).

Concentrations of many of the constituents of the leachate decreased dramatically during the first eight cycles and then declined gradually during the last 32 cycles. Sulfate concentrations in cell 1 decreased from an initial 540 mg/L to 190 mg/L during the eighth cycle (tables 18 and 19). Likewise, sulfate concentrations in cell 2 decreased from 520 mg/L during the second cycle to 160 mg/L during the eighth cycle. At the end of the experiment, sulfate concentrations in both cells were 99 mg/L. The patterns of Zn release (figure 12*B*) and most other elements from the humidity cells containing the fine fraction were very similar to the release of sulfate. Except for the spike during the second cycle in both cells, Zn decreased from an initial concentration of about 80 mg/L to 35 mg/L and 27 mg/L in cells 1 and 2, respectively, during the eighth cycle. Pb release was much lower than the release of Zn and reached a maximum during the third cycle.

SEPARATION TESTS

Separation of Fines and Sands from Gravels

The results of the column leaching tests indicated that the fines and sands physically adhering to the surface of the coarser gravels may have initially controlled the release of metals from the gravel fraction during the column leaching tests. Separation tests were conducted to test this hypothesis and to determine the relationship between the effectiveness of separation and subsequent initial metal release. Separation treatments to remove the finer material from the gravels were conducted using four dry methods (aliquots GS1, GS2, GS5, and GS6), three wet methods using tap water (aliquots GS3, GS7, and GS8), and three wet methods using distilled water (aliquots GS13, GS15, and GS16) (table 1). For the wet methods, the volume of wash water was measured and sampled for pH, cations, and anions. The amount of fines and sands recovered during both wet and dry treatment were measured.

Static tests were then conducted in which the resulting treated gravels were subjected to a 2-h bottle roll with cold distilled water. During this short period, it was assumed that the release of metals occurred through dissolution of soluble salts rather than by the direct oxidation of sulfide minerals. Therefore, static tests should be a good indicator of initial release of metals from treated material. The amount of fines and sands recovered during the static bottle roll tests was also determined for most samples in most experiments.

The fines and sands recovered had either been washed off the larger gravel fraction or been created during the treatment. The aliquot of the test gravel material that did not undergo any further treatment after dry separation (split only) was con- sidered as the control for the amount of fines and sands that could be washed from the gravel fraction. About 4% of the mass of the dry-screened gravel fractions was removed as -1-mm particles during static bottle roll tests (figure 13*A*). About 2% (22.2 g of fines in 993.2 g of charge) was loose dust that was recovered during the 15-min separation in the vibrating, percussion, grain-size Ro-Tap analyzer. The amount of -1-mm material collected after 15 min of tumbling (aliquot GS5) was low (12.0 g) compared to the amount collected from the initial dry screening of other aliquots (23.2 g). Only 2.9 g of the whole sample was lost during tumbling and dry screening (table 20). While the total amount of fines recovered was about 4%, less was recovered during the tumbling and more was recovered during the subsequent bottle roll. This observation suggests that tumbling actually causes the fines to attach more strongly to the surface of the gravels. When milling with media (No. 55 balls) was followed by either dry (aliquot GS6) or wet (aliquot GS8) separation, the amount of fines recovered was much greater than the 4% found as loose dust. More than 5% of the sample was converted to -1-mm material during the dry milling process. In wet treatments for which data on the recovery of fines for both treatment and bottle rolls are available (aliquots GS6, GS15, and GS16), 4% to 5% of the solids were recovered as -1-mm material, with most being recovered during the treatment process. In all the treatments except milling, it appears that most of the -1-mm material recovered in the treatment was merely washed off the gravel fraction rather than being created during the treatments.

Effluents from the static bottle roll tests were also measured for sulfate and metals while a separate aliquot of the effluent was titrated with a known amount of a standardized base to measure the release of acidity. Again, the aliquot receiving no further treatment after dry screening (split only) was considered a control. The results of the static tests of the gravel fraction of the original composite material used in the column tests are included for comparison (table 21).

By comparing the constituents of one bottle roll effluent to another, it is possible to indicate which treatments were most effective at removing salts and other oxidation products that had adhered to the surfaces of the gravels. The effectiveness of each pretreatment was analyzed by two different methods.

Table 16. - Weights and field parameters of the leachate from humidity cell 1

Leaching	Leaching	Weight of cell and sample		Leachate	Weight of C&S	Leachate	Leachate	Leachate	Leachate	Moles of acid titrated	
	time, days	after dry air, gm	after wet air, gm	recovered mL	after leaching, gm	recovered mL	pH	ORP, mV	conductivity mS	to pH 6	to pH 8.3
1	0	988.1	990.4	200	1090.7	96	3.64	287	0.952	0.0001	0.0003
2	7	1048.8	1044.2	147	1083.8	100	3.44	425	0.913	0.0001	0.0004
3	14	1027.2	1022.9	161	1079.6	98	3.34	458	0.821	0.0001	0.0004
4	21	1038.3	1032.7	147	1075.9	100	3.33	450	0.739	0.0002	0.0004
5	28	1036.0	1030.7	145	1073.2	98	3.29	458	0.623	0.0002	0.0004
6	35	1030.7	1025.3	148	1072.6	92	3.23	460	0.567	0.0001	0.0003
7	42	1030.3	1025.9	147	1072.2	92	3.27	453	0.541	0.0001	0.0003
8	49	1014.5	1011.4	161	1070.8	98	3.18	472	0.443	0.0001	0.0003
9	56	1025.8	1022.6	148	1069.3	96	3.18	480	0.451	0.0002	0.0003
10	63	1025.9	1022.4	147	1068.6	94	3.16	485	0.389	0.0001	0.0003
11	70	1020.1	1015.8	153	1068.1	96	3.15	474	0.363	0.0001	0.0003
12	77	1020.6	1015.8	152	1067.5	94	3.19	483	0.412	0.0001	0.0003
13	84	1018.3	1014.6	153	1066.6	92	3.16	466	0.389	0.0000	0.0002
14	91	1019.6	1016.4	151	1066.8	95	3.14	476	0.394	0.0001	0.0003
15	98	1017.3	1013.5	154	1066.6	92	3.36	476	0.394	0.0001	0.0003
16	106	1017.3	1013.3	153	1058.9	90	3.32	487	0.399	0.0001	0.0003
17	112	1007.2	1004.6	154	1066.5	80	3.31	472	0.405	0.0001	0.0002
18	120	1021.9	1017.5	149	1066.0	88	3.28	483	0.419	0.0001	0.0003
19	127	1020.9	1016.3	150	1068.1	92	3.24	474	0.402	0.0001	0.0003
20	134	1021.4	1016.4	152	1065.8	92	3.28	464	0.370	0.0001	0.0002
21	141	1019.5	1014.4	151	1064.7	85	3.12	472	0.405	0.0001	0.0002
22	148	1019.0	1015.3	149	1063.1	94	3.28	472	0.378	0.0001	0.0002
23	155	1015.2	1010.5	153	1063.9	94	3.24	477	0.329	0.0001	0.0002
24	162	1016.0	1013.1	151	1063.3	91	3.28	471	0.372	0.0001	0.0002
25	169	1015.9	1011.9	151	1062.9	95	3.21	483	0.311	0.0001	0.0002
26	176	1016.0	1011.1	152	1062.7	94	3.23	474	0.370	0.0001	0.0002
27	183	1017.0	1009.9	153	1065.2	95	3.25	479	0.339	0.0001	0.0002
28	190	1019.6	1009.7	156	1066.9	99	3.26	474	0.328	0.0001	0.0002
29	197	1011.9	1008.0	159	1063.8	98	3.32	432	0.321	0.0001	0.0002
30	204	1012.7	1007.0	157	1063.7	94	3.26	476	0.325	0.0001	0.0002
31	211	1017.7	1014.8	149	1060.4	94	3.23	449	0.357	0.0001	0.0002
32	218	1011.8	1009.5	151	1061.9	96	3.24	472	0.318	0.0001	0.0002
33	225	1002.2	1001.1	161	1064.0	97	3.26	471	0.282	0.0001	0.0002
34	232	1006.1	1003.5	160	1640.3	99	3.22	480	0.305	0.0001	0.0002
35	239	1016.4	1013.8	151	1062.0	100	3.19	474	0.297	0.0001	0.0002
36	246	1012.3	1008.3	154	1062.5	95	3.35	464	0.289	0.0001	0.0002
37	253	1013.2	1010.4	152	1061.6	93	3.35	467	0.302	0.0001	0.0002
38	260	1012.5	1009.8	152	1061.5	102	3.30	473	0.296	0.0001	0.0002
39	267	1017.2	1013.3	148	1061.1	98	3.32	476	0.277	0.0001	0.0002
40	274	1013.7	1010.4	151	1061.7	99	3.32	476	0.271	0.0001	0.0002
F	281	--	--	300	1062.1	290	3.21	473	0.256	0.0002	0.0005

C&S- Cell and sample.
ORP- Oxidation-reduction potential.
F- Final, no wet-dry air cycle.

Table 17. - Weights and field parameters of the leachate from humidity cell 2

Leaching	Leaching time, days	Weight of cell and sample		Leachate recovered, mL	Weight C&S after leaching, gm	Leachate recovered, mL	Leachate pH	Leachate ORP, mV	Leachate conductivity mS	Moles of acid titrated	
		after dry air, gm	after wet air, gm							to pH 6,	to pH 8.3
1	0	980.0	981.9	200	1079.3	96	3.63	307	0.871	0.0001	0.0003
2	7	1034.8	1030.6	149	1070.5	106	3.48	438	0.911	0.0001	0.0005
3	14	1006.1	1001.1	169	1067.1	100	3.38	447	0.743	0.0001	0.0004
4	21	1020.2	1005.4	162	1061.8	100	3.39	448	0.612	0.0001	0.0003
5	28	1020.3	1014.7	147	1062.6	92	3.34	453	0.594	0.0001	0.0003
6	35	1014.9	1009.6	153	1060.0	92	3.26	458	0.547	0.0001	0.0003
7	42	1016.7	1012.6	148	1057.6	98	3.24	467	0.493	0.0001	0.0003
8	49	995.9	993.1	165	1060.2	94	3.20	470	0.411	0.0001	0.0002
9	56	1010.7	1007.6	153	1057.9	98	3.17	483	0.446	0.0002	0.0003
10	63	1009.4	1005.8	152	1057.1	96	3.18	475	0.388	0.0001	0.0003
11	70	1005.8	1001.0	156	1057.0	96	3.18	468	0.386	0.0001	0.0003
12	77	1007.9	1003.2	154	1056.5	98	3.18	471	0.392	0.0001	0.0003
13	84	1005.5	1002.1	155	1056.7	95	3.18	469	0.396	0.0001	0.0002
14	91	1006.3	1002.8	154	1056.1	98	3.18	463	0.366	0.0001	0.0002
15	98	1006.1	1001.9	154	1055.4	97	3.28	471	0.363	0.0001	0.0002
16	106	1005.9	1001.2	154	1054.7	92	3.28	487	0.387	0.0001	0.0002
17	113	994.2	991.9	163	1058.1	85	3.32	474	0.383	0.0001	0.0002
18	120	1008.4	1003.8	154	1053.7	92	3.29	476	0.374	0.0001	0.0002
19	127	1005.7	1000.4	154	1056.2	96	3.25	468	0.355	0.0001	0.0002
20	134	1008.3	1002.2	154	1056.1	90	3.28	449	0.356	0.0001	0.0002
21	141	1006.3	1000.7	155	1055.4	91	3.13	465	0.359	0.0001	0.0002
22	148	1005.0	1001.1	154	1054.3	95	3.29	452	0.350	0.0001	0.0002
23	155	1003.3	997.8	157	1054.9	95	3.26	467	0.342	0.0001	0.0002
24	162	1005.0	1002.1	153	1054.3	94	3.29	447	0.351	0.0001	0.0002
25	169	1003.9	999.5	155	1054.6	97	3.18	464	0.330	0.0001	0.0002
26	176	1004.6	999.5	155	1054.2	96	3.22	454	0.330	0.0001	0.0002
27	183	1007.8	999.6	155	1054.5	97	3.25	441	0.323	0.0001	0.0002
28	190	1007.9	999.5	155	1053.9	95	3.25	448	0.305	0.0001	0.0002
29	197	1000.8	996.3	158	1055.4	93	3.32	423	0.311	0.0001	0.0002
30	204	1002.5	995.3	160	1054.4	95	3.24	432	0.304	0.0001	0.0002
31	211	1005.3	1002.2	152	1052.0	97	3.22	436	0.332	0.0001	0.0002
32	218	1000.7	998.3	154	1053.2	99	3.25	453	0.305	0.0001	0.0002
33	225	991.2	990.1	163	1055.7	97	3.23	449	0.294	0.0001	0.0002
34	232	994.1	991.6	164	1054.5	100	3.19	454	0.320	0.0001	0.0002
35	239	1006.1	1003.4	151	1052.2	93	3.18	451	0.281	0.0001	0.0002
36	246	1001.5	996.9	160	1053.7	97	3.31	446	0.291	0.0001	0.0002
37	253	1000.8	997.6	156	1051.2	96	3.34	439	0.288	0.0001	0.0002
38	260	1001.2	998.4	153	1051.8	101	3.28	449	0.295	0.0001	0.0002
39	267	1006.0	1001.8	150	152.7	98	3.32	449	0.264	0.0001	0.0002
40	274	1001.0	997.6	155	1051.1	102	3.33	458	0.263	0.0001	0.0002
F		--	--	300	1050.3	300	3.18	468	0.296	0.0002	0.0006

C&S- Cell and sample.
ORP- Oxidation-reduction potential.
F- Final, no wet-dry air cycle.

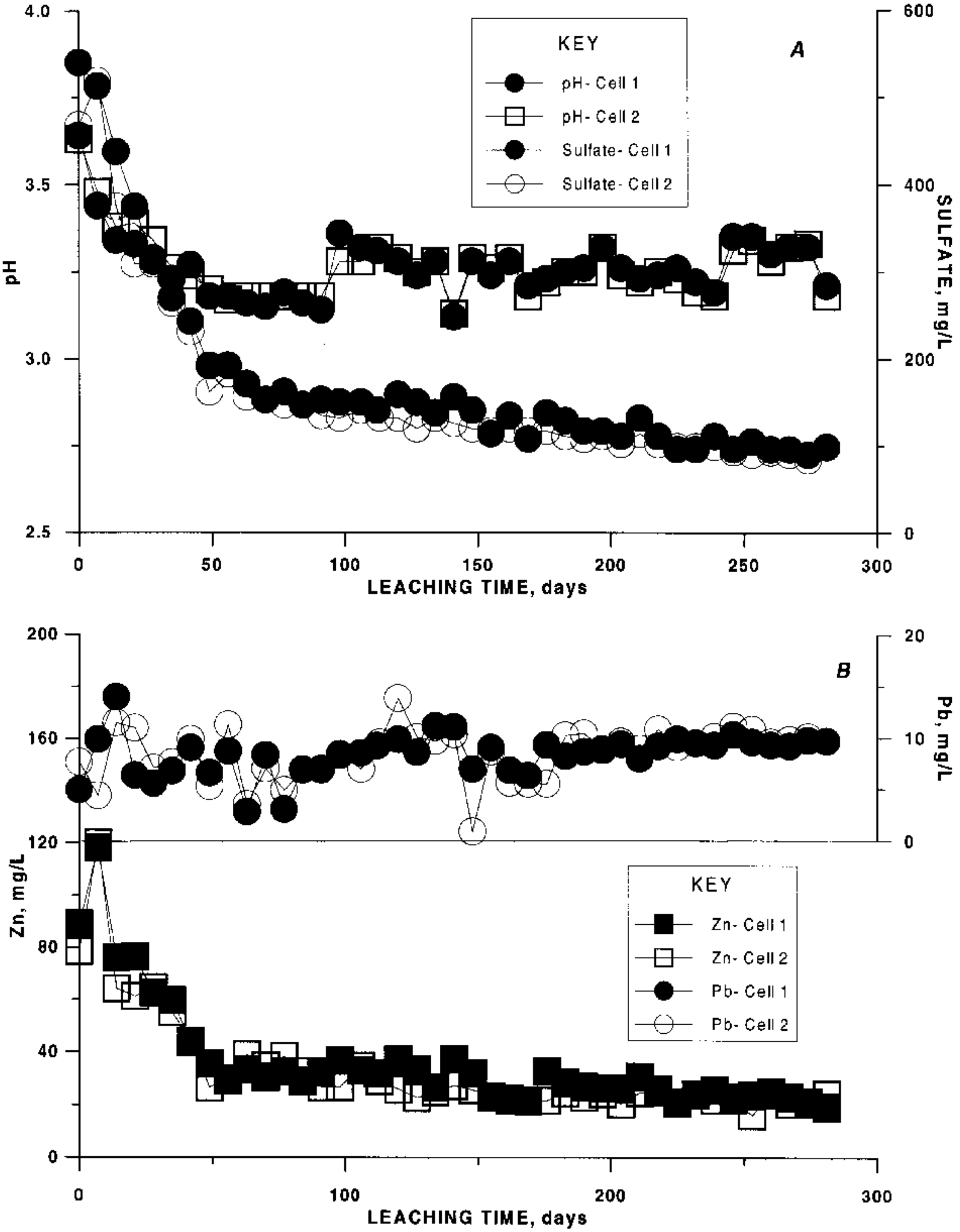

Figure 12.—Results of humidity cell tests. ***A*, pH and sulfate; *B*, Zn and Pb.**

Table 18. - Elemental concentrations of leachates from cell 1, milligrams per liter

Leaching	Leaching time, days	Na	K	Ca	Mg	Al	Mn	Fe	Cu	Zn	Cd	Pb	S
1	0	22	38	59	25	5.5	67	1.50	0.89	89	0.71	4.9	180
2	7	7.2	3.3	51	33	17	60	1.41	2.21	118	1.02	9.8	171
3	14	1.6	10	39	16	8.6	48	2.76	1.68	76	0.88	13.9	146
4	21	6.8	14	40	15	12	34	1.91	2.03	76	0.35	6.3	125
5	28	13	41	30	10.6	11	24	0.28	2.13	63	0.48	5.5	104
6	35	1.9	14	25	8.4	9.8	15.0	1.23	1.97	60	0.40	6.7	90
7	42	1.0	5.8	17	6.3	12	9.9	0.10	2.02	44	0.35	9.0	81
8	49	0.9	12	11.4	4.2	9.1	5.2	0.26	2.05	36	0.28	6.5	64
9	56	5.0	18	10.2	3.6	9.3	4.5	0.78	2.07	29	0.19	8.6	64
10	63	0.9	5.0	8.4	3.2	6.8	3.5	2.54	1.82	33	0.29	2.8	57
11	70	1.0	6.0	5.5	2.2	8.3	2.1	0.62	1.80	31	0.12	8.3	51
12	77	0.7	7.3	5.5	1.9	9.7	2.0	0.06	1.67	32	0.07	3.0	54
13	84	0.3	1.8	1.4	1.3	9.6	1.7	0.02	1.60	29	0.28	6.9	49
14	91	1.3	6.1	4.9	1.4	10	1.6	0.02	1.76	32	0.21	6.9	51
15	98	0.8	10	5.1	2.6	11	1.6	0.42	1.72	37	0.22	8.4	50
16	106	0.8	8.0	4.8	2.4	8.4	1.6	0.14	1.59	33	0.27	8.5	50
17	112	1.9	7.2	2.3	3.2	9.4	1.5	0.04	0.17	32	0.11	9.2	47
18	120	0.8	6.8	2.5	1.6	8.6	1.6	0.08	1.54	37	0.15	9.8	53
19	127	0.5	4.7	2.6	2.9	7.7	1.3	0.03	0.19	34	0.12	8.5	50
20	134	1.2	2.5	2.6	2.5	8.9	1.1	0.03	0.07	27	0.14	11.1	46
21	141	0.4	7.4	3.0	0.8	8.0	1.5	0.08	0.14	37	0.32	11.0	52
22	148	0.8	2.5	3.3	1.5	8.2	1.4	0.03	0.11	32	0.16	6.9	47
23	155	0.4	6.3	2.0	1.9	5.6	0.9	0.15	0.07	23	0.21	9.0	38
24	162	1.5	6.2	1.5	0.8	2.1	1.3	0.06	0.46	22	0.14	6.8	45
25	169	1.5	6.1	1.5	0.8	1.5	1.0	0.05	0.26	22	0.09	6.3	36
26	176	0.2	13	2.1	1.6	7.1	1.4	0.09	0.50	33	0.20	9.3	46
27	183	1.9	5.2	2.0	1.7	6.6	1.2	0.01	0.98	28	0.15	8.2	43
28	190	0.2	7.7	2.8	1.7	6.3	1.1	0.29	0.97	27	0.17	8.6	39
29	197	0.1	5.4	2.5	1.5	5.4	1.1	0.05	0.67	26	0.16	8.8	39
30	204	0.1	3.9	2.6	1.6	5.8	1.1	0.04	0.76	26	0.15	9.4	37
31	211	0.1	4.9	3.2	1.8	7.1	1.3	0.03	0.87	31	0.16	8.0	44
32	218	0.2	9.0	1.4	2.0	6.9	1.1	0.01	0.81	26	0.15	9.2	37
33	225	0.8	4.6	0.6	1.3	4.9	0.9	0.02	0.24	21	0.15	9.8	32
34	232	0.9	5.5	2.8	1.5	5.2	1.1	0.04	0.82	24	0.15	9.4	32
35	239	1.0	5.4	3.1	1.6	5.9	1.1	0.04	0.95	26	0.17	9.3	37
36	246	0.8	5.5	2.7	1.5	5.1	1.1	0.00	0.90	23	0.16	10.3	32
37	253	0.5	13	2.0	1.3	5.6	1.1	0.26	0.09	24	0.21	9.6	35
38	260	0.1	4.7	2.6	1.4	4.9	1.0	0.03	0.79	24	0.15	9.3	32
39	267	0.8	3.7	2.5	1.4	4.6	1.0	0.03	0.73	23	0.16	9.2	32
40	274	0.8	3.9	2.3	1.3	4.3	0.9	0.01	0.68	21	0.13	9.8	30
F	281	0.8	4.1	2.2	1.2	4.0	0.8	0.03	0.62	19	0.13	9.7	33

F- Final, no wet-dry air cycle.

Table 19. - Elemental concentrations of leachates from cell 2, milligrams per liter

Leaching	Leaching time, days	Na	K	Ca	Mg	Al	Mn	Fe	Cu	Zn	Cd	Pb	S
1	0	15	26	53	20	3.2	59	0.12	0.99	79	0.68	7.6	156
2	7	8.1	34	58	23	18	63	0.91	2.61	120	0.30	4.3	173
3	14	1.6	14	35	14	4.6	42	0.85	1.43	64	0.55	11.4	125
4	21	4.7	26	31	12	9.5	28	1.00	1.65	61	0.33	10.9	103
5	28	7.5	37	30	10.0	8.5	25	0.06	2.16	65	0.65	7.0	103
6	35	5.2	16	24	5.8	8.3	16	0.34	1.70	55	0.79	7.5	88
7	42	0.9	5.8	18	5.0	8.9	11.3	0.11	2.01	44	0.35	9.8	77
8	49	0.9	5.4	9.6	4.1	7.6	5.5	0.27	1.74	27	0.08	5.2	54
9	56	8.2	13.2	11.6	3.6	8.7	5.2	0.67	1.83	30	0.08	11.2	61
10	63	0.8	9.6	8.2	3.4	7.1	3.1	0.16	1.73	39	0.44	3.4	52
11	70	0.8	9.4	5.8	2.1	6.7	2.7	0.59	1.57	35	0.26	6.9	51
12	77	0.8	10.5	10.1	2.2	7.4	2.5	0.06	1.43	38	0.21	4.8	49
13	84	0.3	5.1	2.1	2.2	8.6	2.1	0.06	1.48	33	0.22	6.8	49
14	91	0.3	5.1	4.6	1.2	7.5	1.7	0.02	1.45	27	0.20	6.8	45
15	98	1.7	8.0	4.8	2.7	9.4	1.6	0.36	1.44	27	0.19	8.2	44
16	106	0.4	11.0	4.9	2.0	6.8	1.8	0.21	1.37	35	0.18	6.9	47
17	113	1.6	6.7	2.6	2.7	9.3	1.6	0.16	1.46	29	0.10	9.5	44
18	120	0.9	7.8	1.8	1.4	8.0	1.5	0.03	1.26	26	0.20	13.8	44
19	127	0.4	6.9	2.2	1.8	5.8	1.1	0.03	0.07	23	0.04	10.0	40
20	134	0.9	2.5	2.4	2.8	7.6	1.2	0.03	0.07	25	0.04	9.7	44
21	141	0.4	3.6	2.5	0.8	6.6	1.4	0.26	0.08	27	0.19	10.3	42
22	148	0.4	8.0	3.3	1.6	7.4	1.4	0.03	0.11	26	0.12	0.9	40
23	155	0.7	8.3	0.7	2.6	5.9	1.1	0.24	0.07	23	0.17	8.6	39
24	162	1.5	6.2	1.5	0.8	2.0	1.3	0.05	0.24	22	0.05	5.6	40
25	169	1.5	6.2	1.5	0.9	3.8	1.2	0.06	0.65	22	0.05	5.5	39
26	176	1.5	6.2	1.5	0.9	3.8	1.2	0.06	0.65	22	0.05	5.5	39
27	183	0.2	11.9	1.3	1.6	5.7	1.2	0.14	0.30	25	0.19	10.2	37
28	190	0.2	6.6	1.9	1.6	5.8	1.1	0.16	0.84	23	0.10	10.4	36
29	197	0.1	4.9	2.8	1.5	5.5	1.1	0.27	0.65	24	0.15	8.9	37
30	204	0.3	4.0	2.5	1.4	5.1	1.1	0.13	0.60	21	0.11	9.6	34
31	211	0.1	4.4	3.0	1.6	5.9	1.2	0.15	0.74	25	0.11	8.9	38
32	218	0.2	9.6	1.3	1.9	6.2	1.1	0.05	0.75	25	0.17	10.8	34
33	225	0.2	5.3	0.6	1.4	5.1	1.0	0.02	0.26	21	0.15	9.1	33
34	232	0.8	5.3	3.0	1.6	5.4	1.1	0.16	0.82	24	0.15	9.5	33
35	239	0.8	4.9	2.6	1.4	5.3	1.0	0.10	0.85	22	0.14	10.1	33
36	246	0.9	5.1	2.8	1.5	5.1	1.1	0.06	0.86	22	0.14	11.1	31
37	253	0.3	8.0	1.4	1.2	4.6	0.9	0.11	0.05	16	0.09	10.8	30
38	260	0.0	4.6	2.8	1.5	4.9	1.1	0.12	0.78	25	0.15	9.6	31
39	267	0.7	3.5	2.2	1.3	4.1	0.9	0.09	0.63	21	0.13	9.8	30
40	274	0.7	4.1	2.2	1.3	3.9	0.9	0.05	0.62	21	0.12	10.1	28
F		0.7	4.2	2.7	1.3	4.7	1.0	0.05	0.74	24	0.17	9.3	33

F- Final, no wet-dry air cycle.

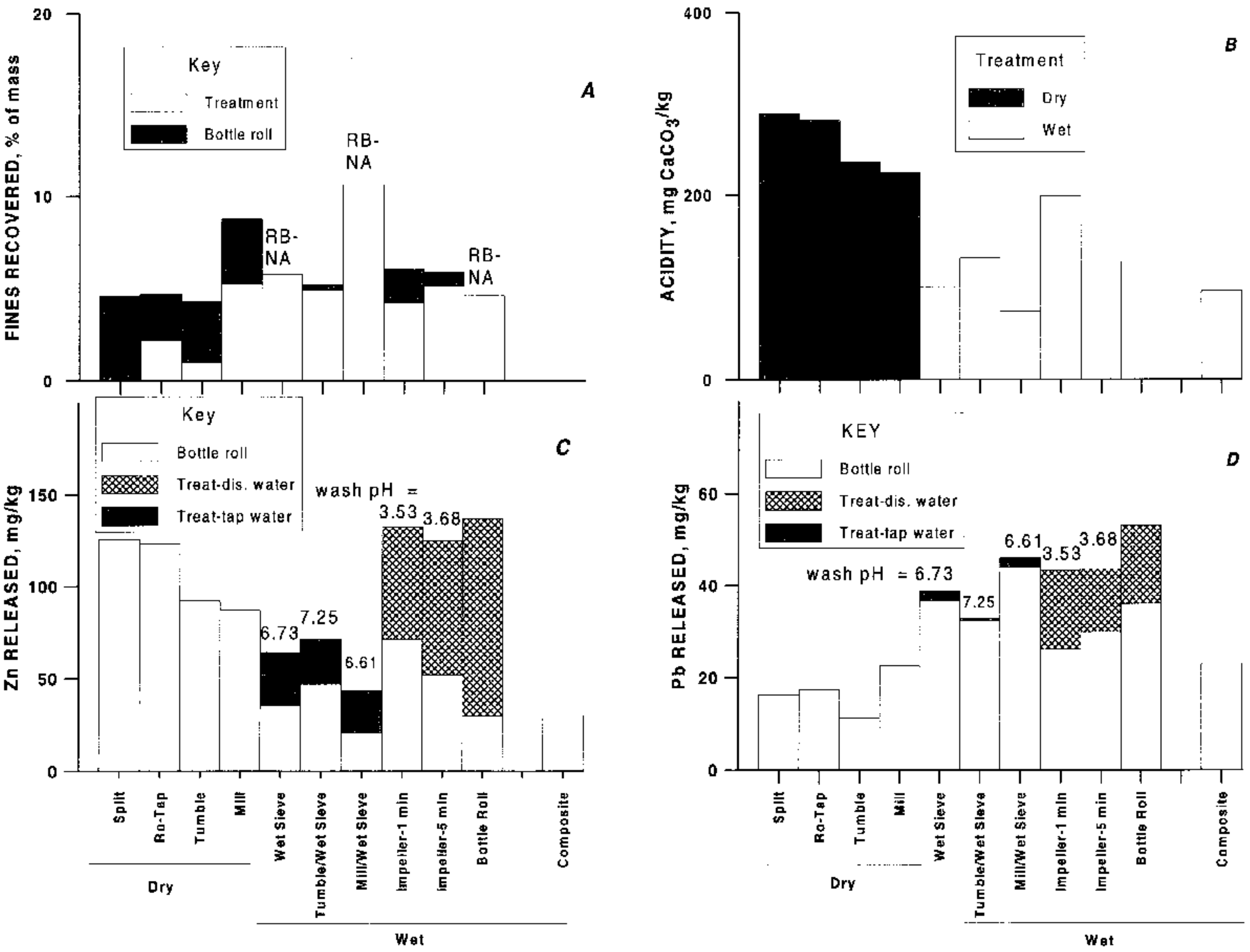

Figure 13.—Results of separating fines and sands from gravels. *A*, Recovery of fines tests; *B*, acidity in leachate from static bottle roll tests following gravel separation; *C*, Zn released during wet treatments with distilled and tap water, and during bottle roll tests; *D*, Pb released. RB-NA—Fines in bottle roll not determined.

Table 20.–**Recovery of solids during separation of fines and sands from gravels, dry grams**

Experiment number	Treatment	Charge	Fines from initial Ro-Tap	Charge after initial Ro-Tap	Fines after treatment	Fines generated during treatment	Charge remaining	Volume of wash water, L
				DRY TREATMENT				
GS1	Split only	1,161						
GS2	Ro-Tap	993.2	22.2	969.6	NA	NA		
GS5	Tumble	1,113			12.0	(1)	1,098	
GS6	Mill	1,173			58.8	35.3	1,095	
				WET TREATMENTS WITH TAP WATER				
GS3	Wet sieve	1,103	25.9			37.6		7.6
GS7	Tumble, wet sieve	1,169	22.9	1,145		34.6		8.5
GS8	Mill, wet sieve	1,096	23.9	1,069		92.8		8.7
				WET TREATMENTS WITH DISTILLED WATER				
GS16	Impeller, 1 min	1,006	21.0	984		21.6		2.0
GS15	Impeller, 5 min	1,081	23.5	1,057		32.2		2.0
GS13	Bottle roll			166		7.7		0.42
Average			23.2					
Std. dev.			1.7					

NA Not analyzed.

[1] Fines after treatment less than average weight of initial loose fines.

Table 21.–**Metals released during bottle rolls after treatment, milligrams per kilogram of solid**

Exper-ment no.	Treatment	Element									SO_4	Acidity released, mg $CaCO_3$/kg	Saturation index for anglesite
		Ca	Mg	Al	Mn	Fe	Cu	Zn	Cd	Pb			
						DRY TREATMENT							
GS1	Split	14	5.9	9.9	17	10.5	0.9	126	0.9	16	450	289	0.04
GS2	Ro-Tap	12	5.7	6.3	22	4.4	4.4	123	0.8	17	408	281	0.05
GS5	Tumble	12	5.1	3.6	17	25	1.2	92	0.6	11	368	236	-0.20
GS6	Mill	14	7.7	1.8	23	27	0.5	87	0.7	23	380	224	0.15
						WET TREATMENTS WITH TAP WATER							
GS3	Wet sieve	4.1	2.0	2.2	4.8	2.4	0.9	36	0.2	37	192	101	-0.20
GS7	Tumble, wet sieve	5.9	2.6	2.5	5.9	4.6	0.7	47	0.3	32	218	132	0.13
GS8	Mill, wet sieve	7.2	2.0	<1.0	3.3	5.7	<0.1	21	0.2	44	192	74	0.23
	Composite	22	2.5	1.6	7.5	0.8	0.2	30	ND	23	131	96	ND
						WET TREATMENTS WITH DISTILLED WATER							
GS16	Impeller, 1 min	4.6	3.3	4.2	9.8	6.3	3.1	71	0.4	26	210	199	0.02
GS15	Impeller, 5 min	3.9	2.5	2.3	7.2	6.2	0.7	52	0.3	30	258	128	0.14
GS13	Bottle roll	4.5	1.8	1.8	4.9	4.0	0.6	30	0.3	36	127	ND	0.06

ND Not determined.

1. The release of acidity from the treated gravels during the static bottle roll tests was compared among the various treatments (table 21) (figure 13*B*). Those treatments yielding the highest amount of acidity were the least effective, while those with the lowest were the most effective. The three dry methods were least effective in removing acidity from the gravels, with only 22% of the acid-generating constituents removed by the most aggressive dry treatment (dry milling). In contrast, the most effective separation method (wet sieving after dry milling) reduced the release of acidic constituents by 74%. The large-volume-batch, wet-screening process used to separate the gravels in the original composite material for the column tests also seemed to be quite effective.

2. The releases of metals during the static bottle roll tests of the gravels after treatment were compared. Zn was selected as the indicator metal because it was present in the greatest concentrations and it is a major contributor to the toxicity of surface waters. The amount of Zn dissolved into solution from the control (aliquot GS1, split only) is considered a measure of easily releasable Zn (table 21). Again, the dry treatments were least effective in preventing Zn release from the treated gravels (figure 13*C*). Dry milling was the most effective dry treatment,

but only reduced easily releasable Zn by 31% relative to the control (split only). In contrast, wet treatments reduced easily releasable Zn between 44% and 83%, with wet sieving after dry milling being the most effective. Again, the large-volume-batch, wet-screening process used to separate the gravels for the column tests also seemed to be quite effective, reducing Zn release in the static test by 76%. It is notable that the 126 ppm of easily releasable Zn in the control (split only) was only 3.5% of the total Zn present in the gravel fraction (3,600 ppm).

In the following discussion, easily releasable Zn is considered a conservative property. Its mass balance includes release into the wash water during wet treatments, removal with fine particles during both wet and dry treatments (not analyzed), or release during the static bottle roll test of the treated gravels. Since the Zn released into solution has been normalized by the liquid-to-solids ratio, the values in tables 21 and 22 for the control (aliquot GS1) can be directly applied to the following mass balance:

126 ppm = release during wet treatments (table 22) + removal with fines during treatment (not measured) + release during bottle roll tests of treated gravels (table 21).

In the dry treatments, any decrease in easily releasable Zn observed in the subsequent static bottle roll tests must have been a result of Zn removal associated with the -1-mm material removed during the initial treatment, because there was no release during treatment. With the wet treatments, decreases in Zn release during the static bottle roll tests could either be a result of removal of Zn with the finer solids or dissolution into the wash water. The fate of the easily releasable Zn during the treatments using distilled water was distinctly different from the fate of Zn during treatments in which tap water was used. When distilled water was used, the amount of Zn released into the wash water (table 22) plus that released during the subsequent static bottle roll tests (table 21) was approximately equal to the Zn released from the control (figure *13C*). This would suggest that only dissolution of easily releasable Zn into the distilled wash water was responsible for the decrease in Zn release in the subsequent static tests. Because the distilled water had no buffering capacity and because the liquid-to-solids ratio was low (between 2.0:1 and 2.5:1) (table 20), the pH of the wash water was below 4. Therefore, the use of distilled water enhanced the solubility of Zn minerals and promoted dissolution into processing water.

The use of tap water, which has much higher liquid-to-solids ratios (7:1 to 8:1), provided enough buffering capacity to keep the pH of the wash water above 6. Zn not found in the wash water or released during the static bottle roll tests must have been adsorbed or precipitated, presumably onto the fines removed during the wet treatments. Geochemical speciation and solubility modeling were undertaken to study the wash water solutions. Because alkalinity was not measured, the ionic charge in the solutions for the three wet treatments in which tap water was used was balanced by a calculated alkalinity concentration. The geochemical model suggests that Zn was near saturation with respect to zinc carbonate ($ZnCO_3$) in these solutions (saturation index between -0.41 and 0.28) (table 22). Because the release of Zn in subsequent bottle roll tests was no greater than with treatments in which distilled water was used, little $ZnCO_3$ seemed to have become attached to the gravels.

The behavior of Pb during the static bottle roll tests after various treatments was different from the behavior of Zn (figure 13*D*). The Pb released after the dry treatments was less than Pb released after the wet treatments. These results can be explained by anglesite solubility. The saturation indices of solutions from the static bottle roll tests fell within a range between -0.2 and 0.2, indicating that sulfate concentrations in the test solutions were controlling Pb release. Because the dry treatments were ineffective in removing soluble sulfate, the high sulfate concentrations in these test solutions suppressed Pb concentrations. However, anglesite solubility cannot explain the low amounts of Pb released during the wet treatments in which tap water was used. The geochemical model indicates that Pb was also supersaturated with respect to lead carbonate ($PbCO_3$) (table 22). The release of Pb during the static bottle roll tests following tap water treatments (37±6 ppm) was only slightly higher than Pb release subsequent to distilled water treatments (31±5 ppm). Any Pb that precipitated onto the gravel fraction as $PbCO_3$ during the tap water treatment and subsequently dissolved during the static bottle roll tests would have come under the influence of the anglesite equilibrium in these test solutions.

The release of acidity, Zn, and Pb from a dry-screened gravel fraction was controlled by sands and fines physically attached to the gravels and soluble salts precipitated onto the surface of the gravels. However, the total amount of -1-mm material removed during treatment was not an accurate predictor of subsequent metal release. Dry treatments were ineffective in reducing metal release in subsequent tests of the treated gravels. Wet treatments were much more effective with wet sieving following dry milling being the most effective (reductions of 76% and 83% for the initial release of acidity and Zn, respectively). The wet screening used to separate the three fractions of the original composite material was the second most effective treatment.

Separation of Metals in Fine Fraction

The fine fraction was subjected to a variety of mineral-processing methods because many of the acid-generating elements (Fe and S) and metals of interest (Pb) were concentrated in the fine fraction (figures 2 and 3). The purpose of these separation methods was both to produce a concentrate that would be sufficiently high grade to smelt and to reduce the environmental complications of disposing of the fine fraction. Gravity separation of fines produced a concentrate that was 30% Pb (as anglesite), which contained 62% of the Pb in 11% of the mass (table 23). However, there were no preferential enrichments of Zn and Cu during gravity separation. Magnetic

Table 22.–Metals released during wet treatments, milligrams of constituent per kilogram of solid

Experiment no.	Treatment	Element									SO_4	pH	Saturation index				
		Ca	Mg	Al	Mn	Fe	Cu	Zn	Cd	Pb			$ZnCO_3$	Malachite	$PbCO_3$	$CaCO_3$	Anglesite
								WITH TAP WATER									
GS3 . . .	Wet sieve	(1)	(1)	<2.6	7.5	0.1	<0.4	28	0.3	2	331	6.73	-0.14	-1.28	0.24	-0.68	-2.06
GS7 . . .	Tumble, wet sieve	(1)	(1)	<2.7	7.7	0.1	<0.4	24	<0.2	<1	387	7.25	0.28	-0.52	-0.08	-0.47	-2.90
GS8 . . .	Mill, wet sieve . .	(1)	(1)	<2.9	13.7	8.6	<0.4	23	<0.2	2	473	6.61	-0.41	-1.42	0.17	-1.18	-2.05
								WITH DISTILLED WATER[2]									
GS16 . .	Impeller, 1 min .	5.9	2.5	3.2	8.0	2.5	5.2	61	0.4	17	228	3.53					0.06
GS15 . .	Impeller, 5 min .	7.9	3.3	4.2	10	5.3	4.4	73	0.4	14	264	3.68					0.05
GS13 . .	Bottle roll	12.9	5.9	4.5	20	6.4	0.3	107	0.7	17	335	NA					0.00

NA Not analyzed.

[1] Ca and Mg concentrations in wash water were within the precision of the analysis of the initial tap water.

[2] Saturation indices of metal carbonate acidic solutions not calculated.

Table 23.–Results of gravity and magnetic separation tests

Test number and	Wt %	Assay, wt %					Distribution, %				
product		Cu	Fe	Mg	Pb	Zn	Cu	Fe	Mg	Pb	Zn
Gravity separation:											
Table concentrate	11.0	0.02	15.4	0.24	29.6	0.23	7.6	18.7	7.95	62.3	11.0
Table tailings	89.0	0.03	8.3	0.35	2.21	0.23	92.4	81.3	92.1	37.7	89.0
Weighted average[1]	100.0	0.03	9.1	0.34	5.22	0.23	100	100	100	100	100
Magnetic separation:											
Magnetic	5.8	0.02	53.4	0.40	2.97	0.095	3.1	26.7	5.8	3.3	1.94
Nonmagnetic	94.2	0.04	9.0	0.41	5.34	0.30	96.9	73.3	94.3	96.7	98.1
Weighted average[1]	100.0	0.04	11.6	0.41	5.20	0.28	100	100	100	100	100

[1] Weighted average of recovered fractions.

Table 24.–Results of flotation tests

Test number and	Wt %	Assay, wt %					Distribution, %				
product		Cu	Fe	Mg	Pb	Zn	Cu	Fe	Mg	Pb	Zn
FS1:											
Rougher concentrate	12.0	0.3	24	([1])	7.00	1.0	31.3	22.9	([1])	19.3	31.3
Tailings	88.0	0.09	11	([1])	4.00	0.3	68.8	77.1	([1])	80.7	68.8
Weighted average[2]		0.12	12.6	([1])	4.36	0.4	100	100	([1])	100	100
FS2:											
Rougher concentrate	19.9	0.1	22	([1])	8.00	0.9	38.3	33.2	([1])	39.9	52.8
Tailings	80.1	0.04	11	([1])	3.00	0.2	61.7	66.8	([1])	60.2	47.2
Weighted average[2]		0.05	13.2	([1])	4.00	0.34	100	100	([1])	100	100
FS3:											
Rougher concentrate	10.9	0.074	11.6	0.37	9.18	0.54	24.6	12.0	9.4	21.9	20.7
Tailings	89.1	0.028	10.4	0.43	4.00	0.25	75.4	88.0	90.6	78.1	79.3
Weighted average[2]		0.03	10.5	0.42	4.56	0.29	100	100	100	100	100
FS4:											
Rougher concentrate	5.1	0.098	15.1	0.36	9.90	1.78	6.34	7.1	4.25	11.0	30.5
Scavenger 1	6.4	0.27	13.4	0.47	9.64	0.33	21.9	7.9	6.86	13.5	7.0
Scavenger 2	9.2	0.23	12.8	0.48	9.28	0.35	26.7	10.9	10.1	18.6	10.8
Tailings	79.3	0.045	10.1	0.43	3.29	0.19	45.1	74.1	78.8	56.9	51.7
Weighted average[2]		0.08	10.8	0.44	4.58	0.30	100	100	100	100	100
FS5:											
Rougher concentrate	5.8	0.14	15.4	0.45	6.91	0.73	11.7	8.0	6.27	9.1	16.2
Scavenger 1	6.6	0.19	15.3	0.47	6.53	0.38	17.3	9.1	7.36	9.8	9.6
Scavenger 2	5.1	0.18	11.5	0.36	7.63	0.46	13.1	5.3	4.41	8.9	8.9
Tailings	82.5	0.05	10.5	0.42	3.84	0.21	57.9	77.7	82.0	72.2	65.4
Weighted average[2]		0.07	11.2	0.42	4.39	0.26	100	100	100	100	100

[1] Mg not determined by x-ray defraction.

[2] Weighted average of recovered fractions.

NOTE.–FS1 and FS2 were analyzed by x-ray defraction; all other flotation samples were analyzed by ICP.

separation concentrated 27% of the Fe into 5.8% of the mass, while Cu, Pb, and Zn were depleted in the magnetic concentrate. However, the high concentrations of Pb in the magnetic concentrate (3 wt %) probably precludes its use as a feedstock for the electronics industry.

In FS 1 performed on fines with no addition of neutralizer (pH = 4), 19% and 31% of the Pb and Zn, respectively, were concentrated in 12% of the mass (table 24). When $NaCO_3$ was added to the fines slurry to achieve a pH of 9 (FS 2), the rougher concentrate constituted 20% of the mass and 40% and 53% of the Pb and Zn, respectively. However, the rougher concentrate was only 8% and 0.9 wt % Pb and Zn, respectively. The addition of Na(OH) to reach a pH of 9 (FS 3) resulted in slightly more enriched Pb in the rougher concentrate but Zn assays that were about half the assays in which $NaCO_3$ was used. Compared to the $NaCO_3$ test, about half the mass and the Pb were distributed to the concentrate, with even less Zn found in the concentrate.

In a staged flotation scheme in which Na(OH) was added to achieve a pH of 9 (FS 4), the most enriched Zn material (1.8 wt %) was produced as the rougher concentrate in which 31% of the Zn was distributed into 5.1% of the mass. The Pb assay of the rougher concentrate was similar to the assays of other rougher concentrates. The scavenger concentrate had a similar Pb assay, but less Zn. In the three-stage flotation scheme, 43% of the Pb and 48% of the Zn were concentrated into 21% of the mass. This recovery was only slightly better than the single-stage scheme in which $NaCO_3$ was used as the neutralizing agent (FS 2). A mixture of the fines from both large-volume batches was used in FS 5. This staged flotation scheme produced a less-enriched concentrate than that formed in FS 4. The low sulfide recoveries in these preliminary tests were indicative of the poor amenability of the fine fraction to flotation. The years of oxidation that this fine material has undergone, as evidenced by the low percentage of sulfide S, precludes the development of mineral-processing methods based on flotation of sulfide minerals to produce a concentrate that could be refined as well as reduce the concentrations of metals in the tailings.

DISCUSSION

GEOCHEMISTRY

Intraelemental Ratios

Prior to evaluating the effects of segregation of mine waste material on metal release rates, the relationships between elemental concentrations in the leachate from the columns were examined to understand the geochemical reactions taking place within the columns. Metal concentrations in leachate within columns are controlled by the balance between the kinetics of dissolution of source material and the kinetics of mechanisms that remove metals. Sources include soluble salts, sulfide minerals that oxidize, and clays that are attacked by acid. Sinks of metals include metal precipitates or metals adsorbed onto mineral surfaces.

Sulfate was chosen as an indicator of the dissolution of sulfide minerals and the subsequent acid attack on gangue minerals. After sulfate was released into solution by the dissolution of metal sulfate minerals or the oxidation of sulfide minerals, it was unlikely to be geochemically reduced in the columns because of the abundance of more reactive electron acceptors (i.e., ferric hydroxides). Secondary sulfate minerals were another possible sink for sulfate. In columns with pH values below 4, gypsum ($CaSO_4$) was the mostly likely sulfate mineral to be supersaturated. The saturation index of gypsum in the sample having the highest sulfate concentration (T1, cycle 5) was -0.13 log units. Because most of the samples had much lower sulfate and Ca concentrations, gypsum probably did not precipitate to any appreciable degree.

Because sulfate was the only significant anion, it is not surprising that many of the cations exhibited correlations with sulfate, because ion balance must be maintained. Linear regression analyses with sulfate were performed for all major cations and are interpreted below in terms of geochemical reactions. Multiple regression analyses were not performed because sulfate is the master independent variable for cations; secondary effects were seen as negative correlations with other cations. Although factor analysis was beyond the scope of this RI, the primary factors could be predicted from the geochemical interpretation of the linear regression analysis.

Examination of the element-element relationships throughout the course of the experiments also provided some indication of the consistency of the dominant geochemical reactions. In addition, the $[Zn]:[SO_4]$ molar ratio provided some indication of what portion of the sulfate was produced by sphalerite oxidation and what portion was generated by pyrite oxidation. The columns containing original composite material exhibited a consistent Zn:S weight ratio throughout the experiment (figure 14*A*). The $[Zn]:[SO_4]$ molar ratios were 0.62, 0.63, and 0.64 for the triplicates, and the regression coefficients (R^2) were greater than 0.93 (table 25). There were no significant differences among the columns, and the regression analysis of the whole set yielded a molar ratio of 0.63. This ratio suggests that about 63% of the sulfate in the leachate from the original composite material originated directly from the oxidation of sphalerite or from the flushing of $ZnSO_4$ generated from previously oxidized sphalerite. The gravels exhibited a slightly lower molar ratio of 0.50, while the ratio for the sand columns was 0.77. In contrast, the molar ratio for the fine column was only 0.04, and the correlation was poor.

Among the different column types, the pH decreased as the $[Zn]:[SO_4]$ molar ratios decreased. Hardly any sulfate originated from sphalerite oxidation in the fine column, which had the lowest pH. In contrast, the sand column exhibited the highest $[Zn]:[SO_4]$ molar ratio in the leachate and had the highest pH. This trend suggests that the pH of a leachate will decrease as the proportion of sulfate originating from pyrite oxidation increases.

The oxidation of pyrite results in the production of both acid and sulfate.

$$FeS_2 + 3.75\ O_2 + 3.5\ H_2O \rightarrow Fe(OH)_3\ (s) + 4H^+ + 2SO_4^{2-}. \tag{A}$$

The oxidation of monosulfide minerals does not produce acid if the cation does not hydrolyze. Therefore —

$$ZnS + 2O_2 \rightarrow Zn^{2+} + SO_4^{2-}. \tag{B}$$

Because sphalerite is usually contaminated with Fe, the oxidation of sphalerite will cause some acid production. The oxidation of ferrous monosulfide (FeS) in the sphalerite lattice to Fe^{3+} and its subsequent hydrolysis and precipitation will produce acid, but only half as much as pyrite oxidation products.

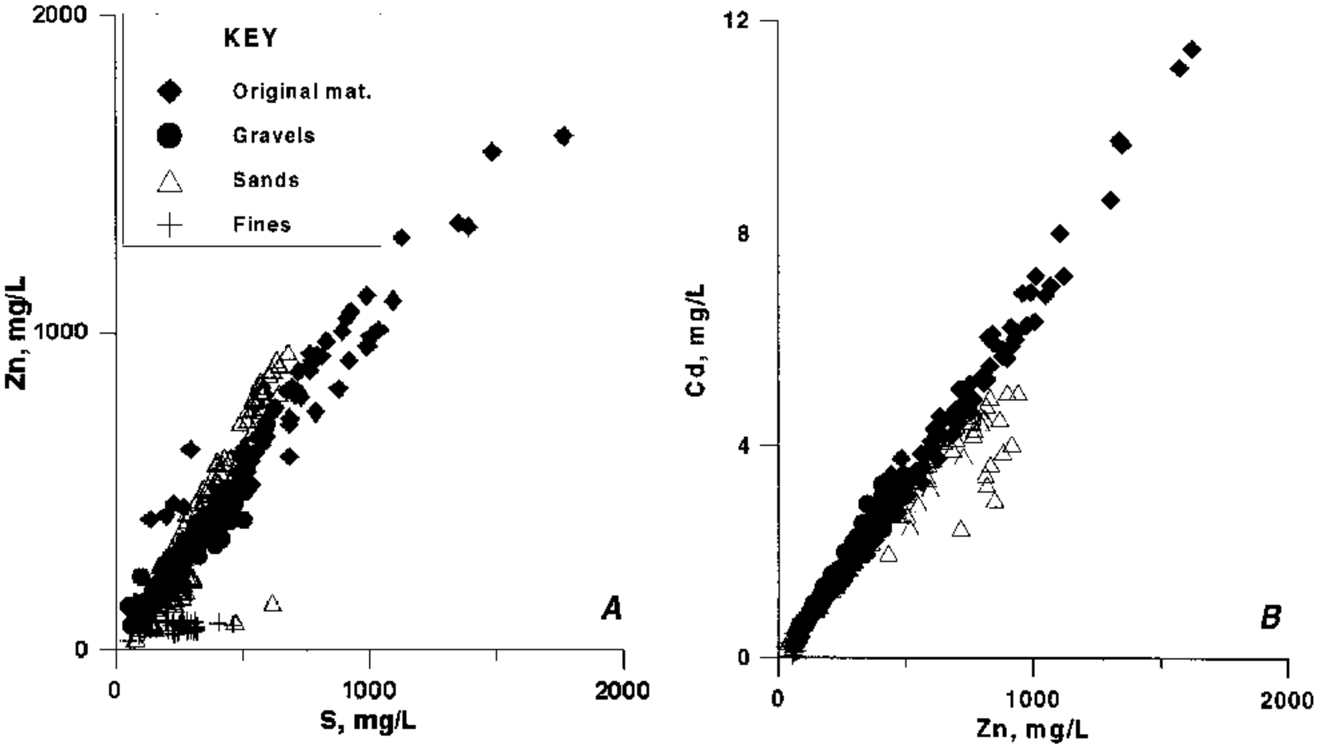

Figure 14.—Comparisons of elements in column leachate. ***A*****, Zn versus S;** ***B*****, Cd versus Zn.**

$$FeS + 2.25\ O_2 + 2.5\ H_2O \rightarrow Fe(OH)_3\ (s) + 2H^+ + SO_4^{2-}. \qquad (C)$$

The Fe^{2+} in sphalerite from mines in the East Fork of Nine Mile Creek ranged from 0.4 wt % to 4 wt % (Fryklund, 1964). Therefore, up to another 7% of the S generated from sphalerite oxidation may have been associated with ferrous monosulfide from contamination of the sphalerite. These reactions indicate it isn't the portion of sulfate generated by pyrite that controls pH, but the amount of pyrite oxidized. During the second wet period (leachings 24 through 33), the average S concentrations were 282, 113, 310, and 270 mg/L for the original composite material, gravel fraction, sand fraction, and fine fraction, respectively. If the portion of S associated with Zn is subtracted from these concentrations (table 25), 260, 104, 71, and 57 mg/L S was generated by other sulfide oxidation reactions (pyrite, chalcopyrite [$CuFeS_2$], FeS in sphalerite) in the fine fraction, original composite material, sand fraction, and gravel fraction, respectively. In general, increasing S generated by reactions other than sphalerite oxidation resulted in decreasing pH's. The higher pH of the sand fraction relative to the pH of the gravel fraction was the exception to this trend, which will be examined later in this section.

It is not known what soil characteristic is responsible for the [Zn]:[SO_4] in the four columns. The lack of visible pyrite in the sand samples examined by SEM explains the high [Zn]:[SO_4] ratio. For the original composite material and the gravel fraction, the oxidation of sphalerite may be outcompeting pyrite for electron acceptors. Despite the slower area-specific oxidation rate of sphalerite relative to pyrite (Rimstidt and others, 1994; Scharer and others, 1994), the overall oxidation of sphalerite was equal to or greater than the oxidation of pyrite in these two types of columns. Therefore, the surface area available for sphalerite oxidation must have been much greater than the area available for pyrite oxidation. A high degree of sphalerite liberation, like that found for the finer fractions examined by SEM, may be responsible for the high reactivity of sphalerite in the columns containing the coarser material.

The geochemical behavior of the oxidation products may also explain the greater reactivity of Zn in the columns containing the original composite material, gravel fraction, and sand fraction. Zn is very mobile and therefore is washed away, leaving new sphalerite surfaces for oxidation. As suggested by the mineralogical analysis, the in situ oxidization of pyrite and the subsequent hydrolysis and precipitation of Fe produces a precipitate, which could act as a barrier to further oxidation. The dominance of sphalerite oxidation over pyrite oxidation in the later stages of the oxidation of tailings would only occur in jig tailings. With waste rock, monosulfides are present in much smaller quantities than pyrite. With flotation tailings, the finer grain size usually limits oxygen diffusion. Rather than being oxidized in situ, the Fe^{2+} produced from the oxidation of pyrite may tend to be transported away from the oxidation site. In contrast, the coarser nature of jig tailings favors oxygen diffusion and in situ oxidation of Fe hydroxides on pyrite

Table 25.—Intraelement correlation statistics for leachate from columns. First row shows slopes for individual columns. Second row (in parentheses) shows slope of correlation when data from all columns of one type are combined with its correlation coefficcient (R^2)

Element versus element	Total	Gravels	Sands	Fines
COLUMNS				
Element versus S:				
Zn	0.62, 0.63, 0.64	0.53, 0.53, 0.48	0.75, 0.76, 0.77	
	(0.63 ± 0.01, 0.98)	(0.50 ± 0.01, 0.93)	(0.77 ± 0.02, 0.93)	(0.04 ± 0.01, 0.17)
Ca	0.13, 0.11, 0.11	0.20, 0.17, 0.18	NC, NC, NC	
	(0.12 ± 0.006, 0.81)	(0.17 ± 0.1, 0.70)	NC	NC
Mg	0.045, 0.047, 0.048	0.091, 0.083, 0.078	NC, NC, NC	
	(0.046 ± 0.002, 0.87)	(0.078 ± 0.002, 0.91)	(0.020 ± 0.005, 0.10)	(0.05 ± 0.008, 0.52)
Mn	0.070, 0.063, 0.066	0.11, 0.10, 0.09	0.032, 0.036, 0.031	
	(0.066 ± 0.003, 0.88)	(0.094 ± 0.02, 0.94)	(0.033 ± 0.002, 0.73)	(0.11 ± 0.02, 0.41)
Na + K	0.016, 0.018, 0.017	0.043, 0.043, 0.034	NC, NC, 0.015	
	(0.017 ± 0.001, 0.76)	(0.035 ± 0.002, 0.73)	(0.014 ± 0.001, 0.46)	NC
Si	0.0027, 0.033, 0.030	0.12, 0.12, NC	0.077, 0.062, 0.070	
	(0.029 ± 0.003, 0.51)	(0.098 ± 0.006, 0.73)	(0.069 ± 0.005, 0.60)	(0.077 ± 0.010, 0.63)
Al	0.14, 0.16, 0.15	0.11, 0.11, 0.13	0.11, 0.07, 0.10	
	(0.15 ± 0.01, 0.85)	(0.13 ± 0.005, 0.88)	(0.091 ± 0.005, 0.72)	NC
Cu	0.0034, 0.0038, 0.0037	NC, 0.005, 0.0042	0.002, NC, NC	
	(0.0035 ± 0.0001, 0.90)	(0.0042 ± 0.0003, 0.60)	NC	NC
Pb	NC, NC, NC	NC, NC, NC	NC, NC, NC	
				(0.0014 ± 0.0002, 0.43)
Cd versus Zn	0.0034, 0.0033, 0.0035	0.0033, 0.0031, 0.0031	0.0028, 0.0020, 0.0025	
	(0.0034 ± 0.00005, 0.99)	(0.0031 ± 0.00005, 0.98)	(0.0025 ± 0.00007, 0.91)	(0.0045 ± 0.0006, 0.51)
Element versus Ca:				
Mg	0.32, 0.31, 0.31	0.31, 0.37, 0.32	0.27, 0.21, 0.25	
	(0.32 ± 0.013, 0.85)	(0.33 ± 0.02, 0.71)	(0.23 ± 0.013, 0.73)	(0.45 ± 0.03, 0.87)
Mn	0.55, 0.53, 0.54	0.39, 0.45, 0.40	0.15, 0.15, 0.15	
	(0.54 ± 0.013, 0.96)	(0.42 ± 0.016, 0.86)	(0.15 ± 0.01, 0.73)	(1.05 ± 0.08, 0.81)
HUMIDITY CELLS, ZN VERSUS S				
Cell 1:				
Beginning (7-49 days)				(0.34 ± 0.03, 0.91)
End (56-281 days)				(0.23 ± 0.03, 0.65)
Cell 2:				
Beginning (7-49 days)				(0.35 ± 0.04, 0.94)
End (56-281 days)				(0.26 ± 0.04, 0.63)

NC Not correlated, $R^2 < 0.40$.

surfaces. The accumulation of Fe hydroxides on the surface of the pyrite would inhibit pyrite oxidation and could lead to dominance of sphalerite oxidation. The coarse nature of jig tailings may explain the high Zn concentrations and circumneutral pH's of pore waters from jig tailings around the Coeur d'Alene Basin.

When Cd concentrations in the leachate were regressed against Zn (figure 14*B*), a remarkably high correlation was found for the original composite material, gravel, and sand columns (R^2 = 0.98, 0.97, and 0.91, respectively) (table 25). The [Cd]:[Zn] molar ratio for the three columns containing the original composite material regressed together was 0.0034 while the molar ratio of the gravel columns was 0.0031 ([Zn]:[Cd] ratios of 292:1 and 316:1, respectively). The sand columns exhibited a lower ratio of 0.0025 ([Zn]:[Cd] ratio of 408:1), even after the last five leachings were eliminated from the regression analysis because they were below the regression line for sand. The quality of these data could not be assured because this was the last analytical run before the laboratory manager left Federal service. The [Cd]:[Zn] regression for the fine column (0.0041, or a [Zn]:[Cd] ratio of 241) produced a higher slope, but Cd was less correlated with Zn (R^2 = 0.51). These molar ratios are consistent with the degree of lattice contamination in sphalerite (0.2 to 0.4 wt % Cd in sphalerite) mined from the East Fork of Nine Mile Creek (Fryklund, 1964). The high degree of Cd correlation with Zn in most of the columns strongly suggests that the Cd originated from lattice contamination of the sphalerite.

Ca, Mg, and Mn in the original composite material columns and the gravel columns (figure 15) were less correlated with S than was Zn (table 25). R^2 for individual columns was greatest for Mn (0.84 to 0.96), followed by Mg (0.81 to 0.91), and finally Ca (0.68 to 0.87). Mn in sphalerite mined from the watershed (0.01 to 0.06 wt %) corresponded to a Mn:Zn ratio between 0.0002 and 0.0011. In contrast, the ratio of Mn:Zn released from the column was between 0.11 and 0.20. Therefore, the most of the Mn could not have originated from sphalerite.

While there were only small differences in the molar ratios within each type of column, significant differences in the [Ca]:[SO_4] and [Mg]:[SO_4] ratios among different types of columns were found. For instance, the [Mg]:[SO_4] ratio in the gravel columns (0.078) was almost twice the [Mg]:[SO_4] ratio of the original composite material column (0.046). The sand columns clearly illustrated that Ca and Mg were highly correlated in their release. The regressions of these elements against S suggest weak correlation (R^2 = 0.21 to 0.37).

The lack of correlation of Ca with S was not random, for the progression of Ca release during the column leaching tests indicated a trend toward lower Ca:S ratios (figure 15*D*). Initially, Ca increased steeply with increasing S at beginning of the experiment. During the first wet period, Ca decreased while maintaining the high slope with respect to S. As Ca increased with increasing S during the first dry period, the slope flattened. Ca decreased much more rapidly with respect to S during the second wet period relative to the first wet period. The slope of the Ca increase with respect to the S increase during the second dry period was much lower than the slope during the first dry period. Mg showed a similar sequential progression and exhibited R^2 with S ranging between 0.08 and 0.17 (not shown). Mn also showed this progression but with a lesser spread between the segments, which resulted in higher R^2 with S for individual columns (R^2= 0.72 to 0.74). When Mg in the sand columns was regressed against Ca (figure 16*A*), much better R^2s were found (R^2 = 0.75 to 0.79). As were the correlations with S, there were some differences in [Mg]:[Ca] molar ratios among the column types, (0.32, 0.36, 0.22, and 0.44 for the original composite material, gravels, sands, and fines, respectively). The Mn:Ca regressions of the leachate from the original composite material and fines were also better correlated than the regressions with S (figure 16*B*). Significant differences in the Mn:Ca ratio were observed among column types.

A correlation between Ca and Mg may suggest a carbonate phase. However, the slightly acidic leachate and the low Ca content of the sand fraction (0.33 wt %) suggest that any carbonate phases originally present probably had already been dissolved during the many decades since these tailings were deposited on the flood plain. The change in the molar ratio of Ca, Mg, and Mn to S of the leachate from the sand columns during the column leaching tests suggests that ion exchange was likely responsible for the correlation between Ca and Mg. It can be seen that [Ca]:[SO_4] and [Mg]:[SO_4] ratios decreased during the first wet-dry cycle for sand column S3 (figure 17). For the [Mg]:[SO_4] molar ratio, the most dramatic decrease occurred during the first wet period. The [Ca]:[SO_4] molar ratio decreased during most of the experiment with the most dramatic decrease occurring during the second wet period. The [Ca]:[SO_4] molar ratio in the leachate seemed to stabilize during the second dry period. With Mg, the most dramatic decrease in the molar ratio of [Mg]:[SO_4] occurred during the first wet period. The Mn:S molar ratios were initially much lower than those of Ca and Mg and decreased only slightly during the column leaching tests. In contrast, the [Zn]:[SO_4] molar ratio increased during the experiment. This would suggest sig- nificant ion exchange during the beginning of the experiment between adsorbed Ca and Mg and soluble Zn produced by the oxidation of sphalerite.

$$X{=}Ca^{+} + Zn^{2+} \rightarrow X{=}Zn^{+} + Ca^{2+}, \tag{D}$$

where the $X{=}Ca^{+}$ = the solid surface with an attached divalent ion. Likewise, the decrease in pH (increase in H^{+}) during the experiment suggests that the following reaction was also occurring initially.

$$X{=}Ca^{+} + H^{+} \rightarrow X{=}H\circ + Ca^{2+}. \tag{E}$$

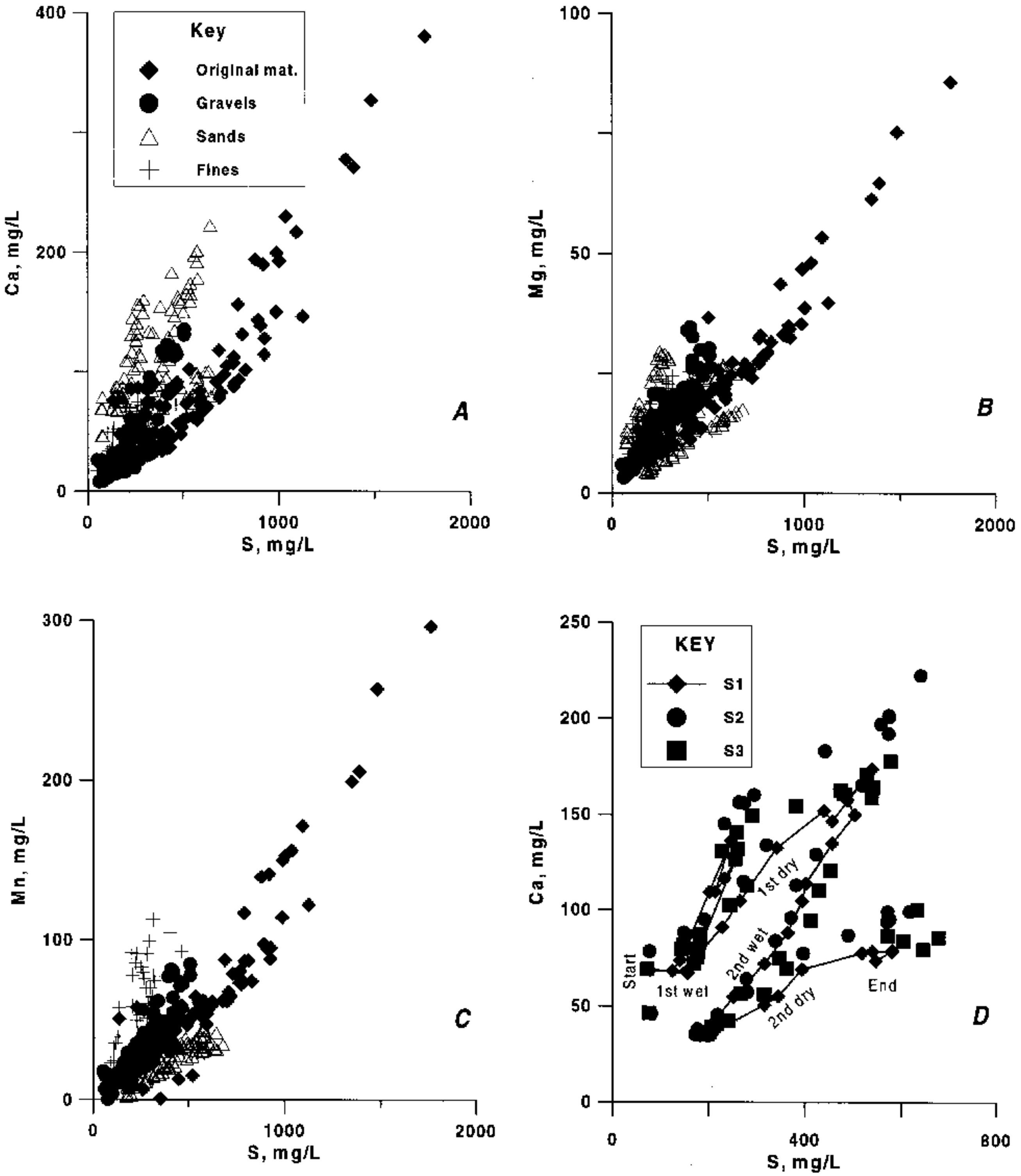

Figure 15.—Comparisons of elements in column leachate. *A*, Ca versus S; *B*, Mg versus S; *C*, Mn versus S; *D*, changing Ca versus S relationship during leaching tests in three columns containing sand fraction.

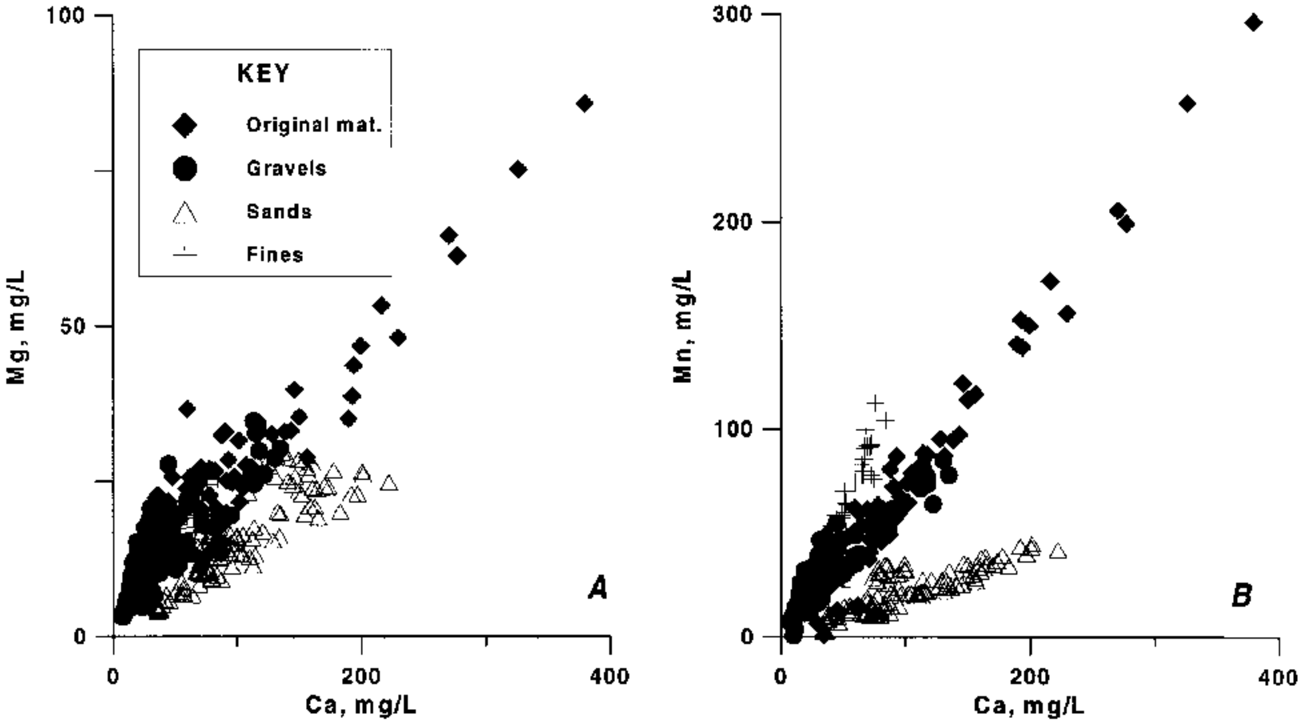

Figure 16.—Comparisons of elements in column leachate. *A*, Mg versus Ca; *B*, Mn versus Ca.

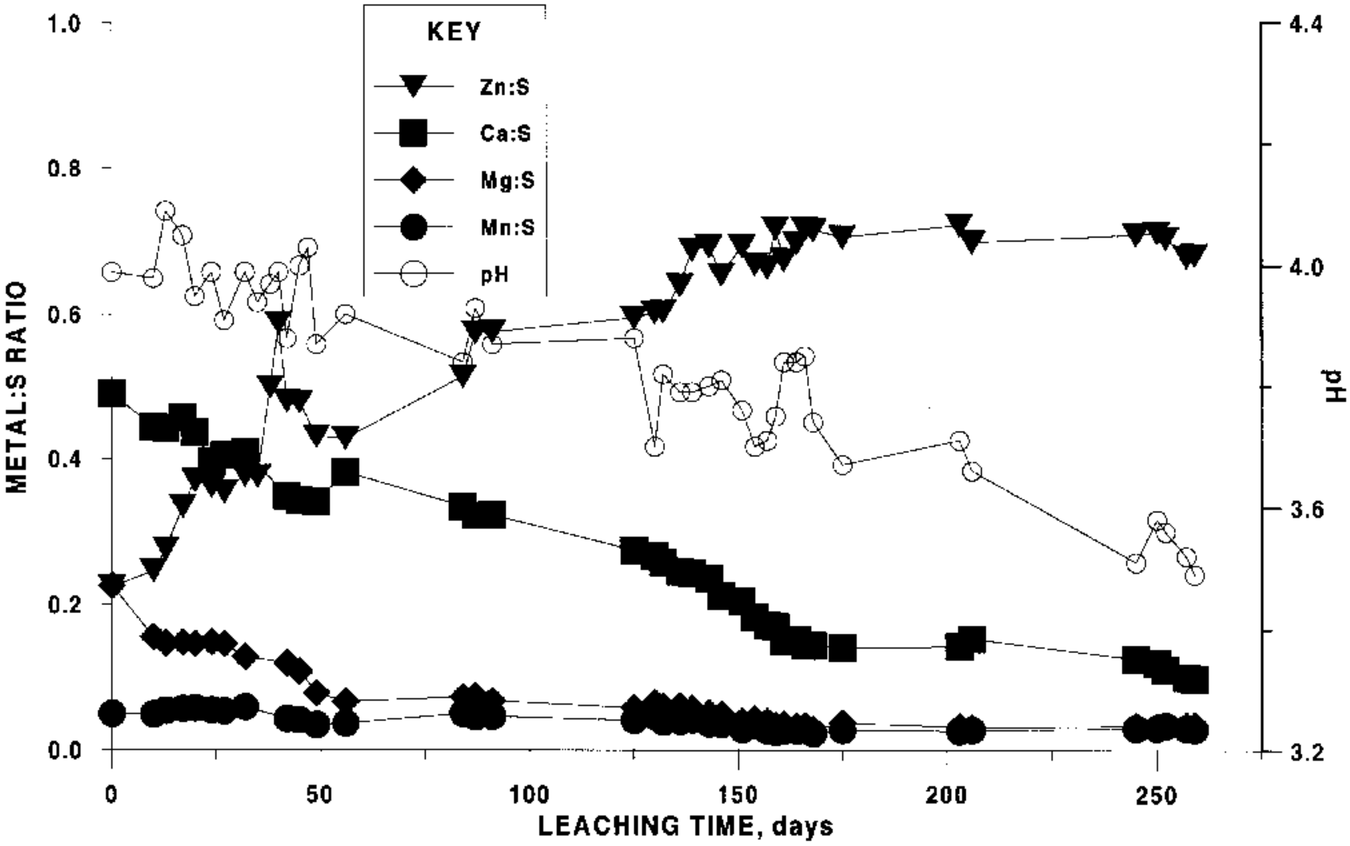

Figure 17.—Metal-to-S molar ratios and pH of leachate from sand column S3.

When all the Ca and Mg on the solid surface had been exchanged, these two reactions ceased and molar ratios then more closely reflected the oxidation reactions. The initial ion exchange of soluble Zn would explain the acceleration of Zn observed in the sand column (figure 7*A*) without a concurrent change in S release (figure 5*B*). While the amount of S released during the first and second dry periods remained about the same, the proportion of cations released changed because of ion exchange. This interpretation suggests that Zn concentrations in the leachate from the sand fraction would follow the cyclic pattern of S and would not continue to increase. It is not known if the uptake of Ca and Mg during the composite separation process was controlled by the nature of the gangue material in the sand fraction or the additional contact of the sand fraction with clean tap water as the fines were washed off. It is also not known what the source was for the low level of release of Ca, Mg, and Mn after the ion-exchange capacity of the sands had been depleted.

Neither Na nor K concentrations correlated with S, Si, or Al concentrations. However, the molar concentrations of Na + K (figure 18*A*) (table 25) were correlated with S for the original composite material and gravel columns (R^2 = 0.72 to 0.98 and 0.80 to 0.89, respectively). Na + K was moderately correlated with S in the sand columns and not correlated in the fine column.

Al concentrations in the columns containing original composite material exhibited initial flushing behavior, were influenced by acid production from oxidation during both cycles, and were highly correlated with S concentrations (R^2 = 0.85) (table 25) (figure 18*B*). The gravel and sand columns also exhibited high correlations with S (R^2 = 0.88 and 0.72, respectively). The release of Al from the fines was low and was not correlated with S. Al was undersaturated with respect to gibbsite [$Al(OH)_3$] and did not seem to be correlated with pH. These observations indicated that Al removal by gibbsite precipitation was not occurring to a significant extent at these low pH’s.

Si in the leachate from the gravel, sand, and fine columns was correlated with S (R^2 = 0.73, 0.60, and 0.63, respectively) (table 25). Si in the columns containing the original composite material reached a maximum of about 70 mg/L regardless of S concentrations (figure 18*C*). The saturation indices shown in figure 10*A* indicate that Si was slightly supersaturated with respect to amorphous silica ($SiO_2 \bullet nH_2O$). Precipitation of silica seemed to be the cause of the lower correlation (R^2 = 0.51) in the columns containing the original composite material.

Significant amounts of Fe were found in the leachate from the fines only when the pH dropped below 3.2 (figure 18*D*). When the ORP was set so that all Fe was assumed to be Fe^{3+}, Fe in the leachate from the fines was undersaturated with respect to amorphous Fe oxide [$Fe(OH)_3$] by about 1.5 log units but supersaturated with respect to goethite [FeO(OH)]. This observation suggests that Fe was probably controlled by some form of ferric oxyhydroxide having an intermediate solubility. This was not surprising considering that the collection bottle, the column inlet, and the column outlet were open to the air. Any oxidation of ferrous Fe that occurred in these column experiments would also occur in a shallow oxygenated aquifer below a mine waste pile.

The correlations of Cu with S (figure 19*A*) were highest in the columns containing the original composite material (R^2 = 0.90) and moderately correlated in two of the three gravel columns (R^2 = 0.72 and 0.73). In contrast, Cu concentrations in the sand and fine columns were low and did not correlate with S. As with Mn, the Cu:Zn ratio in sphalerite mined from the drainage (0.00006 to 0.00012) was much lower than the Cu:Zn ratio released from the columns (0.0026 to 0.005), indicating that Cu was being released from a solid component other than sphalerite.

No significant correlations of Pb with S were found for the columns containing the original composite material, the gravel fraction, and the sand fraction. This observation suggests that any Pb released during the oxidative process was subsequently removed from solution as a result of the higher pH in these columns (pH 3.2 to 4 relative to pH 2.5 of the fine column). At much lower concentrations of adsorptive sites, Pb adsorption onto Fe oxyhydroxides begins at a pH as low as 3.5 (Benjamin, 1978). A moderate negative correlation with S (R^2 = 0.43) was found for the fine column (figure 19*B*). At the lower pH of the fines, adsorption processes were negligible, and Pb concentrations seemed to be controlled by anglesite solubility (figure 11*A*).

The concentrations of leachates from the humidity cells containing the fine fraction were subjected to a limited regression analysis. The regression of Zn with S (as sulfate) was much stronger in the humidity cells (figure 20) relative to the regression for the column containing the fine fraction. However, the [Zn]:[$SO_4^=$] molar ratios in the humidity cells containing the fine fraction (0.23 to 0.35) indicate that pyrite oxidation dominated the reactions, producing sulfate in the humidity cells as it did in the columns containing the fine fraction.

Reconstruction of Geochemical Reactions

The concentrations of dissolved species were influenced by the oxidation of sulfide minerals and the attendant acid production resulting from pyrite oxidation and their removal by geochemical processes. The products of oxidation of sulfide minerals were released either from secondary salts present at the beginning of the experiment, secondary salts formed during the dry periods, or from direct oxidation of sulfide minerals. S was assumed not to have participated in any removal processes and thus was used as a tracer for sulfide mineral oxidation.

The geochemical reactions that occurred in the gravel columns were reconstructed from the element-versus-element plots using the lower estimate of Fe contamination of sphalerite. The series of reactions were normalized to 1 mole of sulfate

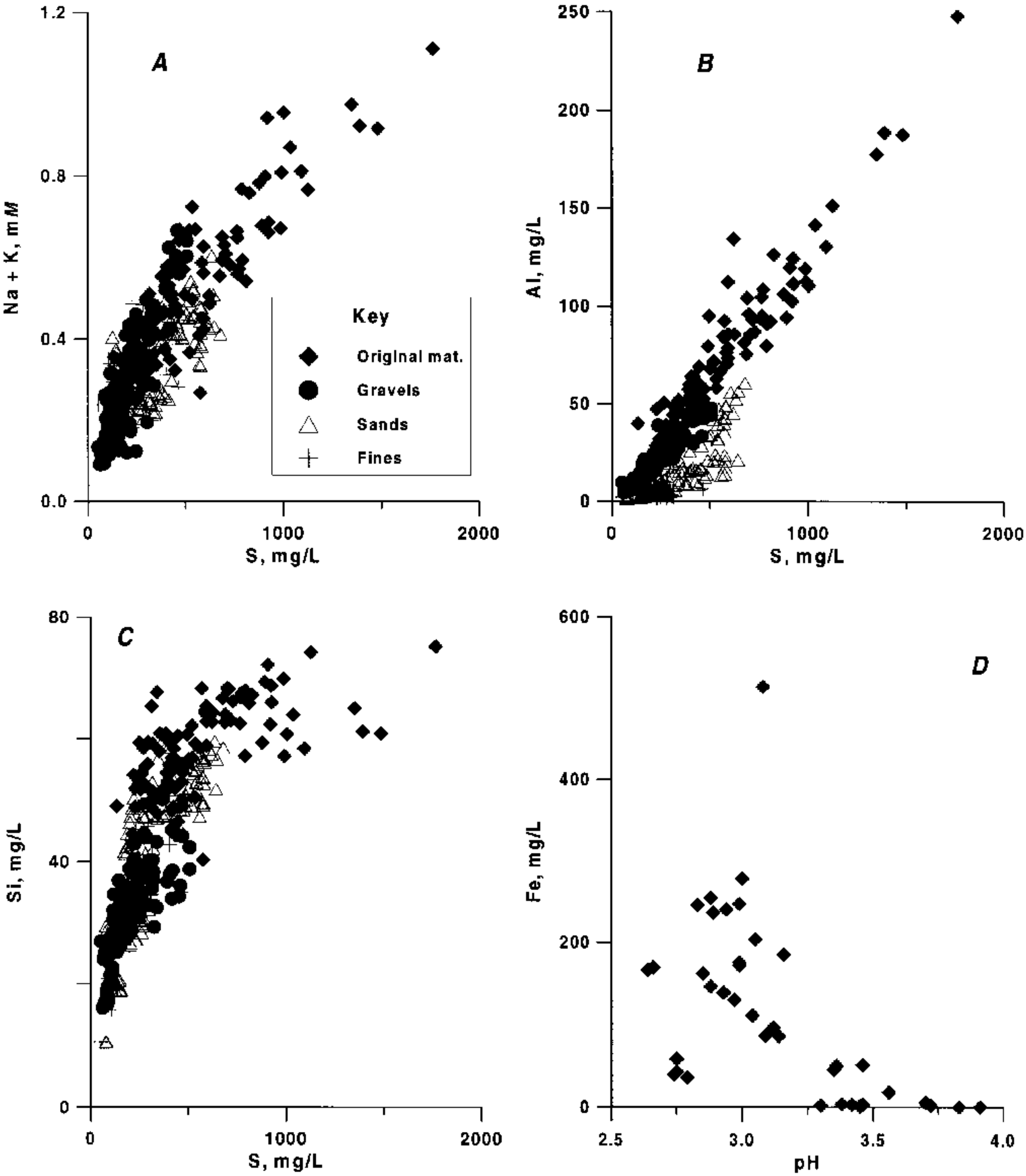

Figure 18.—Comparisons of elements in column leachate. ***A*****, Na + K versus S;** ***B*****, Al versus S;** ***C*****, Si versus;** ***D*****, Fe versus pH in column containing fine fraction.**

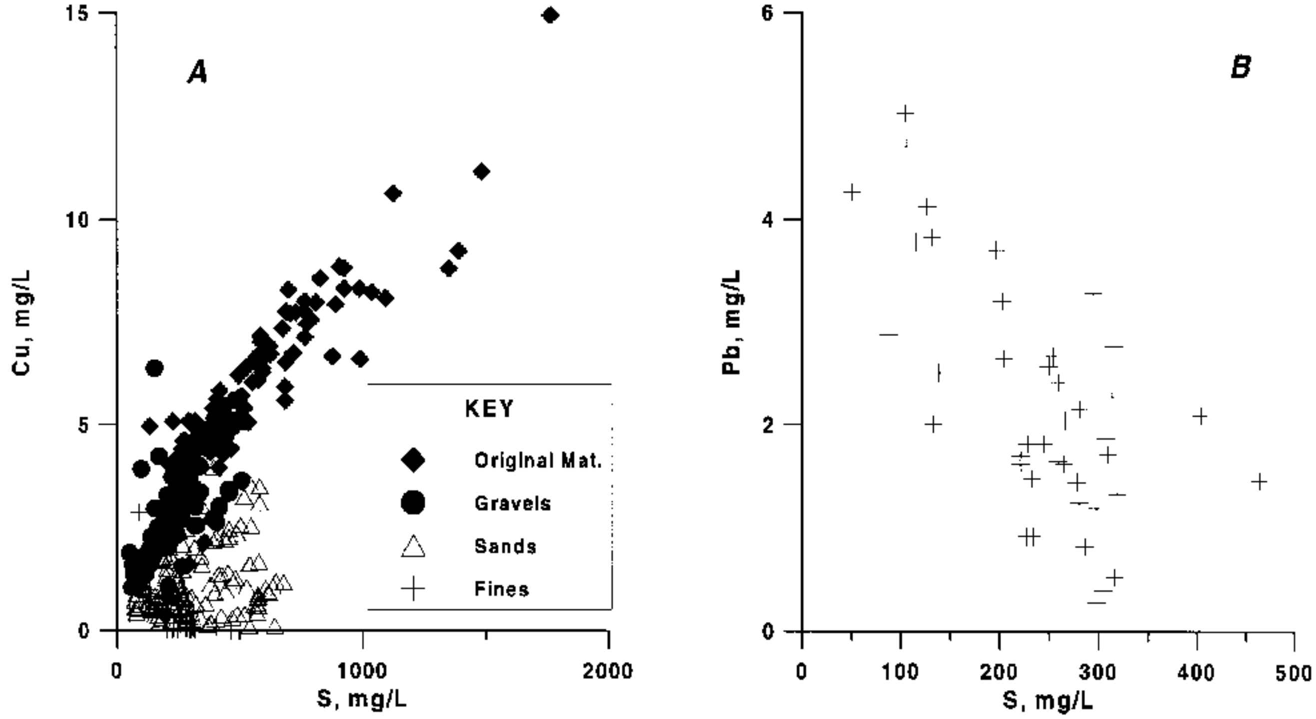

Figure 19.—Comparisons of elements in column leachate. *A*, Cu versus S; Pb versus S in column containing fine fraction.

released (table 26). The stoichiometric coefficients for the reactions were obtained from the regression of the elements against sulfate. Sulfate was produced from the oxidation of sphalerite, pyrite, and chalcopyrite (reactions F, G, and H). The stoichiometric coefficient for Cu in reaction G was obtained from figure 19*A* and table 25. The coefficient for Zn in reaction F was obtained from figure 14*A*. The oxidation of the sulfide in sphalerite and chalcopyrite to sulfate in itself is acid neutral. However, acid is formed by the oxidation and hydrolysis of ferrous Fe to produce ferric hydroxide solids (reaction I). The stoichiometric coefficient for pyrite oxidation (reaction H) is calculated by difference [(1 - (0.53 + 0.068))/2]. For pyrite, acid is produced both by the oxidation of S (-1) and by the oxidation, hydrolysis, and precipitation of Fe.

Since Na, K, Si, and Al probably originated from aluminosilicates, gangue minerals that were present in the sample were examined for their K:Al:Si ratios. The (K + Na):Al:Si ratio of the leachate (1:3:3) was consistent with the dissolution of the muscovite [KAl$_3$Si$_3$O$_{10}$(OH)$_2$] present as a major gangue mineral (reaction J) if Na were allowed to substitute for K. The dissolution of this gangue mineral consumes acid. The ion exchange that was inferred to be occurring within the sand fraction was assumed to be responsible for the release of Ca, Mg, and Mn from the gravel fraction (reaction K).

As shown in reaction A, 2 moles of acid are produced for each mole of sulfate produced by pyrite oxidation. When the sulfate generated only by pyrite (reaction H) and

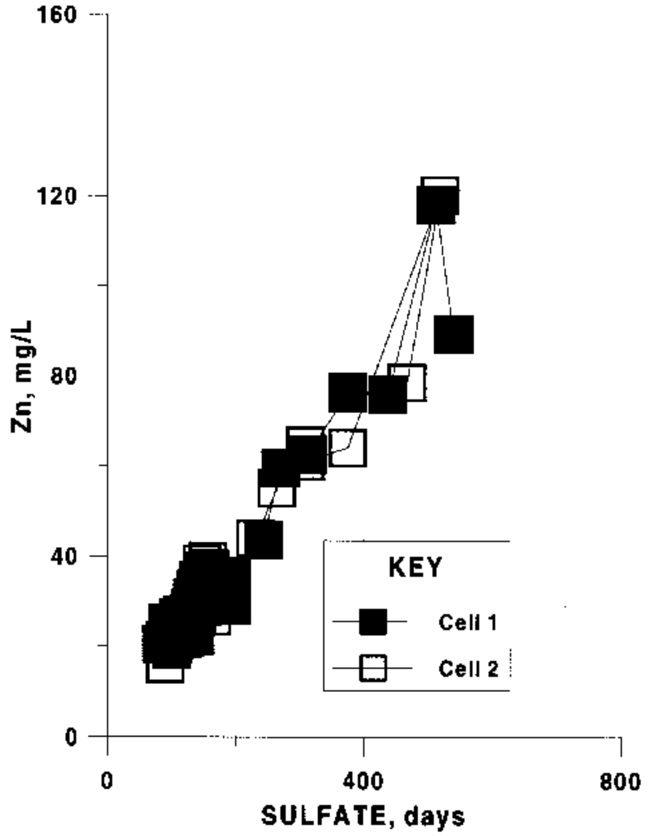

Figure 20.—Zn versus sulfate released from humidity cells containing fine fraction.

Table 26.—Reconstructed reactions for gravel fraction

Equation	Reaction stoichiometry	Reaction
F	$0.53\ (Zn_{0.99}, Fe_{0.01}, Cd_{0.0034})S + 1.18\ 0_2 \neq 0.53\ Zn^{2+} + 0.006\ Fe^{2+} + 0.0020\ Cd^{2+} + 0.53\ SO_4^{=}$	Sphalerite oxidation.
G	$0.034\ CuFeS_2 + 0.136\ O_2 - 0.034\ Cu^{2+} + 0.034\ Fe^{2+} + 0.068\ SO_4^{=}$	Chalcopyrite oxidation.
H	$0.20\ FeS_2 + 0.7\ O_2 + 0.20\ H_2O - 0.20\ Fe^{2+} + 0.40\ H^+ + 0.40\ SO_4^{=}$	Pyrite oxidation.
I	$0.24\ Fe^{2+} + 0.06\ O_2 + 0.6\ H_2O - 0.24\ Fe(OH)_3(s) + 0.48\ H^+$	Fe oxidation, hydrolysis, and precipitation.
J	$0.04\ (Na, K)_1Al_3Si_3O_{10}(OH)_2 + 0.4\ H^+ - 0.04\ (Na^+,K^+) + 0.12\ Al^{3+} + 0.12\ H_4SiO_4$	Muscovite dissolution.
K	$0.4\ X{=}(Ca_{0.5}, Mg_{0.225}, Mn_{0.275}){+}0.4H^+ - 0.4\ X{=}H^o + 0.2\ Ca^{2+}\ 0.09\ Mg^{2+}\ 0.11\ Mn^{2+}$	Ion exchange.
L	$v\ Al^{3+} + v\ H_2O \neq v\ Al(OH)^{2+}{}_1 + v\ H^+$	Al hydrolysis.
M	$w\ PbS + 2w\ O_2 \neq w\ PbSO_4\ (s)$	Galena oxidation and anglesite precipitation.
N	$x\ H_4SiO_4 \neq x\ SiO_2(s) + x\ H_2O$	Silica precipitation.
O	$y\ (Zn_{0.9997}, Cd_{0.003})\ SO_4 - y\ Zn^{2+} + 0.0034\ y\ Cd^{2+} + y\ SO_4^{=}$	$ZnSO_4$ dissolution.

the acid produced from the hydrolysis of Fe^{2+} (reaction I) from reaction H and other reactions (0.04 mole Fe per mole of sulfate in reactions F and G) were summed, 0.88 mole of acid was produced for each mole of sulfate found in the leachate. When ion exchange is assumed to control Ca, Mg, and Mn con- centrations, 0.8 mole of acid is neutralized per mole of sulfate produced (reactions J and K). Within the low pH range of the leachate from the gravel columns (pH 3.5), Al^{3+} is the only element in significant concentrations in solution to provide any buffering capacity through its hydrolysis (reaction L). How- ever, the buffering capacity of Al^{3+} is very limited at a pH 2 logs units away from its acidity constant. More definitive informa- tion of the origin of the Ca, Mg, and Mn in the leachate from all the columns is needed to better define the acid balance.

Given the simplicity of these reactions, this degree of agreement within a wide range of uncertainty suggests that the reactions describe the overall acid-base reactions reasonably well. Several other reactions may also occur that neither produce nor consume acid in this low pH range (< pH 4). The oxidation of galena is acid neutral if Pb is not hydrolyzed at this low pH and if sulfate is the final S product. The presence of anglesite determined by SEM and the high recovery of Pb by gravity separation (i.e., as anglesite) suggest that most of the galena that is oxidized is converted to anglesite (reaction M). At high dissolved Si concentrations, one of the variety of silicate minerals may precipitate (reaction N). The dissolution of $ZnSO_4$ with concurrent Cd release (reaction N) is also acid neutral if it is assumed that the ferrous Fe in the original sphalerite had previously been oxidized and hydrolyzed. As far as the acid-base balance is concerned, the dissolution of $ZnSO_4$ can be substituted for sphalerite oxidation if the effects of the contaminant Fe are ignored.

COMPARISONS OF METAL RELEASE WITH TOTAL ELEMENT CONCENTRATIONS IN THE SOLID PHASE

The releases of metals per a single leaching (milligrams per leaching) were obtained by multiplying the concentrations of elements in the leachate (milligrams per liter) by the volume of water recovered (liters per leaching). This amount of each element was then normalized to the total mass of material the leachant contacted (milligrams per kilogram of material per leaching). In the static tests, there was only one leaching having substantial contact between the water and the solids. Likewise, wet separation of the original composite material into the three size fractions can also be considered a large-volume static test because considerable contact between solids and leachant was achieved. The amount of each element released from the original composite material can be calculated because the concentration of each element was measured in the decant waters and the total volumes of wash water were measured during each of two batch separation processes. Concentrations in the decant water were corrected for the elements originally in the tap water.

In a column leaching kinetic test, contact between the leachant and the solids is much diminished in comparison to contact in a static test. In the column leaching tests, the ratios of the volume of liquid leached to the weight of solids in the columns for each wet-dry cycle (0.24 to 0.41 L/kg) were only one-fifth the ratio maintained in the static tests (2.5 L/kg). Therefore, the release of elements per leaching was summed over a number of leachings to obtain a cumulative release. Releases during each of the two wet-dry cycles of the column tests were summed separately. In contrast, the liquid-to-solids ratio in the humidity cell tests (13.6 L/kg) was much greater than the ratio for the static tests. The releases during the humidity cell tests were summed over the entire 41 leaching tests because these tests did not exhibit the variability found in the column tests. Once the releases of metals during each static and kinetic test were normalized to the amounts of the solids, different leaching treatments for the segregated materials could be compared.

The elements were grouped, first, by the amounts of their release during column experiments with the original composite material relative to total element concentrations in the solid phase and, second, by comparisons of the results of the static and kinetic tests. For many elements studied, only a fraction (< 0.1%) of the total element concentrations were released during the first wet-dry cycle (table 27). This examination of the relationships between the extent of release and total metal

Table 27.—Cumulative metals leached during static, column, and humidity cell tests, milligrams per kilogram

	Liquid:solid ratio, L/kg	Na	K	Ca	Mg	Al	Fe	Mn	Cu	Zn	Cd	Pb	Si	S
						Element								
ORIGINAL COMPOSITE MATERIAL														
Total	NAp	4,700	25,000	2,500	3,400	52,000	74,900	4,200	130	3,600	18	14,400	272,000	8,600
Batch 1	2.3	ND	ND	22	3.0	0.6	<0.2	13	<1	64	0.5	7.7	ND	113
Batch 2	1.6	ND	ND	17	4.6	<0.2	<0.2	14	<1	70	0.6	12	ND	131
Column during 1st cycle	0.23 (0.36)	1.0	2.7	22	5.1	17	<0.05	16	1.5	139	1.26	0.5	10	171
Residence time, years	NAp	1,560	3,090	38	220	3,600	(1)	68	2.9	8.6	4.7	9,600	9,100	17
Weighted average during 1st cycle	NAp	1.9	2.8	17	5.1	4.8	(1)	12	1.6	53	1.43	1.9	9	76
Column during 2nd cycle	0.24 (0.37)	0.6	3.1	11	4.4	14	<0.05	11	1.3	163	0.73	0.5	13	101
Weighted average during 2nd cycle	NAp	0.5	1.7	7	2.6	3.2	(1)	6	0.5	69	0.39	1.2	19	64
GRAVELS														
Total	NAp	3,700	26,000	1,800	3,200	54,000	69,000	3,600	100	3,500	20	9,700	278,000	7,000
Static cold flash shake	2.5	2.3	2.2	1	2.5	1.7	0.87	7.5	0.3	28	0.17	23	<3	44
Column during 1st cycle	0.41 (0.47)	2.1	3.2	10	4.6	6	<0.1	9	2.2	59	1.94	2.3	9	69
Column during 2nd cycle	0.42 (0.47)	0.4	1.2	7	2.4	4	<0.1	5	0.6	62	0.34	0.9	15	39
SANDS														
Total	NAp	7,000	31,000	3,300	3,200	54,000	77,000	3,200	100	5,200	30	12,900	282,000	7,000
Static cold flash shake	2.5	ND	21	29	4.7	1	2	14	0.45	47	<0.3	19	4.3	70
Column during 1st cycle	0.41 (0.47)	1.5	2.6	38	6.5	3	<0.1	8	0.74	68	1.13	1.5	11	123
Column during 2nd cycle	0.42 (0.47)	0.8	3.0	25	3.5	7	<0.1	6	10.7	228	3.9	0.8	15	127
FINES														
Total	NAp	5,900	19,900	3,400	3,900	54,000	127,600	4,200	400	3,300	<10	49,400	243,000	12,000
Column during 1st cycle	0.40 (0.36)	1.6	2.1	18	5.2	2.5	31	25	0.51	33	0.48	1.3	9	76
Column during 2nd cycle	0.33 (0.37)	0.7	2.2	11	4.8	1.0	38	13	0.20	20	0.13	0.6	5	68
Humidity cell	13.6 (21.4)	25	120	121	54	94	2.4	1,000	13.9	470	3.10	12.5	ND	749

NAp Not applicable. ND Not determined.

[1] Release from gravels was less than detection limit.

NOTE.– For column and humidity cell tests, the liquid-to-solid ratio is based on water recovered, the value in parentheses is based on water added.

concentrations was consistent with reactions F through O. Na, K, Al, and Si were released at a very slow rate by the acid attack on aluminosilicate minerals. For the elements associated with muscovite dissolution (Na, K, Si, and Al), the plots of element versus S suggest that the release of these elements was dependent on how the controlling geochemical oxidation reactions and subsequent dissolution proceeded. Because of the stoichiometry of these elements (i.e., low stoichiometric co- efficients for the overall reaction), release was low even at the fairly low pH's found in the leachates. The low release of Pb (<0.03%) seemed to be controlled by anglesite solubility. Fe release was only found in the fine fraction (0.02% of the total) and was probably controlled by ferric hydroxide solubility.

A rough estimate of the time before the original composite material might leach significant amounts of elements under these laboratory conditions can be made by dividing total element concentration by the leaching rate. The leaching rate for the first wet-dry cycle in milligrams of element per kilogram of solids of the original composite material per one-third year (column leaching during first cycle in table 27) was used. This residence-time calculation assumes that the leaching rate for the second wet-dry cycle continues at the same rate throughout the entire time of the estimate. Many physical and geochemical conditions tend to slow down the leaching rate with time, and thus a longer period of time is required to leach the same amount of an element. Implicit in this calculation is the as- sumption that the mineral being dissolved or oxidized during these leaching tests contributes most of the mass of the element. If the element were also present in less reactive minerals, then the time-to-consumption of the dissolving phase will be overestimated to the extent that other nonreactive phases are present. In addition, missing leachate concentration data will underestimate the release, which results in an overestimation of residence time.

Although the original composite material was only one sample and the laboratory conditions did not precisely simulate environmental conditions, these calculations gave a rough estimate of the time the reactions could continue at their present rate. For K, Na, and Al, residence times between 1,500 and 3,600 years were calculated under these acidic conditions, while the residence time for Si was 9,000 years. The predominance of less reactive quartz in the gangue minerals explains the much longer residence time for Si.

The remaining elements (Ca, Mg, Mn, Zn with Cd, and S) had higher stoichiometric coefficients, and their releases were greater than 0.3% of their metal concentrations during the first leaching cycle. Cu concentrations in both the solids and liquids were too low for a definitive pattern to be discerned. During the first wet-dry cycle, about 4% of the Zn was released from the original composite material. Therefore, if release continued at this rate, Zn minerals having the same reactivity as those that were solubilized during the leaching experiment would be consumed in 25 one-third-year periods, or 8.6 years. About 2% of the S was released during the first wet-dry period, resulting in a residence time of 17 years.

The residence times for Ca, Mg, and Mn were calculated to be 37 years, 222 years, and 88 years, respectively. As shown with the sand fraction, the ion-exchange capacity of the solids can be depleted quickly. Clearly, the nature and kinetics of Ca, Mg, and Mn releases from more refractory forms will dictate their eventual time to consumption.

COMPARISONS OF METAL RELEASE BETWEEN STATIC AND KINETIC TESTS

The elements that were released in significant amounts can be divided according to whether most of the release was through dissolution of water-soluble minerals or through oxidation and the attack of the resulting acid. Dissolution of soluble minerals was responsible for most of the release during the short time of a static test because in situ oxidation was unlikely to occur at a rate sufficient to release significant amounts of metals. In contrast, the releases of elements during column tests were a result of both dissolution of soluble minerals and oxidation that occurred during the test. Thus, the ratio of release during the static tests relative to release during the column tests gives some indication which process predominated during the column tests.

Moderate releases of Ca, Mg, and Mn associated with ion exchange were found both in the static tests and the first cycle of the column leaching tests. More than 80% of the Ca, Mg, and Mn released during the first wet-dry cycle of the column test was released during the static test. In contrast, between 50% and 70% of the Zn and S released during the column tests was released during the static test, indicating the presence of soluble $ZnSO_4$ in the original composite material. Therefore, Zn and sulfate in the column tests were released both from the dissolution of soluble $ZnSO_4$ salts and from the oxidation of sphalerite.

Both the humidity cell and column leaching tests were conducted on the wet-screened fine fraction for about 270 days. Therefore, estimates of the acceleration of weathering processes in humidity cells can be made by comparing the release rates from the two different tests. In addition to the weekly wet air-dry air cycle in which the nature of the contact between water and solids was changed, the humidity cells were leached with 34 times as much water as the columns (13.6 L/kg versus 0.40 L/kg). The ratio of humidity cell release to the release from the columns containing the same material was 8.9 and 5.2 for Zn and S, respectively. The ratios for elements associated with ion exchange ranged between 2.6 for Mn to 6.4 for Ca. The ratios for elements associated with the gangue minerals ranged between 2.7 for Al to 23 for K. The higher liquid-to-solid ratios for the humidity cell experiments resulted in less concentrated leachates and a higher pH. This higher pH inhibited the release of Fe from the humidity cells, which was lower than the Fe release from the column tests by a factor of 3. The ratios for Cu and Pb were 19 and 7, respectively. Although the humidity cells accelerated the release of all elements except Fe, much of this accelerated release may have been the result of greater flushing of the material with more water. On the basis of these data, it cannot be determined if the acceleration in weathering in the humidity cells was a result of greater oxidation during the dry periods or by the more effective flushing of oxidation products from the humidity cells by the greater amounts of water.

EFFECTS OF SEPARATION ON METAL RELEASE IN COLUMN TESTS

The effects of segregating the original composite material can be determined by comparing metal release from the original composite material with metal release from the segregated material, weighted according to their respective contributions to the original composite material. In general, the weighted-average metal release from the segregated material was less than the metal release from the original composite material (table 27). Some of this decrease was caused by changing the interaction between water flow and the geochemical reactions. Some of the decrease was a result of washing soluble salts off the original composite material during the wet- separation process. It was assumed that this flushing effect was limited to the first wet-dry cycle. Therefore, the release of an element from the original composite material during the first wet-dry cycle was compared to the summation of the weighted-average release of elements from the segregated fractions plus the elements released during the batch separation. For the comparisons of the second wet-dry cycle, metal release from the original composite material was compared directly to the weighted-average release from the segregated material.

Zn is considered in detail below to illustrate the concepts behind the comparisons of metal release. The release per leaching for columns containing the original composite material and the three segregated fractions is shown in figure 21*A*. The high release of Zn from the columns containing the original composite material during the initial leaching cycles was probably a result of the dissolution of soluble Zn salts. Since these salts were removed to a large extent during the wet screening while the segregated fractions were being prepared, the releases of Zn from these segregated fractions were much less. Consequently, the calculated weighted-average release of Zn from the segregated fraction was also lower than releases from the original composite material. The cumulative release of Zn from the original composite material during the first wet-dry cycle (to the third cycle after the dry period at 139 days) was 139 milligrams of Zn per kilogram of solids (figure 21*B*) (table 27). In contrast, the weighted-average release of the segregated fractions was only 53 mg/kg. Much of this difference can be explained by the dissolution of soluble Zn salts during wet screening (average 67 mg/kg for the processing of the two batches). The cumulative difference between the release from the original composite material and the weighted average of the segregated fractions is also shown in figure 21*C*. The dissolution of Zn salts during the wet-screening process (average 67 mg/kg) can account for this cumulative difference in release between the original composite material and the weighted average of the segregated columns only through the first 50 days of leaching.

The cumulative release of Zn from the gravel fraction during the second wet-dry cycle (59 mg/kg) was similar to that of the first wet-dry cycle (62 mg/kg) (table 27). During the last six leachings of the second dry cycle (last 75 days), Zn release from the sand fraction accelerated, resulting in releases from the sand columns that were higher than the releases from the original composite material. The cumulative Zn release from the sand fraction increased from 68 mg/kg during the first cycle to 228 mg/kg during the second cycle. The cumulative releases from the fine column during the two cycles were much lower (33 and 20 mg/kg, respectively). Despite the acceleration of Zn release from the sand fraction, the cumulative weighted-average release of the segregated fractions during the second wet-dry cycle (69 mg/kg) was still lower than that from the original composite material (163 mg/kg).

The weighted-average Zn release and the contribution of Zn from the gravel fraction are normalized to release of the original composite material for each specific leaching in figure 22. The weighted-average release simulates remediation options in which all materials are left on site after separation. During the initial stages of the column tests, when the effects of the wet screening were operating, and during the wet period of the second cycle, the weighted-average release was less than 40% of the release from the original composite material. The higher release from the sand fraction after the second dry period increased the weighted-average release to 60% of the release from the original composite material. Overall, during the two wet-dry cycles, the release of Zn from the original composite material was 302 mg/kg while the weighted-average release from the segregated fractions was 122 mg/kg. Only 67 mg/kg of this 180 mg/kg difference can be attributed to washing of soluble Zn salts during the wet-screening process. Therefore, 67% (113 of 180 mg/kg) of this difference in the cumulative release must have been a result of changing the geochemical or hydrological flow characteristics of the columns as a result of the separation process.

When only the gravel fraction was simulated as remaining on site, the gravels contributed only 20% of the release from the original composite material during the period in which the effects of the wet screening were operating and during both wet periods. During the dry periods, removal of the sand and fine fractions (40% of the mass) resulted in a 60% decrease in release.

The cumulative S release from the columns containing the original composite material during the first cycle (171 mg/kg) (table 27) was significantly higher than the weighted-average S release from segregated columns (76 ppm). As with Zn, this

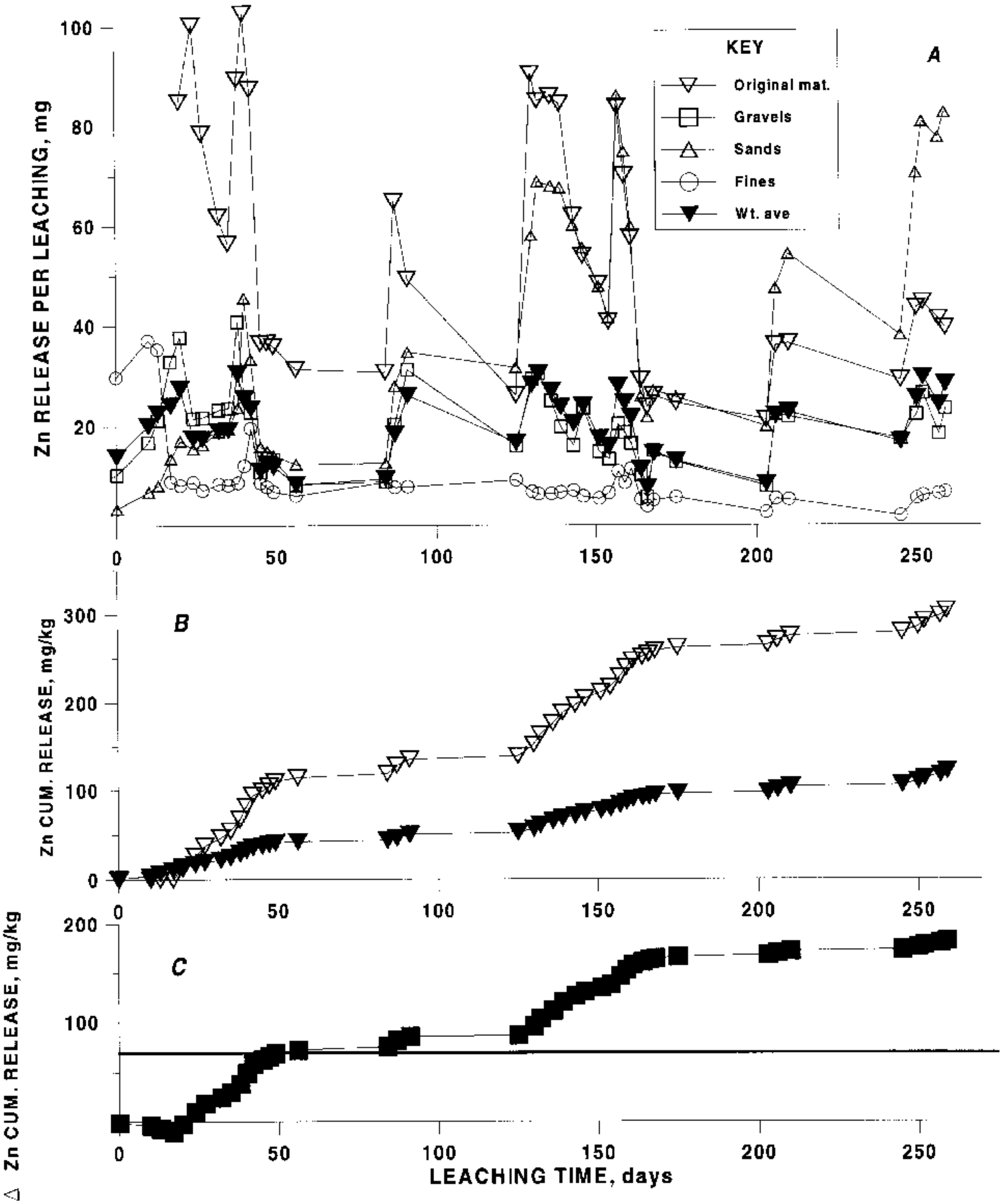

Figure 21.—Average release of Zn from triplicate columns containing original composite material, gravel fraction, and sand fraction, and from single column containing fine fraction. Weighted-average concentrations were calculated from concentrations of three fractions and their respective contributions to mass of original material (61%, 15%, and 25%). *A*, Zn release per leaching; *B*, cumulative Zn release; *C*, difference in cumulative release between original composite material and weighted average. Horizontal line indicates release during wet screening.

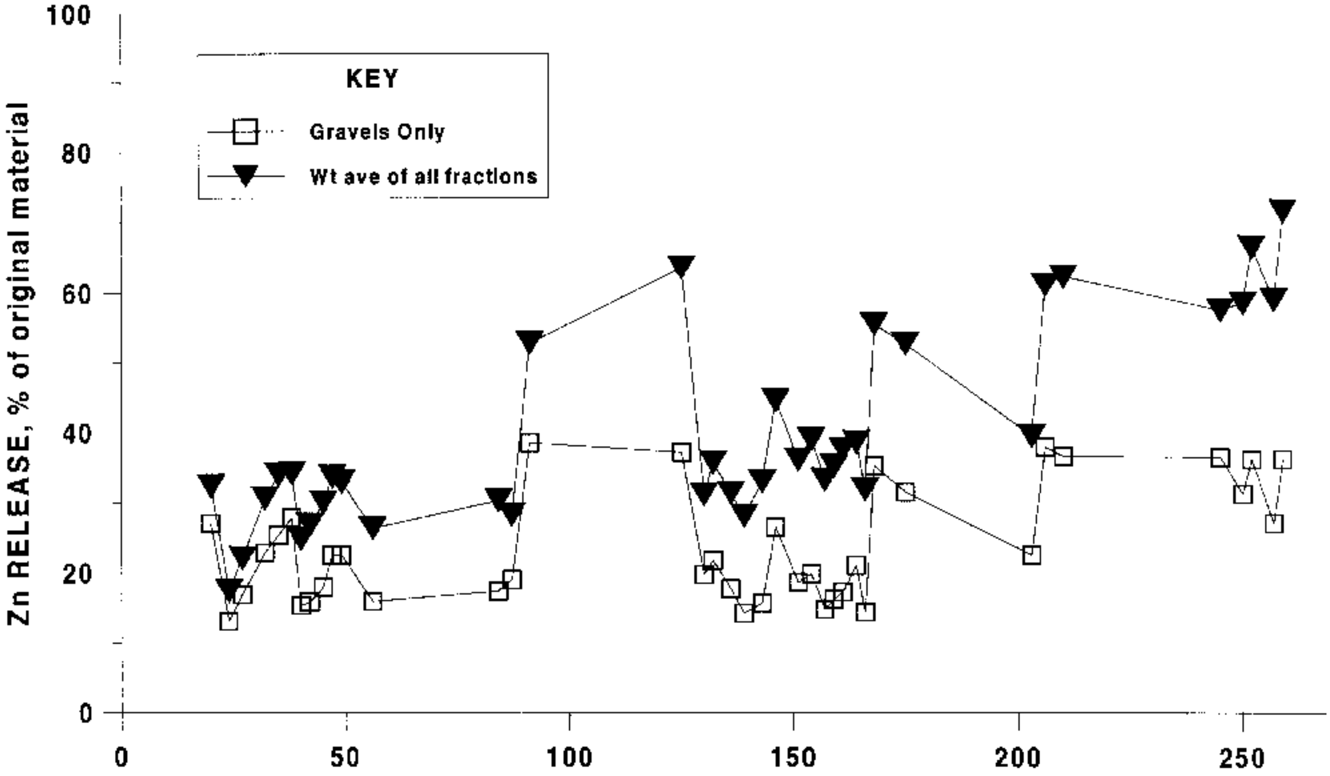

Figure 22.—Release of Zn from gravel fraction and weighted average of segregated fractions compared to release from original composite material. Weighted-average release simulates release if all fractions are left on site, while release from gravel fraction simulates removal of 40% of material contained in fine and sand fractions.

difference can be accounted for by the release of S into the processing water during the wet-screening process (average 122 mg/kg). However, S release from the original composite material (101 mg/kg) during the second cycle was still twice that of the weighted-average release from the segregated fractions (54 mg/kg).

For the major cations, releases were much smaller than the releases of Zn and sulfate. The differences between the cumulative release from the original composite material during the first cycle and the calculated weighted average from the segregated material were somewhat diminished because the segregated columns had significant releases during the first four leachings when no water was recovered from the columns containing the original composite material. The release of Ca from the original composite material was 22 mg/kg during the first cycle. Of the 17 ppm of Ca released from the segregated columns during the first cycle, 5 mg/kg was released during the first four leachings. Likewise, 2.1 of the 5.1 ppm Mg and 5 of the 16 ppm Mn were released during the first four leachings. The cumulative releases for both the original composite material and the weighted average of the segregated fractions during the second cycle were lower than the releases during the first cycle. The weighted-average releases of the segregated columns during the second cycle were lower than releases from the original composite material. The resulting cumulative releases were less than 6 and 3 mg/kg for K and Na, respectively.

The cumulative release of Al from the original composite material during both cycles was 31 mg/kg, while the cumulative release from the segregated fractions was 8 mg/kg. The releases of Cu and Cd from the original composite material were small (2.8 and 2.0 mg/kg, respectively) and similar to those of the weighted average (2.1 and 1.9 mg/kg, respectively).

The behavior of Pb was anomalous in that the segregation of the material increased the amounts of Pb released from the columns. The release from the columns containing the original composite material during the two cycles was 1.0 mg/kg, while that of the weighted average was 3.1 mg/kg. Much of this increase is attributable to Pb release from the gravel columns, which was 3.2 mg/kg during the two cycles. As shown in figure 11*A*, Pb concentrations in the column leachates seemed to be controlled by anglesite solubility. The remediation option of separation was partially successful in reducing Zn and sulfate release. However, such success had the adverse consequence of diminishing the effect that high sulfate concentrations had on limiting Pb solubility. The anglesite control of Pb release from the gravel fraction emphasizes the need for effective separation treatments because the anglesite was concentrated in the fine fraction.

PHYSICAL SEPARATION AS A MEANS TO REDUCE METAL LEACHING RATES

The separation of the porous gravel fraction from the chemically reactive sand and fine fractions of the original composite material did change the interaction between the hydrology and geochemistry of the columns in a manner that reduced metal loadings. However, the gravel fraction continued to release significant amounts of metals. In an experiment ancillary to the leaching tests, dry-screened gravel from the same original composite material was cleaned using a variety of wet and dry methods, and the resulting solids were subjected to a static leaching test (table 1). The results of this experiment clearly showed that the chemically reactive fines and sands adhering to the surfaces of the gravels controlled the initial release of metals. To remove the finer material from the surfaces of the coarser gravel, water must be used (table 21). Wet screening of the gravels and wet rolling in a bottle produced low initial Zn releases (75% reduction from the control material). Wet screening after dry milling of the gravels produced the lowest initial Zn release (85% reduction), but also generated additional fine material because of attrition of the gravels.

Any remediation option that includes separation and on-site disposal of the coarser fraction must pay particular attention to the efficiency of separating the finer fraction of the soil that adheres to the material that will remain on site. The finer fraction left on the surfaces of the gravel will control initial metal release. Trommels are widely used in the initial separation step. However, if not properly operated, a significant amount of fines can be rejected along with the coarser material (EPA, 1995). An additional washing of the rejected coarse material from trommels is suggested in which the cost of treating the water is balanced against the value of further reducing initial release.

In this demonstration, the gravel fraction continued to release metals after the effects of the adhered fine fraction had diminished. Both the mineralogical analysis and the wet cycle-dry cycle data (figure 6*B*) indicated that the gravels in this original composite material had an inherent ability to release metals because they contained sulfide minerals. In retrospect, the reach on the East Fork of Nine Mile Creek was not the ideal site from which to collect the original composite material because a mill was once located there. Much of the coarser fraction may have been brought to the site for milling rather than being transported by fluvial processes. In addition, the hydrological isolation of part of the original composite material may have skewed the results of these experiments. On the other hand, these isolated pockets of material may be widespread at mine waste sites, and the original composite material may be representative of many sites.

For on-site disposal of the coarser fractions after separation and washing to be effective, the coarser fraction must be much less likely to inherently release metals by oxidation of sulfide minerals. On-site disposal of the coarser fraction will probably have limited success when the entire size spectrum of the soil contains unoxidized sulfides, such as this original composite material did. On-site disposal of the coarser fraction as the only remediation process is more suited to a stream reach where the coarser fraction is primarily natural alluvial gravels.

The fine fraction was subjected to a variety of mineral-processing techniques to further reduce the portion of material required to be disposed of in a mine waste repository. Gravity separation was a fairly successful technique in concentrating Pb, probably as anglesite. However, the removal of the Pb as anglesite would have to be much more efficient in order to reduce Pb release. Pb release is controlled by sulfate concentrations in interstitial waters through anglesite solubility, rather than by the oxidation of galena. Therefore, any anglesite present can release Pb at low sulfate concentrations. This separation would only be feasible if it were economical to smelt the gravity concentrate (30% Pb). While concentration of 27% of the Fe into the magnetic fraction is interesting, little of the metals of interest are associated with this magnetic component. Only if the magnetic component, with its moderate metal contamination, was valuable as a feedstock would magnetic separation be beneficial. Conventional flotation was ineffective in concentrating the elements of interest, probably because of the extent of oxidation.

Although removal of the sand and fine fractions caused a disproportionate decrease in Zn release, the effects of changing the chemistry or hydrology of the gravel fraction were not sufficient to suggest an on-site remediation option in which the physical separation of a size fraction is the only treatment. However, this research does suggest some disposal options. If this material were to be disposed of in a repository, strategically placing different size fractions into different layers might minimize the amount of metal released by the actions of any water that did percolate through the system (figure 23). If the repository were isolated from ground water by placing the most reactive fraction on the bottom and covering it with the finer fraction, water percolation could be minimized (recall that one column of fine material clogged, indicating limited hydrological conductivity). The coarser fraction could then be placed over the finest fraction to act as a drain for any percolating water. The discontinuity in hydrological conductivity at the gravel-fines boundary would minimize water transport through the fine fraction (Richardson effect) and maximize drainage through the less reactive material. This separation process could be combined with other chemical stabilization processes, such as neutralization, addition of reducing agents to limit oxygen penetration, or providing a chemically reactive underliner.

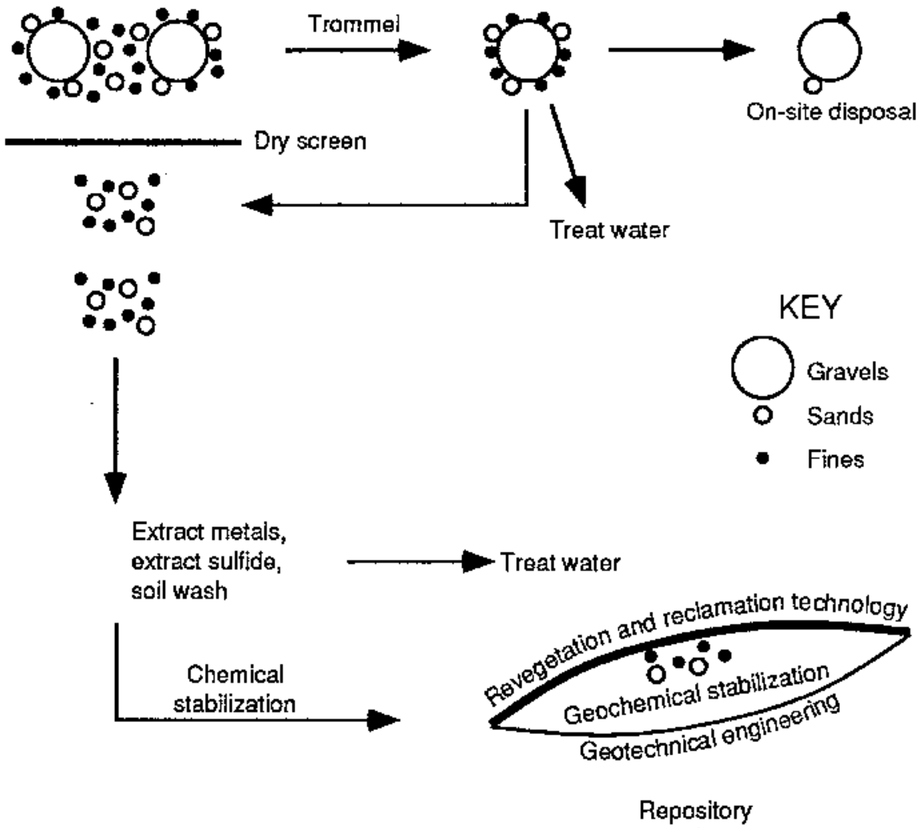

Figure 23.—Schematic of hybrid approach of using size fractionation in conjunction with disposal in repository.

CONCLUSIONS

Mine waste from the East Fork of Nine Mile Creek was tested to determine the feasibility of size separation as a primary remediation option. The hypothesis to be tested was that separating the porous gravel fraction from the chemically reactive fine fraction would change the geochemical and hydrologic interactions and thus reduce the overall release of metals. The element-element ratios of leachate from columns containing the original composite material and columns containing the three size fractions were consistent with the oxidation of sphalerite, chalcopyrite, and pyrite. The acid produced from oxidation was partially neutralized by the dissolution of muscovite. The effect of exchange of Ca and Mg on the surfaces of the sand fraction was clearly evident. It is not known how ion exchange affected metal release in the original composite material and the other segregated fractions. In this open system, Fe seemed to be controlled by the solubility of a ferric hydroxide mineral. Dissolved Si concentrations were controlled by silica solubility, while Pb was controlled by anglesite solubility. The initial release of metals from the coarser fraction was controlled by the sands and fines remaining on the surfaces of the gravel, a result of incomplete size separation.

When releases of metal from the original composite material were compared to the weighted-average releases from the three size fractions, size separation reduced Zn release by 60%. While two-thirds of this reduction was a result of changing hydrogeochemistry, one-third was the result of the flushing action of the water used during the separation process. Because Pb concentrations were controlled by anglesite solubility, decreased dissolved sulfate in the segregated material actually allowed more Pb to be dissolved.

For on-site disposal of the coarser fraction of mine-waste-contaminated soils to be a reliable remediation option, the coarser fraction must have a low sulfide mineral content and must be thoroughly cleaned of fines. Sulfide minerals in the coarser fraction of this original composite material probably originated in material brought to the millsite, rather than being transported by fluvial processes. More dramatic reductions in metal releases would be expected if the coarser fraction were composed mostly of alluvial gravels. To limit initial release rates of metals, aggressive water treatments would be necessary to wash off soluble salts and fine material adhering to gravel surfaces.

The fine fraction was subjected to a variety of mineral-processing techniques to concentrate metals into a useable product and to reduce metal releases. Conventional sulfide mineral flotation failed because of the extensive oxidation that had already taken place during the decades that this mine waste has been deposited on the flood plain. Gravity separation produced a concentrate that was fairly high in Pb, probably as anglesite. The high Fe concentration in a concentrate separated by magnetic properties was interesting, but did not achieve either goal.

The goal of changing the hydrogeochemistry of mine waste by size separation to reduce release of metals was achieved in this study, albeit not to the extent that would allow on-site disposal of the coarser fraction as the only remediation action. However, a hybrid approach in which size separation is an integral part of a variety of remediation schemes is suggested.

ACKNOWLEDGMENTS

The authors wish to thank the many scientists from the Spokane Research Center (SRC), the Reno Research Center (RERC), and the Salt Lake City Research Center (SLRC) of the former U.S. Bureau of Mines who made this project possible. We recognize and express our appreciation to Juan Salcedo, physical science aide, for his dedication to careful performance of the humidity cell tests at RERC. Farril Jackson, Robert Larson, and Eddie Sullivan, physical science technicians, assisted in the gravel separation experiment at SLRC.

The ICP analyses at SRC were performed by Keith Weverstad, engineering technician, and John Bertagolli, chemist, while those at SLRC were performed by William Lockman, chemist. Fern Stones, chemist, performed the AA analyses at SLRC. Pam Drake, research chemist, performed the IC anion analyses for SRC while Dwight Hammargren, chemist, performed similar analyses at SLRC. Kim Harbaugh, chemist, performed the dissolution of solids at SLRC, while Jim Sjoberg, senior chemical analyst, conducted the mineralogical analysis and performed the characterization study at RERC. J. Scott Clark, physical science aide, assisted in data entry at SRC. Also at SRC, Priscilla Wopat, technical publications editor, provided preliminary editorial review with the assistance of Colleen Cook, editorial assistant, who prepared some of the tables, and Ken Strunk, engineering draftsman, who assisted with graphics.

The authors acknowledge the benefit of the scientific discussions with William White, physical scientist, SLRC. Technical review of an earlier manuscript was provided by Dr. Katie Walton-Day, research hydrologist, Colorado District Office (WRD) of the U.S. Geological Survey, and Kim Lapakko, senior engineer, Minnesota Dept. of Natural Resources.

REFERENCES

Allen, J. P. Mineral Processing Pretreatment of Con- taminated Sediments. Report prepared by USBM for U.S. EPA, Great Lakes National Program Office, Chicago, IL. 1994.

Allen., J. P., and L. Polls. Physical Separation Technology: A First Step in Contaminated Sediment Treatment. Paper in Proceedings of Assessment and Treatment of Contaminated Sediments in the North Branch Chicago River (Glencoe, IL, Oct. 19-20, 1992). NE IL Plan. Commis., Chicago, IL, 1993.

Benjamin, M. M. Effects of Complexing Metals and Com- plexing Ligands on Trace Metal Adsorption at the Oxide/ Solution Interface. Ph. D. Dissertation, Stanford Univ., 1978, 228 pp.

Collcott, S. B. Water Quality Along the South Fork of the Coeur d'Alene River, 1966-1988. M.S. Thesis, ID Univ., 1989.

Doepker, R. D. Enhanced Heavy Metal Mobilization from Unsaturated Mine Tailings. Transactions of SME, v. 288, 1991, pp. 1801-1805.

Fryklund, V. C. Ore Deposits of the Coeur d’Alene District, Shoshone County, Idaho. U.S. Geol. Surv. Prof. Paper 445, 1964, p.12.

Gillette, G., and D. R. Ralston. Hydrogeologic Analysis and Reclamation Alternatives for the Jack Waite Mine, Shoshone County, Idaho. Completion Report Prepared for U.S. Forest Service. ID Univ., Moscow, ID, 1979, 186 pp.

Horning, C. E., D. A. Terpening, and M. W. Bogue. Coeur d'Alene Basin EPA Water Quality Monitoring. EPA, Seattle, WA, EPA-910/9-88-26, 1988, 3 pp.

Ioannou, C. Distribution, Transport and Reclamation of Abandoned Mine Tailings Along the Channel of the South Fork of the Coeur d'Alene River and Tributaries, Idaho. M.S. Thesis, ID Univ., 1979, 156 pp.

Johnson, H. E., and C. L. Schmidt. Clark Fork Basin Project Status Report and Action Plan, Clark Fork Basin Project. Office of the Governor, Helena, MT, 1988.

Lauch, R., B. B. Locke, M. Dosani, E. Alperin, and A. Groen. Evaluation of Treatment Technologies for Contaminated Soils and Debris. Paper in Third International Conference on New Frontiers for Hazardous Waste Management (Cincinnati, OH). EPA, EPA/600/9-89/072, 1989, pp. 1-12.

Masters, H., and B. Rubin. EPA's Mobile Volume Reduction Unit for Soil Washing. EPA, EPA 600D/91/202, 1991, pp. 89-104.

McCulley, Frick and Gilman, Inc., Boise, ID. Upstream Surface Water Sampling Program: Spring 1991 High Flow Event, South Fork of the Coeur d'Alene River Basin Above the Bunker Hill Superfund Site. Report Prepared for Trustees for the Natural Resource Damage Trust Fund, Boise, ID. 1991, 31 pp.

_____ Upstream Surface Water Sampling Program: Fall 1991 Low Flow Event. South Fork of the Coeur d'Alene River Basin Above the Bunker Hill Superfund Site. Report Prepared for Trustees for the Natural Resource Damage Trust Fund. 1992, 31 pp.

Nordstrom, D. K. Aqueous Pyrite Oxidation and the Consequent Formation of Secondary Iron Minerals. Paper in Acid Sulfate Weathering, ed. by J. A. Kittrick, D. S. Fanning, and L. R. Hossner. Soil Sci. Soc. Am., Madison, WI, 1982, pp. 37-56.

Parkhurst, D. I., D. G. Thorstenson, and L. N. Plummer. PHREEQ–A Computer Program for Geochemical Calculations. U.S. Geol. Surv. Water Resour. Invest. 80-96, 1980, 193 pp.

Paulson, A. J. Fate of Metals in Surface Waters of the Coeur d’Alene Basin, Idaho. USBM RI 9620, 1996, 75 pp.

Rimstidt, J. D., J. A. Chermak, and P. M. Gagen. Rates of Reaction of Galena, Sphalerite, Chalcopyrite, and Arsenopyrite with Fe(iii) in Acidic Solutions. Paper in Environmental Geochemistry of Sulfide Oxidation, ed. by C. N. Alpers and D. W. Blowes. Am. Chem. Soc., 1994, pp. 1-13.

Scharer, J. M., R. N. Nicholson, B. Halbert, and W. J. Snodgrass. A Computer Program to Assess Acid Generation in Pyritic Tailings. Paper in Environmental Geochemistry of Sulfide Oxidation, ed. by C. N. Alpers and D. W. Blowes. Am. Chem. Soc., 1994, pp. 14-30.

Skougstad, M. W., M. J. Fishman, L. C. Friedman, D. E. Erdmann, and S. S. Duncan, eds. Technique of Water-Resource Investigations of the United States Geological Survey: Methods for Determination of Inorganic Substances in Water and Fluvial Sediments. Book 5, Laboratory Analysis. U.S. Geol. Surv., 1979.

Sobek, A. A., W. A. Schuller, J. R. Freeman, and R. M. Smith. Field and Laboratory Methods Applicable to Overburden and Mine Soils. EPA 600/7-78-054, 1978, 203 pp.

Stogran, S. W., and R. H. O. Wagner. General Overview of Mineral Processing Techniques Used for Site Remediation. Presented at Ninth Intern. Symp. on Heavy Metals in the Environ. (Toronto, ON, Sept. 12-17, 1993). Lakefield Res., Lakefield, ON, 1993, 4 pp.

U.S. Environmental Protection Agency, Office of Solid Waste and Emergency Response. Innovative Technology Soil Washing. Directive 9200.5-250FS, 1989, 2 pp.

_____, Office of Research and Development. Bergmann USA Soil Sediment Washing Technology–Applications Analysis Report. EPA/540/AR-92/075, 1995, 57 pp.