

**RI 9599**

**REPORT OF INVESTIGATIONS/1996**

# **Environmental Impacts of Cemented Mine Waste Backfill**

**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 9599**

# **Environmental Impacts of Cemented Mine Waste Backfill**

**By R. L. Levens, A. D. Marcy, and C. M. K. Boldt**

**UNITED STATES DEPARTMENT OF THE INTERIOR**  
**Bruce Babbitt, Secretary**

**BUREAU OF MINES**  
**Rhea Lydia Graham, Director**

International Standard Serial Number  
ISSN 1066-5552

## CONTENTS

	<i>Page</i>
Abstract .....	1
Introduction .....	2
Background .....	2
Purpose and objectives .....	2
Hydrochemistry .....	2
Air permeability and water saturation of backfill .....	3
Related research .....	4
Methodology .....	5
Laboratory data collection .....	5
Field data collection .....	6
Data presentation and analysis .....	7
Assay and leachability of sample CN .....	7
Particle-size distribution .....	8
Neutralizing capacity of cemented backfill .....	8
Deionized water wash .....	9
Sulfuric acid wash .....	10
Field water quality .....	13
Discussion and conclusions .....	15
References .....	16

## ILLUSTRATIONS

1. Cross section through Tempe pressure cell .....	17
2. Schematic of mine workings and test stope .....	18
3. Particle-size distribution of tailings samples .....	19
4. pH of H <sub>2</sub> SO <sub>4</sub> wash leachate, sample CN .....	20
5. pH of H <sub>2</sub> SO <sub>4</sub> wash leachate, sample SO .....	21
6. pH of H <sub>2</sub> SO <sub>4</sub> wash leachate, sample SN .....	22

## TABLES

1. Mineralogical analyses of tailings used in backfill .....	6
2. Chemical assay of backfill materials .....	7
3. ICP-AES data from analysis of strong acid extraction of backfill materials .....	8
4. Acid-neutralizing capacity of portland cement in backfill samples .....	9
5. Acid-neutralizing capacity of tailings in backfill samples .....	9
6. Acid-neutralizing capacity of cemented backfill samples .....	9
7. Element concentrations in samples containing cement after washing with deionized water for 7 days .....	10
8. Maximum neutralizing potential of cemented backfill samples .....	11
9. Neutralizing potential of cemented backfill samples .....	12
10. Element concentrations in cemented backfill samples after washing in H <sub>2</sub> SO <sub>4</sub> for 227 days .....	13
11. Average and range of element concentrations in water samples from cemented backfill from test mine .....	14
12. Saturation indices of water samples .....	15

## UNIT OF MEASURE ABBREVIATIONS USED IN THIS REPORT

cm	centimeter	mm	millimeter
cm <sup>3</sup>	cubic centimeter	mmho/cm	millimho per centimeter
g	gram	mol	mole
h	hour	Mpa	megapascal
kg	kilogram	m/s	meter per second
L	liter	mV	millivolt
m	meter	pct	percent
mequi.	Miliequivalent	ppm	part per million
mg	milligram	S	siemens
mg/g	milligram per gram	t	metric ton
mg/L	milligram per liter	°C	degree Celsius
mL	milliliter	µm	micrometer

Reference to specific products does not imply endorsement by the U.S. Bureau of Mines.

# Environmental Impacts of Cemented Mine Waste Backfill

By R. L. Levens,<sup>1</sup> A. D. Marcy,<sup>2</sup> and C. M. K. Boldt<sup>3</sup>

---

## ABSTRACT

Researchers at the U. S. Bureau of Mines conducted investigations to evaluate the potential for ground water contamination by mine waste used as backfill. Samples of cemented waste backfill and water discharging from drillholes and seeps were collected to use in chemical analyses and laboratory tests to determine the physical and chemical factors that control release of heavy metals to ground water.

Greater water retention by cemented backfill (as compared to uncemented sandfill) reduces the surface area exposed to oxidation, which in turn reduces the amount of acid produced. The acid is neutralized by the cement and minerals contained in the backfill. The grain-size distribution of tailings used for backfill affects the structural integrity of cemented backfill under attack by acidic water; breakdown of the backfill structure releases neutralizing materials faster. Backfilled stopes in rock with low hydraulic conductivities will constitute preferential flow paths after mine flooding; however, the rate of flow through backfill will be much slower than when the stope is partially saturated during mine operation. Considering all factors, acid generation and release of metal ions from cemented backfill should be less than in uncemented sandfill.

---

<sup>1</sup>Hydrologist.

<sup>2</sup>Research chemist.

<sup>3</sup>Civil engineer.

Spokane Research Center, U.S. Bureau of Mines, Spokane, WA.

## INTRODUCTION

### BACKGROUND

The Safe Drinking Water Act was enacted in 1974 by Congress to develop regulations to protect the Nation's underground sources of drinking water. One result was the Underground Injection Control program (UIC), promulgated in 1981 by the U.S. Environmental Protection Agency (EPA). Under the provisions of the UIC, a Class V well includes "Sand backfill and other backfill wells used to inject a mixture of water and sand, mill tailings or other solids into mined-out portions of subsurface mines whether what is injected is a radioactive waste or not" [40 CFR 146.5(e)(8)]. A well is broadly defined as either a dug hole or a bored, drilled, or driven shaft whose depth is greater than its largest surface dimension.

Because placement of mine waste backfill in underground openings is considered to be underground injection under UIC regulations, the effect on mine backfilling practices could be extensive. Currently, over 20 metal mines in the United States use backfill materials ranging from quarried rock to cemented mill tailings. The major purpose of the backfill is to support the ground during mining; however, backfill is increasingly considered a means of minimizing surface disposal of mine waste.

Water affected by backfill during active mining is usually pumped to the surface, where its disposal is regulated as surface discharge. Backfilled areas may become flooded after a mine is closed, possibly resulting in contamination of ground water. Therefore, in contrast to regulations addressing surface disposal, regulations concerning the contamination of ground water after mine closure will be a primary focus under the UIC program.

Returning mine waste to the original excavation is an attractive option because the original minerals are stable in that environment. However, oxidation of the backfill after it is placed underground and prior to flooding after mine closure may release metals and produce secondary mineral precipitates that are more soluble than the original minerals. Because many mines remain open for decades, dissolution of secondary minerals stored in partially saturated backfill can be a significant source of metals contamination of ground water after mine closure.

Addition of cement to backfill changes both the chemical and physical characteristics of the backfill. The addition of cement will buffer acid-producing oxidation reactions, resulting in less

mobilization of metals. More important, changes in the physical structure of the backfill resulting from the addition of cement may increase the capacity of the backfill to retain water prior to mine closure. Greater water retention will reduce the permeability of the backfill to air and decrease the total surface area of sulfides available for direct oxidation. Furthermore, the addition of cement reduces the hydraulic conductivity of backfill significantly, which acts to reduce transport of metals by reducing the groundwater flow rate through the backfill once it's flooded.

The mechanisms controlling dissolution of minerals in cemented backfill and the mobility of heavy metals change when a mine becomes flooded after mine closure. Reduced amounts of oxygen will limit the oxidation of sulfides as well as the precipitation of metal hydroxides. The nature of the changes likely to occur after mine flooding must be considered in order to estimate the impacts of placed mine waste backfill on ground water.

### PURPOSE AND OBJECTIVES

The purpose of this research by the U.S. Bureau of Mines (USBM) was to study the possible impacts of cemented mine waste backfill on the quality of ground water in the rock surrounding a stope. Both field and laboratory studies were conducted on the mobilization and transport of metals from cemented backfill. The objectives of the field work were to (1) document the impacts of cemented backfill on water being discharged from a selected stope, (2) investigate how the mobility of metals retained in cemented backfill differed from their mobility in uncemented mine waste sandfill, and (3) discuss the long-term impacts of cemented backfill after mine closure and subsequent mine flooding. Laboratory studies were conducted to (1) measure changes in acid-neutralization capacity that result from adding cement to backfill, (2) measure the rate of neutralization processes, (3) evaluate the impact of differences in grain-size distribution on the strength of the cemented backfill and the rate of chemical attack, and (4) investigate the effect of adding cement to backfill on hydraulic conductivity and water saturation.

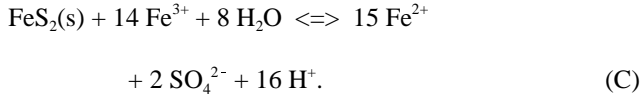
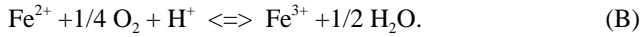
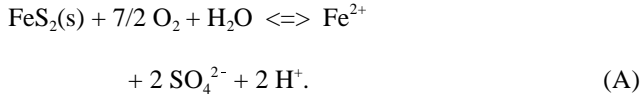
## HYDROCHEMISTRY

Oxidation of acid-producing sulfides, such as pyrite ( $\text{FeS}_2$ ), and associated dissolution of other minerals control the chemical composition of water draining from sulfide mines.

Initially, pyrite is oxidized by molecular oxygen ( $\text{O}_2$ ) in the presence of water, yielding sulfate ion ( $\text{SO}_4^{2-}$ ), ferrous ion ( $\text{Fe}^{2+}$ ), and hydrogen ion ( $\text{H}^+$ ). Next,  $\text{Fe}^{2+}$  is oxidized by  $\text{O}_2$  to



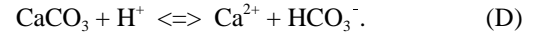
ferric ion ( $\text{Fe}^{3+}$ ). This second step is catalyzed by the bacteria *Thiobacillus ferrooxidans*. Pyrite is oxidized by  $\text{Fe}^{3+}$ , yielding additional  $\text{Fe}^{2+}$ ,  $\text{SO}_4^{2-}$ , and  $\text{H}^+$  in the final step (Lowson, 1982). The three steps of the oxidation of pyrite are given below.



$\text{Fe}^{2+}$ ,  $\text{SO}_4^{2-}$ , and  $\text{H}^+$  are released into solution through pyrite oxidation.  $\text{Fe}^{3+}$  may precipitate as ferrihydrite [ $\text{Fe}(\text{OH})_3$ ], goethite [ $\text{FeO}(\text{OH})$ ], or jarosite [ $\text{KFe}_3(\text{SO}_4)_2(\text{OH})_6$ ], which are collectively known as "yellow boy." The solubility of  $\text{Fe}^{3+}$  increases at low pH values ( $<4.5$ ) and is reduced during oxidation of additional pyrite.  $\text{Fe}^{3+}$  becomes the dominant oxidizing agent below pH 3.0. The presence of *T. ferrooxidans* greatly increases the rate at which  $\text{Fe}^{2+}$  is oxidized, thereby perpetuating the oxidation of pyrite by  $\text{Fe}^{3+}$ .

The  $\text{H}^+$  produced during oxidation of pyrite may be consumed in reactions involving carbonate and silicate minerals, releasing major ions, including calcium ( $\text{Ca}^{2+}$ ),

magnesium ( $\text{Mg}^{2+}$ ), sodium ( $\text{Na}^+$ ), potassium ( $\text{K}^+$ ), bicarbonate ( $\text{HCO}_3^-$ ), and silicic acid ( $\text{H}_4\text{SiO}_4$ ). Typical reactions involving calcite ( $\text{CaCO}_3$ ) and olivine ( $\text{Mg}_2\text{SiO}_4$ ) are given below.



Metals other than Fe also may be leached from ore, backfill, or country rock by acidic water created by oxidation. The resulting concentrations of heavy metals are controlled by the buffering capacity of the geochemical system, oxidation-precipitation reactions, dissolution-precipitation reactions, or desorption-adsorption reactions. The buffering capacity of the system is determined to a great extent by the geochemistry of the major ions. Therefore, knowledge of the dissolution and precipitation reactions involving the major ions is a key to understanding the mobility of metals.

Oxidation of sulfide minerals contained in backfill that has been partially saturated prior to mine closure and flooding produces secondary minerals that are retained in the backfill. The solubility of these minerals will increase after the backfill becomes saturated, leading to the possible release of metals. Dissolution of secondary minerals containing  $\text{Fe}^{3+}$  may release this oxidizing agent, resulting in a temporary continuation of sulfide oxidation after the backfill has been flooded.

## AIR PERMEABILITY AND WATER SATURATION OF BACKFILL

The permeability of porous materials such as backfill to air ( $k_{\text{nw}}$  for permeability of nonwetting phase) is a function of pore geometry and the amount of water in pores. Geometric properties of pores include porosity, shape, and dimensions of pore spaces, and tortuosity of flow pathways through interconnected pore spaces; these properties are usually combined into a single coefficient, the pore size distribution index ( $\lambda$ ).

Water saturation is usually expressed as effective saturation ( $S_e$ ) when considering air or water flow;  $S_e$  is defined as the fraction of the voids that water actually flows through ( $0 \leq S_e \leq 1.0$ ). Effective saturation is a function of capillary pressure ( $P_c$ ), defined as the difference between air and water pressures in pore spaces, which in turn is a function of pore geometry. Displacement pressure ( $P_d$ ) is the  $P_c$  where  $S_e$  drops below 1.0 during drainage of pore water. The fraction of the total pore volume that does not contribute to flow ( $S_e = 0$ ) is defined as the residual saturation ( $S_r$ ). Residual saturation ranges from 0.05 to 0.40 and is reached when water is held in pores that are smaller than the majority of pores. Larger values of  $S_r$  and smaller values of  $\lambda$  are usually associated with finer materials.

Equations by Corey (1986) for  $S_e$  and  $k_{\text{nw}}$ , as well as the generalized Kozeny-Karmen equation of air flow ( $q_{\text{nw}}$ ), are presented below.

$$S_e(P_c) = (P_d/P_c)^\lambda, \quad (1)$$

$$k_{\text{nw}}(S_e) = k (1-S_e)^2 (1-S_e^\gamma), \quad (2)$$

$$\text{and} \quad q_{\text{nw}} = k_{\text{nw}}/\mu_{\text{nw}} (-\partial p_{\text{nw}}/\partial x + \rho_{\text{nw}}g), \quad (3)$$

$$\text{where} \quad \gamma = (2+\lambda)/\lambda,$$

$$\mu_{\text{nw}} = \text{dynamic viscosity of air,}$$

$$p_{\text{nw}} = \text{pressure of air,}$$

$$\rho_{\text{nw}} = \text{mass density of air,}$$

$$\text{and} \quad g = \text{acceleration of gravity.}$$

When backfill drains after placement, saturation will be approximately equal to  $S_r$ . Effective saturation will increase and  $k_{nw}$  will decrease if water continues to flow into the backfill from the country rock. Air permeability decreases rapidly as  $S_e$  increases, decreases for common materials by a factor of 10 for  $S_e = 0.6$ , and reaches 0 when  $S_e = 1.0$ . Oxidation of sulfides is effectively shut off because the amount of  $O_2$  dissolved in the incoming water is very low.

Many porous materials have distinctively different pore sizes that exhibit different saturation, permeability, and flow characteristics. Fractured rock in which water flows through primary pores and/or secondary fractures is one example. Under saturated conditions, water flows preferentially through the fracture network; however, when  $S_e$  drops below 1.0, the larger fractures are the first pores to drain. At some intermediate  $S_e$  value, flow through the primary pores becomes dominant, and when  $S_e$  approaches 0, water will be held in primary pore spaces while the fractures will be dry.

Water flow through cemented backfill that has shrinkage cracks or gaps at rock-backfill interfaces will behave in a similar manner to fractured porous rock. The intact backfill and the secondary cracks and openings will have separate  $S_e(P_c)$  and  $k_{nw}(S_e)$  relationships, and the importance of each will depend on the rate of water inflow from the country rock. Under dry conditions, water will be held in the intact backfill and secondary openings will be dry, while under wetter conditions, flow through the larger openings will increase. When backfill is flooded after mine closure, flow will be primarily through the secondary openings.

The  $S_r$ , as well as the  $S_e(P_c)$  and  $k_{nw}(S_e)$  relationships, for a given backfill will affect the oxidation of sulfide minerals during active mining while the backfill is partially saturated. The larger the  $S_r$ , the more pores will remain saturated, resulting in less mineral surface area available to be oxidized. Surface area available for oxidation will be less under wetter conditions ( $S_e > 0$ ). The formation of shrinkage cracks and gaps will increase oxidation when they are drained under dry conditions.

## RELATED RESEARCH

Several studies have addressed the effects of coal and uranium backfill materials on ground water. The contamination potential of coal waste backfill in surface and underground mines has been studied by Henderson and Norton (1984), Geidel and Caruccio (1982), McCurry and Rauch (1986), and Senyur (1989). The important considerations in these studies were the potential for acid production and the amount of water flow through the wastes. Snow<sup>4</sup> concluded that flooding mine workings to control acid mine drainage is difficult when the workings are located above the mine level where drainage occurs. Sealing mines with fly ash was proposed to facilitate flooding above the drainage level under these circumstances. Senyur (1989) observed decreases in the permeability of backfill and the rate of water flow through the backfill over time.

The applicability of coal mine case studies in an investigation of the environmental impacts of backfill in metal mines is limited, however. The primary difference between the two types of mines is that heavy metals are released in metal mines as a result of oxidation of sulfides, whereas in coal mines, relatively smaller amounts of heavy metals are contained in wastes, resulting in less metals release.

Studies of the impacts of uranium mill tailings backfill have been extensive (Longmire and others, 1981; Brookins and others, 1982; Thomson and Heggen, 1982; Thomson and others, 1986). Field samples of tailings and backfill, and studies of water discharging from backfill were used to interpret geochemical transformations in backfill. The fate of heavy metals contained in the uranium tailings was considered as well as the fate of radioactive constituents. The authors concluded that the short- and long-term environmental impacts of backfill associated with active mining and postclosure activities were negligible.

Factors controlling metals release from surface tailings impoundments have been investigated through the use of leaching columns and simulated rain water to analyze tailings (Doepker and O'Conner, 1990a, 1990b; Doepker, 1991a, 1991b). The factors investigated included degree of saturation; availability of  $O_2$ ; wet-dry cycles; leachate residence time; buffering capacity of tailings; evaporation of pore waters; composition of host rock; composition, amount, and rate of formation of secondary minerals; and leachant pH, ionic strength, and types of ions present.

The major cause of metal dissolution was found to be oxidation of sulfide minerals by atmospheric  $O_2$  under partially saturated conditions. Enhanced metal dissolution was observed following alternating wet and dry periods or after extended drying periods; the degree of enhanced metal dissolution was affected by the percentage of water removed during a dry period

<sup>4</sup>R. E. Snow, "Estimation and Control of Ground Water Inflow and Discharge from Underground Mines." Paper presented at the annual meeting of the Society for Mining Engineers, Salt Lake City, UT, Feb. 26-Mar. 1, 1990. 9 pp.

(Doepker and O'Conner, 1990a). Furthermore, reduced partial pressure of O<sub>2</sub> was determined to be the only way to minimize metals release from sulfidic tailings. Concentrations in leachates from well-oxidized tailings differed from concentrations from fresh tailings because secondary minerals were more or less soluble than primary minerals. Secondary minerals formed in backfill under partially saturated conditions before mine flooding may dissolve after flooding, which may cause a temporary increase in metal mobility. The oxidation of cemented backfill and subsequent release of metals and formation of secondary minerals are expected to be less than what would occur in uncemented sandfill because of increased residual water saturation and decreased surface area resulting from the addition of cement.

Several factors affecting metal dissolution from submerged tailings were investigated using batch tests (Doepker and Drake, 1990, 1991). Oxidation of sulfide minerals in submerged tailings was much slower than oxidation in nonsubmerged tailings because O<sub>2</sub> diffuses slowly in water. However, metals were released from submerged, oxidized tailings even when they were neutralized because of the dissolution of secondary minerals. Thus a short-term release of metals

from secondary minerals may occur as a backfilled stope becomes submerged. However, metals release would be expected to decrease as secondary minerals were depleted from the tailings.

The impacts of mine waste sandfill on groundwater quality surrounding a stope was investigated in a study parallel to the one being presented here (Levens and Boldt, 1992). Concentrations of metals in water collected as it left a sandfilled stope were below or slightly above the maximum concentration levels (MCL's) allowed under the Safe Drinking Water Act. The lack of metals release from the sandfill was attributed to the buffering of acid by dissolution of carbonate minerals.

The primary issues identified in earlier research were a reduction in O<sub>2</sub> and oxidation reactions resulting from flooding of placed backfill, the detrimental effects of allowing tailings to dry out or of mechanically dewatering backfill prior to backfilling, the buffering capacities of backfill, and the extent of backfill oxidation prior to flooding (Brookins and others, 1982; Thomson and others, 1986; Doepker and Drake, 1990; Levens and Boldt, 1994).

## METHODOLOGY

This research is part of a larger effort in which the impacts of mine waste backfill on water quality are being investigated in four underground sulfide mines (Levens and Boldt, 1992). Backfill materials used in the four mines included cemented, total-gradation tailings; uncemented, classified sand; and uncemented, low-grade gob. Important consequences of adding cement to backfill include (1) reduced mineral dissolution resulting from enhanced buffering capacity, (2) reduced oxidation of sulfide minerals resulting from greater water retention, (3) reduced migration of metals from backfill into ground water because of lower hydraulic conductivity, and (4) increased strength and reduced chemical attack attributable to differences in backfill grain-size distributions.

Backfill samples were analyzed to identify mineralogy and to determine the maximum amounts of metals that could be leached. Leachability tests using deionized water and sulfuric acid were conducted to characterize neutralization capacities and rates. Grain-size distributions were plotted from sieve analyses, and capillary pressure-saturation relationships were determined using Tempe pressure cells.

### LABORATORY DATA COLLECTION

A sample of dewatered, freshly milled tailings used in backfilling in the test mine (sample CN), as well as samples of sandfill from a

comparison mine (samples SO and SN) (Levens and Boldt, 1994) were obtained for chemical analyses and laboratory tests. Two separate samples were collected at the comparison mine, one of oxidized backfill from a 10-year-old stope (sample SO) and the other of new tailings from the secondary cyclone (sample SN). These samples were similar in particle-size distributions and mineralogy, differing only in age.

The three samples were sent to the USBM's Reno Research Center for chemical assay and mineral identification by X-ray diffraction. The chemical assay method used was lithium borate fusion followed by acid digestion using hydrochloric acid (HCl) and inductively coupled plasma (ICP) analysis. A maximum leachability assay of 1 g of each backfill sample was also conducted using a mixture of HCl (2 cm<sup>3</sup>), nitric acid (HNO<sub>3</sub>) (4 cm<sub>3</sub>), and water (20 cm<sup>3</sup>) at the USBM's Spokane Research Center (SRC). The samples were placed on a shaker overnight and the supernatant liquid was filtered and analyzed by inductively coupled plasma-atomic emission spectroscopy (ICP-AES). The maximum leachability extraction procedure can be assumed to dissolve 100 pct of the water-soluble salts (chlorides, sulfates, and nitrates), as well as the water-insoluble salts (sulfides and carbonates). The metal oxides will also be solubilized. Maximum leachability data, in combination with X-ray diffraction data (table 1), provide the information necessary to determine the source of metals that can be released in an acidic environment.

**Table 1.—Mineralogical analyses of tailings used in backfill<sup>1</sup>**

Mineral	CN sample	SO sample	SN sample
Quartz . . . . .	Major.	Major.	Major.
Muscovite . . . . .	Trace.	Trace.	Trace.
Pyrite . . . . .	None.	Trace.	Trace.
Calcite . . . . .	None.	None.	None.
Siderite . . . . .	Trace.	Trace.	Trace.
Galena . . . . .	Trace.	Possible trace.	None.
Unidentified . . . . .	Trace.	Trace.	Trace.

<sup>1</sup>Major = 30 to 100 pct. Minor = 10 to 30 pct. Trace = 1 to 10 pct. Accuracy was approximately  $\pm 25$  pct of amount present.

Leaching investigations were conducted in a controlled environmental chamber to ascertain the neutralization capacities of the three backfill samples and to measure the rate of neutralization. Each sample was mixed with 4-pct-by-weight Type I, II portland cement at 70-pct slurry density (weight of solids  $\div$  weight of slurry). The mixes were poured into three replicate 5-cm cube molds and allowed to cure for 28 days in a fogroom maintained at 100-pct humidity. Two of the three cubes of each cemented backfill sample were placed into glass jars and placed in the environmental chamber. The third cube of each sample was kept in the fogroom to be used as a control sample in strength tests.

Each of the jars in the environmental chamber was filled with 2,500 mL of distilled water. Distilled water was circulated over the samples for the first 7 days using small pumps. The electrical conductivity (EC), pH, and temperature of the distilled water leachate was measured daily; after 7 days, water samples were collected for anion and cation analyses.

At the end of 7 days, 1.4 mL of concentrated H<sub>2</sub>SO<sub>4</sub> was added to the leachate circulating over the sample. The pH, EC, and temperature of the leachate were measured daily. As evaporation occurred in the chambers, distilled water was added to maintain the total volume of the leachate at approximately 2,500 mL. When the pH of the leachate on any of the samples increased to about 6, 1.4 mL of concentrated H<sub>2</sub>SO<sub>4</sub> was added to lower the pH. Samples were collected at 2- to 4-week intervals for analysis of cations and anions.

Relationships between capillary pressure and backfill saturation were determined for uncemented tailings and for tailings mixed with 6 pct cement by weight using Tempe pressure cells equipped with 0.1 MPa, ceramic, porous plates (figure 1). Four replicate cemented samples were cast in the test cylinders used in the Tempe cells and cured for 4 weeks in the fogroom. Samples were submerged in a water-lime solution to maintain saturation and to prevent dissolution of the cement while curing. The bottom port of the Tempe cell was connected to an adjustable burret to maintain the outflow water head at the level of the ceramic plate. Capillary pressure was increased

by increasing nitrogen (N<sub>2</sub>) pressure at the top port. Saturation changes were determined from the volume of water displaced into the burret and from sample porosity.

## FIELD DATA COLLECTION

Samples of tailings (sample CN) and water were collected from a test stope in an underground sulfide mine for analysis. The rock types in the test stope consisted of Precambrian metasediments, including argillite, sericitic quartzite, and vitreous quartzite. Massive tetrahedrite (Cu<sub>12</sub>Sb<sub>4</sub>S<sub>13</sub>), galena (PbS), and sphalerite (ZnS) with quartz (SiO<sub>2</sub>) and siderite (FeCO<sub>3</sub>) gangue compose the ore mineralogy. The stope extends approximately 120 m along strike of the vein and is mined by underhand longwall cut-and-fill with backfill. The backfill consists of cemented tailings in which most of the fines have been retained. The underhand longwall cut-and-fill method differs from overhand cut-and-fill by progressing downward in successive slices instead of overhead. Mining proceeds after the previous cut has been backfilled with cemented tailings and is allowed to set; consequently, the back, or roof, of the stope consists of reinforced cemented backfill.

Groundwater recharge to the Precambrian metasediments near the test mine is primarily the result of infiltration from overlying surface drainage basins. The drainage basin above the mine is underlain by variably fractured bedrock except where narrow strips of alluvium are found along stream channels.

The unfractured rock surrounding the mine has very low hydraulic conductivity; consequently, water percolates along fractures and faults. Similarly, water from the bedrock enters the mine where fractures and faults are intersected by backfilled or open mine workings or by boreholes. The hydraulic conductivity of similarly fractured metasediments was estimated at  $1 \times 10^{-7}$  m/s by Lachmar (1988). Water entering the mine drains to collection sumps and is pumped to the surface for discharge. For comparison, the hydraulic conductivity of intact backfill with 6 pct cement added was calculated to be less than  $1 \times 10^{-9}$  m/s in a laboratory permeameter. Placed backfill will probably have shrinkage cracks that may increase the bulk hydraulic conductivity of the backfill two or more orders of magnitude.

Water sampling was initiated in November 1990 and continued on a monthly basis through April 1993; the stope advanced 32 m, and 53,500 t of ore were extracted during this time period. Samples were collected both before and after the water was in contact with the cemented backfill in order to determine the impacts of placed mine waste backfill on water quality. Water was collected from exploratory boreholes that intersected accessible drifts on three levels, and additional samples were taken from seeps in the advancing stope

and from a sump that received commingled drainage on sampling level 2 (figure 2). Data from the boreholes represent water quality within the country rock, whereas the commingled water and seeps that contact the backfill represent water quality affected by backfilling. The advancing underhand cut-and-fill stope cut through a sampling borehole on level 2; probably as a consequence, the borehole dried up after the seventh sampling visit.

The pH, EC, redox potential (Eh), temperature, and alkalinity of samples were measured in the field. Samples were vacuum

filtered through 0.45- $\mu\text{m}$  filters and placed in flexible 50-mL polyethylene bottles. Separate bottles were filled for cation analysis using the Perkin-Elmer Plasma II ICP and for anion analysis using a Dionex Series 4000i gradient ion chromatograph (IC). Samples for cation analysis were preserved with  $\text{HNO}_3$  according to EPA procedures (1983) for stabilizing ions in solution. Samples were then transported to the chemistry laboratory at SRC and stored in a refrigerator until being tested.

## DATA PRESENTATION AND ANALYSIS

Mineral assays of backfill prior to the addition of cement, published mineralogic descriptions, and information from mine records, in combination with the X-ray diffraction data, provide the information necessary to determine the sources of metals that can be expected to be released in an acidic environment. The differences between the results of the mineral assay and data from the maximum leachability tests using tailings from the test mine are compared to similar data from a sandfilled test mine discussed by Levens and Boldt (1994). This comparison provides a baseline for determining the role of cement in controlling leaching of metals from backfill.

Particle size and capillary pressure-water saturation measurements provide information about the susceptibility of a backfill to oxidation prior to flooding. Particle-size analysis also may explain variations in cemented backfill strengths that, in turn, lead to variations in the degree of chemical attack by acidic solutions. Hydraulic conductivity measurements indicate whether water will flow preferentially through the cemented backfill after flooding.

Leaching experiments conducted in an environmental chamber shed light on the susceptibility of cemented backfill to leaching by external sources of acidic water. Calculated neutralization capacities based on the amount of cement added and mineral assay data are calculated first. The pH and ion concentrations of leachates from the deionized water wash and the  $\text{H}_2\text{SO}_4$  wash demonstrate the effects of different chemical and physical factors on dissolution of minerals in backfill by acidic water.

The ultimate use of the laboratory data is to determine factors that explain the chemical makeup of water collected in a test mine. Cation and anion levels in water samples were compared to determine if significant differences could be detected and attributed to the backfill material, in this case, cemented tailings. A thermodynamically based geochemical computer model, WATEQ4F (Ball and others, 1987), was used to investigate element speciation and mineral saturation in water samples. Saturation indices calculated by WATEQ4F provide a basis for evaluating the potential for dissolution and precipitation reactions among minerals in backfill and infiltrating water.

Knowledge of the ranges of reaction kinetics and mineral stability is necessary to interpret the validity of the thermodynamic approach used by WATEQ4F. Also, chemical reactions may be slowed because tailings particles become coated with cement and because of increased water saturation; the first factor limits diffusion of water to reactive minerals while the second factor limits diffusion of  $\text{O}_2$  into small pores.

### ASSAY AND LEACHABILITY OF SAMPLE CN

Analysis by X-ray diffraction indicated sample CN consisted of quartz with traces of muscovite [ $\text{KAl}_2(\text{AlSi}_3\text{O}_{10})(\text{OH})_2$ ], siderite, and galena. Chemical assays showed that, prior to the addition of cement, approximately one-third of the backfill used in the test stope consisted of silica (Si) (table 2). Significant quantities of aluminum (Al), Ca, Mg, K, chromium (Cr), copper (Cu), nickel (Ni), lead (Pb), and zinc (Zn) were also detected.

Table 2.—Chemical assay of backfill materials, parts per million

Analyte	CN sample	SO sample	SN sample
Al	19,000	15,000	14,000
As	<300	500	1,500
Ba	200	80	44
Ca	2,300	3,300	3,700
Cd	16	8	13
Co	10	20	30
Cr	90	80	100
Cu	210	250	620
Fe	53,000	57,000	54,000
K	5,500	5,800	5,100
Mg	1,900	2,400	1,400
Mn	5,600	5,000	1,600
Mo	<50	<50	<50
Na	400	600	500
Ni	200	330	240
P	<1,000	<1,000	<1,000
Pb	1,800	1,500	1,500
Si	334,000	348,000	358,000
Zn	4,300	2,500	5,800

The maximum leachability assay using a mixture of HCl and HNO<sub>3</sub> yielded significant concentrations of Ca and Mg as well as the metals Fe, manganese (Mn), Pb, and Zn (table 3). Assuming that the Ca extracted by the acid exists as CaCO<sub>3</sub>, the CN sample contains 0.58 pct CaCO<sub>3</sub>. Lesser amounts of silver (Ag), arsenic (As), cadmium (Cd), Cr, Cu, and Ni were also leached. The Ca concentration in the acid leachate indicates a low acid-neutralization capacity in the tailings while low Si and Al concentrations indicate the tailings have very little reactive aluminosilicate minerals that might contain trace metals.

**Table 3.—ICP-AES data from analysis of strong acid extraction of backfill materials, milligrams per liter**

Analyte	CN sample	SO sample	SN sample
Ag .....	0.04	0.02	0.03
Al .....	2.1	2.0	1.9
As .....	1.2	6.0	10.4
Ba .....	0.3	0.03	0.02
Ca .....	23.0	35.4	38.8
Cd .....	0.17	0.21	0.34
Cu .....	0.69	0.56	0.69
Fe .....	306	312	186
K .....	0.9	0.9	0.8
Mg .....	11.2	12.4	6.4
Mn .....	32.4	29.4	9.5
Na .....	0.52	0.12	0.41
Pb .....	32.0	21.6	27.8
S .....	7.8	37	86
Si .....	2.2	2.2	1.7
Zn .....	21.9	14.9	35.4

The Pb and Zn contained in the leachate from the CN sample were 32.0 and 21.9 ppm, respectively. Both these elements should exist as sulfides because the sample was collected from fresh tailings; however, there is about half the necessary sulfur (S) to account for dissolution of galena and sphalerite. Fe probably occurs primarily as siderite because the sample was fresh and therefore contained little iron oxide from oxidation.

The mass of the CN sample dissolved during the maximum leachability assay was estimated by converting concentrations to oxides of Si, Na, K, and Al; carbonates of Ca, Mg, and Fe; and sulfides of Pb, As, and Zn for all element concentrations above 1 mg/L. When these values were converted to milligrams per gram, the amount of sample dissolved was 111 mg/g, or about 11 pct. Less than this quantity of tailings will react, leaving at least 89 pct of the sample to be bound by cement.

## PARTICLE-SIZE DISTRIBUTION

Particle-size distributions relate to the structural integrity of the tailings-cement matrix and therefore to the susceptibility of acemented backfill to chemical attack. Particle-size distributions of samples CN, SO, and SN are shown in figure 3. A comparison of the curves shows that samples SN and SO have similar narrow ranges of particle sizes while sample CN has a wider range with significantly finer particles. Sample CN had a coefficient of uniformity (a measure of the gradation range of the particle-size curve) of 14 and a coefficient of curvature (a measure of the shape of the particle-size curve) of 1.28; on the basis of these values, sample CN is classified as a well-graded sand. The coefficients of uniformity for samples SN and SO were 3 and 6, respectively, and the coefficients of curvature were 0.69 and 0.85, respectively. Samples SN and SO are classified as uniform, poorly graded sands.

Differences in particle-size distributions are expected to affect the strength and structural integrity of cemented backfill and, as a consequence, the degree of degradation when the material is attacked by acid solutions. Therefore, the results of particle-size analyses are considered in the following discussion of the laboratory leaching experiments.

## NEUTRALIZING CAPACITY OF CEMENTED BACKFILL

Water retention characteristics of cemented backfill affect the access of air to sulfide minerals and therefore oxidation rates. Leachate analyses from both the deionized water and acid wash experiments indicate the contribution of cement to acid neutralization relative to the contribution from minerals contained in the tailings.

The resistance of the cemented backfill samples to attack by acidic water depends on the neutralizing capacity of the backfill and the rate at which acidic water diffuses into the samples. Neutralizing capacity is calculated from the ratio of the weight of the cement to the weight of the backfill and the composition of each as determined from published values and chemical analyses.

The average composition of compounds in Type I, II portland cement that will contribute to acid-neutralization capacity are 65.9 pct calcium oxide (CaO), 2.3 pct magnesium oxide (MgO), and 0.72 pct potassium oxide (K<sub>2</sub>O). Based on the quantity of cement used to make the samples, the milliequivalents (mequi.) of neutralizing capacity from each component were calculated and then totaled to obtain the total neutralizing capacity of the cement in each sample (table 4).

For example, the contribution from CaO in the CN sample would be

$$\text{CaO} = \frac{0.066 \text{ kg CaO}}{0.1 \text{ kg cement}} \times \frac{0.072 \text{ kg cement}}{2.694 \text{ cement}} \times \frac{0.744 \text{ kg}}{3 \text{ cubes}} \times \frac{2,000 \text{ mequi.}}{0.056 \text{ kg CaO}} \times 2 \text{ cubes} = 314.0 \text{ mequi.}$$

The neutralizing capacities of the uncemented tailings samples were calculated on the basis of maximum leachability data and estimated mineralogy (table 5). Ca, Mg, and Mn were assigned to carbonate minerals whereas Na

The neutralizing capacities of the uncemented tailings samples were calculated on the basis of maximum leachability data and estimated mineralogy (table 5). Ca, Mg, and Mn were assigned to carbonate minerals whereas Na

$$\text{CaCO}_3 = \frac{23.0 \text{ mg Ca}}{1 \text{ L}} \times \frac{0.1 \text{ L}}{1 \text{ g tailings}} \times \frac{1.814 \text{ kg tailings}}{2,694 \text{ kg sample}} \times \frac{0.744 \text{ kg}}{3 \text{ cubes}} \times \frac{2 \text{ mequi.}}{40.04 \text{ mg}} \times 2 \text{ cubes} = 38.4 \text{ mequi.}$$

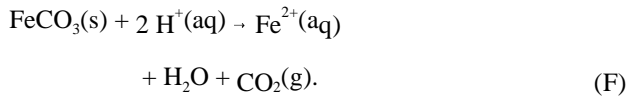
**Table 4.—Acid-neutralizing capacity of portland cement in backfill samples, milliequivalents**

Sample	CaO	MgO	K <sub>2</sub> O	Total
CN . . . . .	314.0	25.2	2.0	341.2
SN . . . . .	264.4	21.2	1.6	287.2
SO . . . . .	344.6	27.6	2.2	374.4

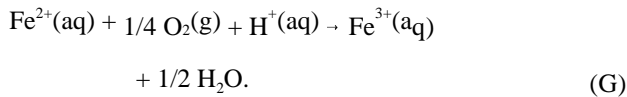
**Table 5.—Acid-neutralizing capacity of tailings in backfill samples, milliequivalents**

Sample	Sum of Ca, Mg, Mn, K, and Na	Fe	Total
CN . . . . .	109.7	366.6	476.3
SN . . . . .	80.2	124.4	204.6
SO . . . . .	142.2	403.2	545.4

If Pb and Zn were present as sulfides and sulfates, then the remaining small amount of S was assigned to Fe in a molar ratio for pyrite; the remainder of the Fe was assigned to siderite. The reaction between siderite and H<sub>2</sub>SO<sub>4</sub> is—



Oxidation of Fe<sup>2+</sup> is—



Hydrolysis of Fe<sup>3+</sup> is—



Reactions F and G consume 3 mol of H<sup>+</sup> for each mol of siderite. However, depending on the extent of hydrolysis of Fe<sup>3+</sup> (equation H), 3 mol of H<sup>+</sup> may be produced. Therefore, dissolution of siderite may result in net acid consumption ranging from 0 to 3 mol of H<sup>+</sup> per mol of siderite.

Sample CN had all the measured S required for Pb and Zn compounds. Therefore, in agreement with the mineralogical analyses, all Fe in the sample was assigned to siderite in calculations of neutralization capacity. Samples SO and SN had small amounts of Fe assigned to pyrite with the rest considered to be siderite. The value for siderite in sample SO is probably too high because some Fe probably has oxidized to goethite; however, an approximation can be completed using lesser amounts of Fe and taking this first calculation as an extreme value.

The total neutralization capacity of the cemented backfill calculated as the sum of the capacities of the cement and the backfill is given in table 6. The neutralizing capacity of the cemented tailings compared to tailings alone, and not including contributions from siderite, was approximately 3.6 times greater in the SO sample, 4.1 times greater in the CN sample, and 4.6 times greater in the SN sample. The quantity of siderite dissolved is important from the perspective of the physical strength of the sample even if no acid is consumed. Because siderite is part of the particles being bound together by cement, its destruction will weaken the sample.

**Table 6.—Acid-neutralizing capacity of cemented backfill samples, milliequivalents**

Sample	Sum of Ca, Mg, Mn, K, and Na	Fe	Total
CN . . . . .	450.9	366.6	817.5
SN . . . . .	367.4	124.4	491.8
SO . . . . .	516.6	403.2	919.8

## DEIONIZED WATER WASH

High concentrations of Na, K, and Ca were detected in the deionized water used to flush the surfaces of the cemented backfill cubes prior to washing with H<sub>2</sub>SO<sub>4</sub> (table 7). Hydroxides and sulfates of these elements derived from the cement were probably flushed from the surfaces of the samples. Also, the amounts of Al and Si detected were low, which would

be expected because minerals containing these elements have low solubilities. No measurable amounts of trace metals were dissolved.

**Table 7.—Element concentrations in samples containing cement after washing with deionized water for 7 days, milligrams per liter**

Analyte	CN sample	SO sample	SN sample
Al	0.2	2.2	0.2
Ba	0.17	0.08	0.06
Ca	54.2	96.1	183
Cu	0.04	0.09	ND
Fe	0.2	0.2	0.1
K	7.3	15.5	26.6
Mn	ND	0.1	ND
Na	7.9	14.7	14.0
Pb	0.06	ND	0.02
Si	6.6	6.7	8.5
Zn	0.06	ND	0.05
pH	8.6	8.6	8.0
SO <sub>4</sub>	86.1	130	366

ND No data.

### SULFURIC ACID WASH

Tables 8 and 9 show the amount of H<sub>2</sub>SO<sub>4</sub> added and the remaining acid-neutralization capacities of the three samples of cemented backfill during the H<sub>2</sub>SO<sub>4</sub> wash test. The values in table 8 include the potential contribution of siderite, whereas the values presented in table 9 include only the contributions of Ca, Mg, and Mn carbonates and K and Na oxides. The values in table 9 are based on the assumption that acid consumption (equations F and G) is balanced by acid production by hydrolysis (equation H). Large amounts of oxyhydroxides precipitated on the surface of the three samples is evidence that siderite was reacting and that the hydrolysis reaction occurred to a limited extent. Therefore, the values in tables 8 and 9 are reasonable bounds for actual remaining neutralization capacities.

Figures 4, 5, and 6 show the pH of the fluid washing the samples as a function of time after H<sub>2</sub>SO<sub>4</sub> was added. The pH of the wash solution dropped from about 8 to less than 3 for all samples after the H<sub>2</sub>SO<sub>4</sub> wash began. The pH of the wash from samples SO and SN increased to the basic range after 72 h, indicating an aggressive attack of the samples by the acid, resulting in neutralization of the H<sub>2</sub>SO<sub>4</sub>. Sample CN had a slower reaction rate as indicated by an increase in pH in the wash to only 4.93. Samples SO and SN had similar particle-size distributions, whereas sample CN had a higher percentage of both large and fine particles. The broader particle-size distribution of sample CN may have promoted the formation of a more resistant cement-tailings matrix, which would limit

penetration of the acid. Degradation of the structural integrity of the SO and SN samples apparently allowed penetration of the acid, leading to the rapid reactions observed.

The pH of the wash solution from sample CN showed a slow rise after each addition of H<sub>2</sub>SO<sub>4</sub>, becoming significantly slower as the test progressed. Early in the test, acid neutralization took place more rapidly as reactions occurred on the surface of the cubes, but over time, the surface of the sample accumulated reaction products (such as gypsum and iron oxyhydroxides) that slowed penetration of additional acid into the cube. Also, the acid had to diffuse into the sample to greater depths each time the acid was added, slowing the rate of neutralization. As shown in figure 4, the sample was still neutralizing acid at the end of the experiment.

Sample SO rapidly neutralized each addition of acid, and pH recovered more slowly as the test progressed. After 70 days, pH remained nearly constant, gaining only 0.2 pH units over the period of the rest of the experiment. It appears that most of the material available for acid neutralization had been consumed by that time.

Sample SN responded differently to the acid wash than either of the two other samples. Spikes of increased pH similar to those shown by the SO sample occurred during the first few days. The acid appeared to penetrate the sample rapidly, so that all the easily accessible basic material was consumed in about 10 days. Then pH decreased for the rest of the experiment while no more acid was added. The continuing decrease in pH can be attributed to the presence of reduced iron sulfide compounds, such as pyrite, in the sample, which would oxidize over the course of the experiment and produce acid, which would lower the pH. The pyrite in the sample was calculated as 0.112 mol, which would produce 450 mequi. of acidity if oxidized and precipitated as ferrihydrite; this amount was greater than the amount of basic material in the sample. Oxidation of sulfides at a faster rate than acid neutralization would also explain the continued decline in pH, even though calculations showed that significant quantities of basic material remained in the SN sample.

The results of the chemical analyses of the acid wash solutions are given in table 10. All washes showed increased concentrations of metals at the end of the experiment as compared to the beginning. WATEQ4F was used to evaluate solubility controls of the Pb and Zn ions in the SN sample wash because concentrations of these elements were high in the tailings. Zn concentrations continued to increase throughout the experiment, but concentrations were probably limited by diffusion of the acid into the tailings to oxidize and dissolve the sphalerite present. Pb concentrations did not increase above 4 mg/L.



Table 8.—Maximum neutralizing potential of cemented backfill materials

Elapsed time, days	CN			SN			SO		
	mL of acid added	mequi. remaining	pH	mL of acid added	mequi. remaining	pH	mL of acid added	mequi. remaining	pH
0 .....	0.0	818	8.01	0.0	492	8.05	0.0	920	8.65
3 .....	1.4	768		1.4	442		1.4	870	
5 .....		718	<sup>1</sup> 4.93	1.4	392	<sup>1</sup> 7.43	1.4	920	<sup>1</sup> 8.18
6 .....		718	2.59	1.4	342	<sup>1</sup> 7.44	1.4	770	<sup>1</sup> 7.92
7 .....		718	2.90		342	5.27	1.4	720	<sup>1</sup> 6.73
8 .....		718	2.85	1.4	292	<sup>1</sup> 6.28	1.4	670	<sup>1</sup> 7.54
9 .....		718			292			670	
10 .....		718	3.20	1.4	242	<sup>1</sup> 6.69	1.4	620	<sup>1</sup> 6.94
11 .....		718	3.57		242	3.85		620	3.35
12 .....		718			242			620	
13 .....		718	4.19		242	4.92		620	5.46
14 .....		718	4.31		242	4.96	1.4	570	<sup>1</sup> 7.01
15 .....		718			242			570	
16 .....		718			242			570	
17 .....		718	4.73		242	4.48		570	5.09
18 .....		718	4.91		242	4.65		570	5.79
19 .....		718	5.44		242	5.04	1.4	520	<sup>1</sup> 6.59
20 .....		718	5.12		242	4.81		520	3.04
21 .....		718			242			520	
22 .....		718			242			520	
28 .....		718	4.76		242	5.92		520	5.70
31 .....	1.4	668	<sup>1</sup> 6.18		242	4.82		520	5.36
32 .....		668	2.27		242	4.67	1.4	470	<sup>1</sup> 6.24
33 .....		668	2.42		242	4.66		470	2.47
42 .....		668	3.07		242	4.40		470	3.93
60 .....		668	5.16		242	4.12		470	4.73
		668			242			470	
81 .....	1.4	618	<sup>1</sup> 6.10		242	3.64		470	5.06
82 .....		618	2.24		242	3.63		470	5.04
		618			242			470	
109 .....		618	4.06		242	3.52		470	5.06
		618			242			470	
136 .....		618	5.28		242	3.31		470	4.97
		618			242			470	
158 .....	1.4	568	<sup>1</sup> 6.49		242	3.02		470	4.82
159 .....		568	2.31		242	3.09		470	4.85
		568						470	
223 .....		568	4.72		242	2.28		470	4.83
		568		One cube of SN disintegrated.				470	
		568						470	
238 .....		568	5.19			2.17		470	4.84
Total mL of acid added: .....	7.0			7.0			12.6		
Total mequi. of acid added: .....	250			250			450		

<sup>1</sup>pH prior to addition of acid.

NOTE.—Blank cells indicate no data.

Table 9.—Neutralizing potential of cemented backfill materials, excluding  $\text{FeCO}_3$ 

Elapsed time, days	CN			SN			SO		
	mL of acid added	mequi. remaining	pH	mL of acid added	mequi. remaining	pH	mL of acid added	mequi. remaining	pH
	0.0	451	8.01	0.0	367	8.05	0.0	517	8.65
0 .....	1.4	401	<sup>2</sup> 1.87	1.4	317	<sup>2</sup> 2.57	1.4	467	<sup>2</sup> 2.17
3 .....	1.4	351	<sup>1</sup> 4.93	1.4	267	<sup>1</sup> 7.43	1.4	417	<sup>1</sup> 8.18
5 .....		351	2.59	1.4	217	<sup>1</sup> 7.44	1.4	367	<sup>1</sup> 7.92
6 .....		351	2.90		217	5.27	1.4	317	<sup>1</sup> 6.73
7 .....		351	2.85	1.4	167	<sup>1</sup> 6.28	1.4	267	<sup>1</sup> 7.54
8 .....		351			167			267	
9 .....		351			167			267	
10 .....		351	3.20	1.4	117	<sup>1</sup> 6.69	1.4	217	<sup>1</sup> 6.94
11 .....		351	3.57		117	3.85		217	3.35
12 .....		351			117			217	
13 .....		351	4.19		117	4.92		217	5.46
14 .....		351	4.31		117	4.96	1.4	167	<sup>1</sup> 7.01
15 .....		351			117			167	
16 .....		351			117			167	
17 .....		351	4.73		117	4.48		167	5.09
18 .....		351	4.91		117	4.65		167	5.79
19 .....		351	5.44		117	5.04	1.4	117	<sup>1</sup> 6.59
20 .....		351	5.12		117	4.81		117	3.04
21 .....		351			117			117	
22 .....		351			117			117	
28 .....		351	4.76		117	5.92		117	5.70
31 .....	1.4	301	<sup>1</sup> 6.18		117	4.82		117	5.36
32 .....		301	2.27		117	4.67	1.4	67	<sup>1</sup> 6.24
33 .....		301	2.42		117	4.66		67	2.47
42 .....		301	3.07		117	4.40		67	3.93
60 .....		301	5.16		117	4.12		67	4.73
		301			117			67	
81 .....	1.4	251	<sup>1</sup> 6.10		117	3.64		67	5.06
82 .....		251	2.24		117	3.63		67	5.04
		251			117			67	
109 .....		251	4.06		117	3.52		67	5.06
		251			117			67	
136 .....		251	5.28		117	3.31		67	4.97
		251			117			67	
158 .....	1.4	201	<sup>1</sup> 6.49		117	3.02		67	4.82
159 .....		201	2.31		117	3.09		67	4.85
		201			117			67	
223 .....		201	4.72		117	2.28		67	4.83
		201		One cube of SN disintegrated.				67	
		201						67	
238 .....		201	5.19			2.17		67	4.84
Total mL of acid added: .....	7.0			7.0			12.6		
Total mequi. of acid added: ...	250			250			450		

<sup>1</sup>pH prior to addition of acid.<sup>2</sup>pH after addition of acid.

NOTE.—Blank cells indicate no data.

**Table 10.—Element concentrations in cemented backfill samples after washing with H<sub>2</sub>SO<sub>4</sub> for 227 days, milligrams per liter**

Analyte	CN sample	SO sample
SN	sample	
Al	.....	54.00.4480.1
Ba	.....	0.010.003ND
Ca	.....	640716623
Cd	.....	0.010.321.8
Cu	.....	0.100.070.68
Fe	.....	6.66.897.6
K	.....	3.91.4 3.0
Mg	.....	95.2125110
Mn	.....	52.865.364.8
Na	.....	8.08.79.4
Pb	.....	0.901.63.9
Si	.....	14.634.7157
Zn	.....	0.9733.7336
pH	.....	4.94.72.2
SO <sub>4</sub>	.....	1,8072,0503,622
ND	No data.	

Early in the experiments, Ca concentrations reached a plateau, apparently limited by gypsum (Ca<sub>2</sub>SO<sub>4</sub> · 2H<sub>2</sub>O) solubility. It was obvious from the sample analyses that iron oxyhydroxides precipitated during dissolution of the cemented backfill and limited the solubility of Fe.

In the CN sample wash, all concentrations of metal ions (except Mn) stayed below 10 mg/L. This result can be attributed to the stability of the sample and its acid-neutralization capacity. The pH at the end of the experiment was about 5.5.

Concentrations of several metals were greater in the SO sample than in the CN sample. pH was about the same, so solubility was probably not limiting; it is suspected that more of the SO sample had been attacked and more metal ions were freed.

**FIELD WATER QUALITY**

Concentrations of As, barium (Ba), and Pb exceeded the primary MCL's specified under the Safe Drinking Water Act in selected samples (table 11). Also, concentrations of Fe, Mn, and SO<sub>4</sub> exceeded secondary MCL's. However, during most visits, all concentration levels were below or near the MCL's.

EC was highest in the sample from the sump and lowest in sample DH1 from level 1. Higher EC correlated most closely

with higher concentrations of Ca, K, Mg, and SO<sub>4</sub>. No meaningful differences in pH, Eh, or most heavy metals were detected; an exception was that Pb and Zn concentrations were higher in specific samples from the sump on level 2.

Concentrations of Ca, Mg, K, and SO<sub>4</sub> were higher in the sump and stope samples than in the drillhole samples. The higher concentrations of Ca, Mg, and SO<sub>4</sub>, in conjunction with near-neutral pH values, suggest that acid production by oxidation of sulfide minerals is being buffered by dissolution of carbonate minerals, or more significantly, the cement added to the backfill. High concentrations of Na balanced by high concentrations of HCO<sub>3</sub> were detected in some samples; this occurrence appears to be unrelated to chemical reactions within the backfill.

The saturation indices (SI) calculated using WATEQ4F (Ball and others, 1987) indicate equilibrium or slightly undersaturated conditions for most minerals (-1 ≤ SI ≤ 1) (table 12). Ferrihydrite is one of few minerals that was supersaturated (SI ≥ 1), indicating a potential to precipitate. Other minerals, such as gypsum, that commonly precipitate from water discharging from sulfidic wastes were undersaturated (SI ≤ -1) and therefore were not expected to precipitate. Mixing water high in HCO<sub>3</sub><sup>-</sup>, a condition observed at several sites, with water in equilibrium with calcite may result in precipitation of calcite.

Table 11.—Average and range (in parentheses) of element concentrations in water samples from cemented backfill in test mine

Analyte	DH1 (22)	DH2 (14)	DH3 (7)	DH4 (8)	Sump (10)	Stope (9)
Element, mg/L:						
Al	0.20 (0.01-0.66)	<0.01 (<0.01-0.64)	0.45 (0.08-0.66)	0.03 (0.01-0.10)	0.29 (0.01-1.19)	0.10 (0.01-0.65)
As	<0.10 (<0.10-0.40)	<0.10 (<0.10-0.22)	<0.10	<0.10	<0.10 (<0.10-0.20)	<0.10 (<0.10-0.60)
Ba	1.12 (0.59-1.79)	0.88 (0.74-1.02)	0.22 (0.17-0.27)	0.39 (0.26-0.44)	0.06 (0.02-0.09)	0.08 (0.06-0.12)
Ca	25.81 (12.20-35.60)	27.38 (24.00-29.01)	27.72 (23.00-36.50)	28.38 (21.80-32.63)	230.50 (10.62-434.30)	66.42 (29.16-99.70)
Cu	0.04 (0.01-0.09)	<0.01 (<0.01-0.06)	0.04 (0.02-0.06)	<0.01	0.04 (<0.01-0.20)	<0.01 (<0.01-0.04)
Fe	0.57 (0.05-2.46)	0.39 (0.06-0.47)	0.61 (0.27-0.94)	0.22 (0.10-0.31)	1.56 (<0.01-8.70)	0.23 (0.02-0.56)
K	20.27 (12.90-58.10)	21.96 (17.40-24.70)	11.55 (7.70-15.10)	11.38 (9.50-17.16)	44.79 (9.40-124.80)	51.35 (41.10-75.29)
Mg	2.46 (1.39-3.07)	3.45 (2.97-3.83)	2.51 (1.86-3.21)	2.00 (1.83-2.33)	38.48 (1.85-66.76)	7.17 (3.05-11.45)
Mn	0.17 (0.05-0.44)	0.08 (0.07-0.11)	0.06 (0.03-0.08)	0.05 (0.03-0.08)	0.86 (0.02-1.69)	0.41 (0.18-0.89)
Na	57.97 (34.69-84.41)	184.44 (157.17-245.06)	179.58 (136.39-244.92)	221.31 (54.12-302.73)	72.18 (13.70-170.64)	211.21 (183.67-262.93)
P	0.18 (0.03-1.04)	0.08 (0.03-0.27)	0.10 (0.03-0.27)	0.10 (0.03-0.41)	0.22 (<0.05-1.47)	0.33 (0.03-1.20)
Pb	<0.05 (<0.05-0.13)	0.06 (<0.05-0.10)	0.06 (<0.05-0.08)	<0.05 (<0.05-0.08)	1.01 (0.06-6.84)	0.17 (<0.05-0.46)
Si	9.45 (3.85-12.80)	7.96 (3.11-8.91)	13.33 (10.20-17.29)	10.70 (5.99-12.73)	9.60 (5.22-12.36)	13.68 (8.45-19.45)
Zn	0.05 (<0.01-0.34)	0.02 (<0.01-0.05)	0.04 (0.01-0.07)	<0.01 (<0.01-0.03)	0.42 (0.25-0.79)	0.04 (<0.01-0.16)
HCO <sub>3</sub> , mg/L	261.53 (235.00-290.00)	617.58 (549.00-866.00)	484.33 (450.00-518.00)	672.43 (638.00-762.00)	134.75 (79.00-366.00)	304.10 (234.00-518.00)
SO <sub>4</sub> , mg/L	3.18 (0.15-8.4)	9.84 (2.10-16.20)	39.78 (33.85-46.13)	17.45 (7.12-20.67)	663.10 (140.27-1595.45)	384.94 (271.81-503.58)
EC, S	0.46 (0.25-0.52)	1.08 (1.00-1.13)	.98 (0.85-1.09)	1.41 (1.32-1.45)	1.83 (0.54-3.02)	1.60 (1.26-2.01)
Eh, mV	180.77 (88.00-265.00)	160.36 (-68.00-238.00)	170.67 (80.00-282.00)	144.86 (0.00-194.00)	208.90 (177.00-256.00)	150.67 (3.00-207.00)
pH	7.21 (6.29-7.98)	7.36 (7.02-7.58)	7.15 (6.69-7.42)	7.13 (7.06-7.26)	7.46 (6.50-9.35)	7.63 (6.98-8.17)
Temp., °C	29.59 (26.60-31.90)	34.58 (33.20-37.50)	33.33 (31.40-36.00)	40.63 (39.00-42.30)	27.38 (25.30-31.40)	35.68 (31.40-40.60)

Table 12.—Saturation indices of water samples

Mineral	DH1	DH2	DH3	DH4	Sump	Stope
Albite .....	-0.518	NC	0.040	0.523	-1.284	-0.158
Calcite .....	-0.325	0.200	0.860	-0.119	0.086	0.282
Dolomite .....	-1.801	-0.559	0.597	-1.362	-0.978	-0.396
Gypsum .....	-3.414	-3.027	-1.274	-2.401	-2.779	-0.587
Illite .....	3.910	NC	2.808	4.638	0.677	4.667
Kaolinite .....	5.621	NC	3.353	6.291	2.979	12.905
Ca-montmorillonite .....	4.584	NC	2.451	5.527	1.503	4.868
Siderite .....	-0.305	NC	NC	NC	NC	NC
Silica gel .....	-0.505	-0.631	-0.416	-0.394	-0.563	-0.473

NC Not calculated.

## DISCUSSION AND CONCLUSIONS

Previous research into the environmental impacts of mine waste sandfill demonstrated that sandfill mineralogy, as well as exposure to O<sub>2</sub> and water prior to mine flooding, will control the release of metals to ground water. Secondary minerals formed when sandfill is exposed to O<sub>2</sub> during mine operations will be dissolved, and oxidation of sulfides by Fe<sup>3+</sup> may occur after the sandfill is flooded. Addition of cement is expected to decrease the surface area of sulfides exposed to oxidation, to decrease the diffusion of air into the backfill prior to flooding by increasing residual water saturation, and to augment the buffering capacity provided by the natural mineralogy. These factors should result in the release of less metals than would occur from sandfill alone.

The addition of cement affected the chemistry of backfill under the influence of an external source of acidic water. Sufficient H<sub>2</sub>SO<sub>4</sub> was added to the solution contacting the cemented backfill to drop the pH to ~2.0. In three different tailings samples, the pH of the solution contacting the backfill increased. The acid-neutralization capacity, as well as the acid-neutralization rate, of all three samples was different.

Particle-size distribution of the tailings used to make a cemented backfill appeared to be very important in controlling the rate of chemical attack. Material with a wider distribution of particle sizes created concrete with a slower chemical reaction rate with acid than material with uniform sizes of particles. It is possible that the slower reaction rate results from slower diffusion of acid into the sample, which in turn may be caused by smaller pore sizes.

The SN and SO samples had very similar distributions of particle sizes and smaller ranges of sizes than the CN sample. These samples exhibited very rapid neutralization of the acid wash flowing over the surface of the cemented tailings, which suggests a rapid penetration rate. This, in turn, could be interpreted as related to the pore size of the concrete.

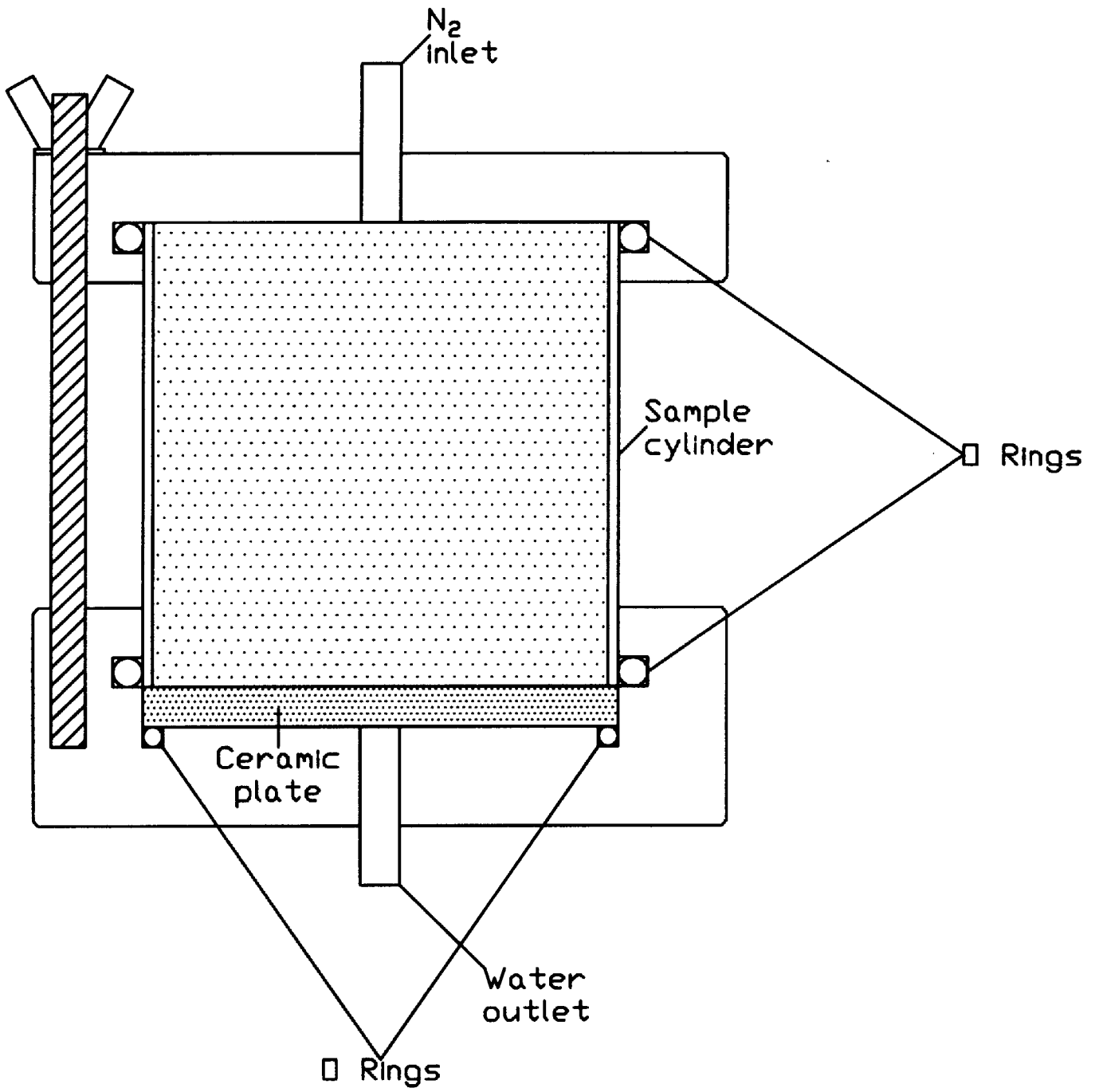
The presence of sulfide minerals in the tailings is important in determining the acid-neutralization capacity of the tailings. The main difference between the SO and SN samples was the estimated pyrite content; the quantity of Ca and Mg carbonates, as estimated from the strong acid dissolution, was approximately the same. Therefore, the SN sample had a greater potential to generate acidic water than did the SO sample. After an approximately equivalent period of acid neutralization by the two samples, the wash contacting the SN sample remained acidic. It appears that the additional acid exposed sufficient reduced sulfide minerals to allow oxidation and acid production. The acid-producing capacity of tailings will be an important consideration prior to their use as cemented backfill.

Backfilled stopes in rock with low hydraulic conductivities will probably constitute preferential flow paths after mine flooding; however, the rate of flow through the backfill will be much less prior to flooding. Furthermore, addition of cement decreases the hydraulic conductivity of backfill, which will result in less water flow through the backfill than if uncemented sandfill is used. Preferential flow may develop where shrinkage occurs near stope boundaries or where the backfill has deteriorated because of sulfide oxidation. However, the effect of increased flow will be offset by decreased surface area contact and by armoring of preferential flow paths by insoluble precipitates.

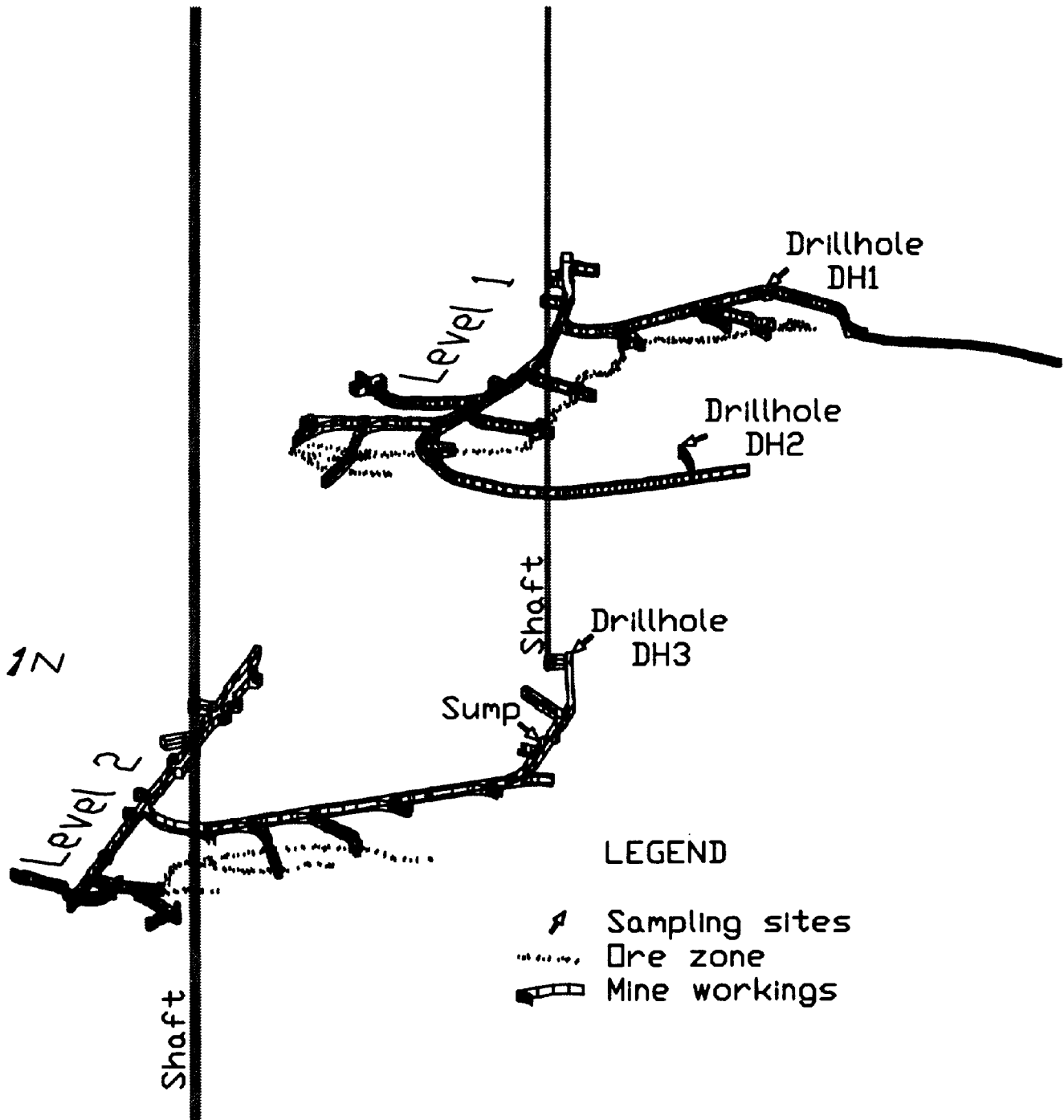
Considering all factors, the overall impact of cemented backfill should be less than the effect of uncemented sandfill. Factors relevant to the contamination potential of cemented backfill that warrant further study include (1) the relationship between residual saturation of backfill and the addition of cement, (2) the reduction in sulfide oxidation and buffering resulting from armoring of preferential flow paths, (3) changes in the strength of cemented backfill in the long term caused by sulfide oxidation, and (4) the quality of residual pore water after backfilling.

## REFERENCES

- Ball, J. W., D. K. Nordstrom, and D. W. Zachmann. WATEQ4F-A Personal Computer FORTRAN Translation of the Geochemical Model WATEQ2F With Revised Data Base. U.S. Geol. Surv., OFR 87-50, 1987, 108 pp.
- Brookins, D. G., B. M. Thomson, and P. A. Longmire. Early Diagenesis of Uranium Mine Stope Backfill. Paper in Uranium Mill Tailings Management, Proceedings of the Fifth Symposium (Ft. Collins, CO, 1982). Civil Eng. Dep., CO State Univ., 1982, pp. 27-37.
- Corey, A. T. Mechanics of Immiscible Fluids in Porous Media. Water Res. Publ. (Littleton, CO), 1986.
- Doepker, R. D. Column Leach Study IV: Factors Affecting the Dissolution of Metals from Sulfidic Mine Tailings. Paper in Proceedings, 2nd International Conference on the Abatement of Acidic Drainage (Montreal, PQ, Sept. 16-18, 1991). Centre de Recherches Minerales, Quebec, PQ, v. 1, 1991a, pp. 115-138.
- \_\_\_\_\_. Enhanced Heavy Metal Mobilization From Unsaturated Mine Tailings. Trans. of SME, v. 288, 1991b, pp. 1801-1805.
- Doepker, R. D., and P. L. Drake. Laboratory Study of Submerged Metal-Mine Tailings 1: Effect of Solid-Liquid Contact Time and Aeration on Contaminant Concentrations. Trans. of SME, v. 288, 1990, pp. 1826-1830.
- \_\_\_\_\_. Laboratory Study of Submerged Metal-Mine Tailings 3: Factors Influencing the Dissolution of Metals. Paper in Proceedings, 2nd International Conference on the Abatement of Acidic Drainage (Montreal, PQ, Sept. 16-18, 1991). Centre de Recherches Minerales, Quebec, PQ, v. 1, 1991, pp. 139-158.
- Doepker, R. D., and W. K. O'Conner. Column Leach Study I: Heavy Metal Dissolution Characteristics from Selected Copper Mine Tailings. Paper in 5th Billings Symposium on Disturbed Land Rehabilitation (Billings, MT, Mar. 25-30, 1990). Reclamation Research Unit, MT State Univ., Bozeman, MT, Publ. No. 9003, v. 1, 1990a, pp. 27-40.
- \_\_\_\_\_. Column Leach Study II: Heavy Metal Dissolution Characteristics from Selected Lead-Zinc Mine Tailings. Column Leach Study II: Heavy Metal Dissolution Characteristics from Selected Lead-Zinc Mine Tailings. Chapter 9 in Mining and Mineral Processing Wastes: Proceedings of the Western Regional Symposium on Mining and Mineral Processing Wastes, ed. by F. M. Doyle (Berkeley, CA, May 30-June 1, 1990). Soc. Min. Eng., 1990b, pp. 69-80.
- Geidel, G., and F. T. Caruccio. Acid Drainage Response to Surface Limestone Layers. Paper in Proceedings, 1982, Symposium on Surface Mining, Hydrology, Sedimentology and Reclamation, ed. by D. H. Graves (Lexington, KY, Dec. 6-10, 1982). Coll. Eng., Univ. KY, 1982, pp. 403-406.
- Henderson, R. M., and P. J. Norton. A Method of Predicting the Pollution Potential of Surface Mining Backfill. Intern. J. Mine Water, v. 3, No. 1, 1984, pp. 41-55.
- Lachmar, T. Analysis of an Acid-Producing Underground Lead-Zinc Mine, Coeur d'Alene Mining District, Idaho. Ph.D. dissertation, Univ. ID, Moscow, ID, 1988, 207 pp.
- Levens, R. L., and C. M. K. Boldt. Hydrochemical Impacts of Mine Waste Backfill in Underground Sulfide Mines. Paper in Environmental Issues and Management of Waste in Energy and Mineral Production. Proceedings: Second International Conference, ed. by R. K. Singhal, A. K. Mehrotra, K. Fytas, and J.-L. Collins (Calgary, AB, Sept. 1-4, 1992). Balkema, vol. 2, 1992, pp. 891-902.
- \_\_\_\_\_. Environmental Impacts of Mine Waste Sandfill. USBM RI 9493, 1994, 12 pp.
- Longmire, P. A., R. T. Hicks, and D. G. Brookins. Aqueous Geochemical Interactions Between Ground Water and Uranium Minestope Backfilling-Grants Mineral Belt, New Mexico: Application of Eh-pH Diagrams. Paper in Uranium Mill Tailings Management, Proceedings of the Fourth Symposium (Ft. Collins, CO, Oct. 26-27, 1981). Civil Eng. Dep., CO State Univ., 1981, pp. 389-414.
- Lowson, R. T. Aqueous Oxidation of Pyrite by Molecular Oxygen. Chem. Rev., v. 82, No. 5, 1982, pp. 461-497.
- McCurry, G. N., and H. W. Rauch. Characterization of Ground Water Contamination Associated With Coal Mines in West Virginia. Paper in Proceedings of the Sixth Annual Symposium and Exposition on Aquifer Restoration and Ground Water Monitoring (Columbus, OH, May 1986). NWWA, 1986, pp. 669-685.
- Senyur, G. The Time Effect on Flow Through Mine Backfill Materials. Paper in Innovations in Mining Backfill Technology. Proceedings of 4th International Symposium on Mining With Backfill, ed. by F. P. Hassani, M. J. Scoble, and T. R. Yu (Montreal, PQ, Oct. 2-5, 1989). Balkema, 1989, pp. 415-423.
- Thomson, B. M., and R. J. Heggen. Water Quality and Hydrologic Impacts of Disposal of Uranium Mill Tailings by Backfilling. Management of Wastes From Uranium Mining and Milling, International Atomic Energy Agency, IAE-SM-262/51, Vienna, Austria, 1982, pp. 373-384.
- Thomson, B. M., P. A. Longmire, and D. G. Brookins. Geochemical Constraints on Underground Disposal of Uranium Mill Tailings. Appl. Geochem., v. 1, 1986, pp. 335-343.
- U.S. Environmental Protection Agency. Methods of Chemical Analysis of Water and Wastes. Publ. EPA-600/4-79-020, 1983, 298 pp.

*Figure 1**Cross section through Tempe pressure cell.*

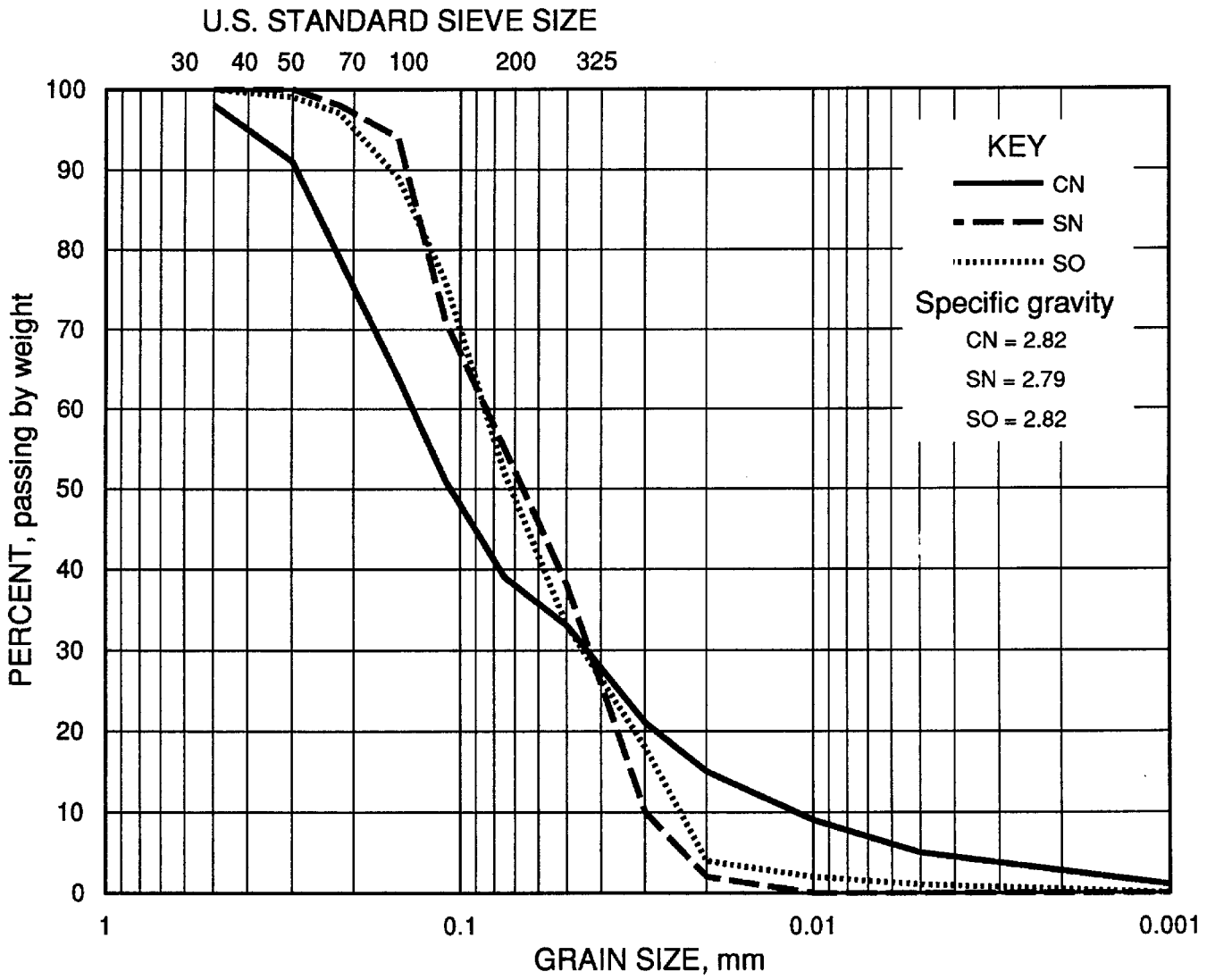
**Figure 2**



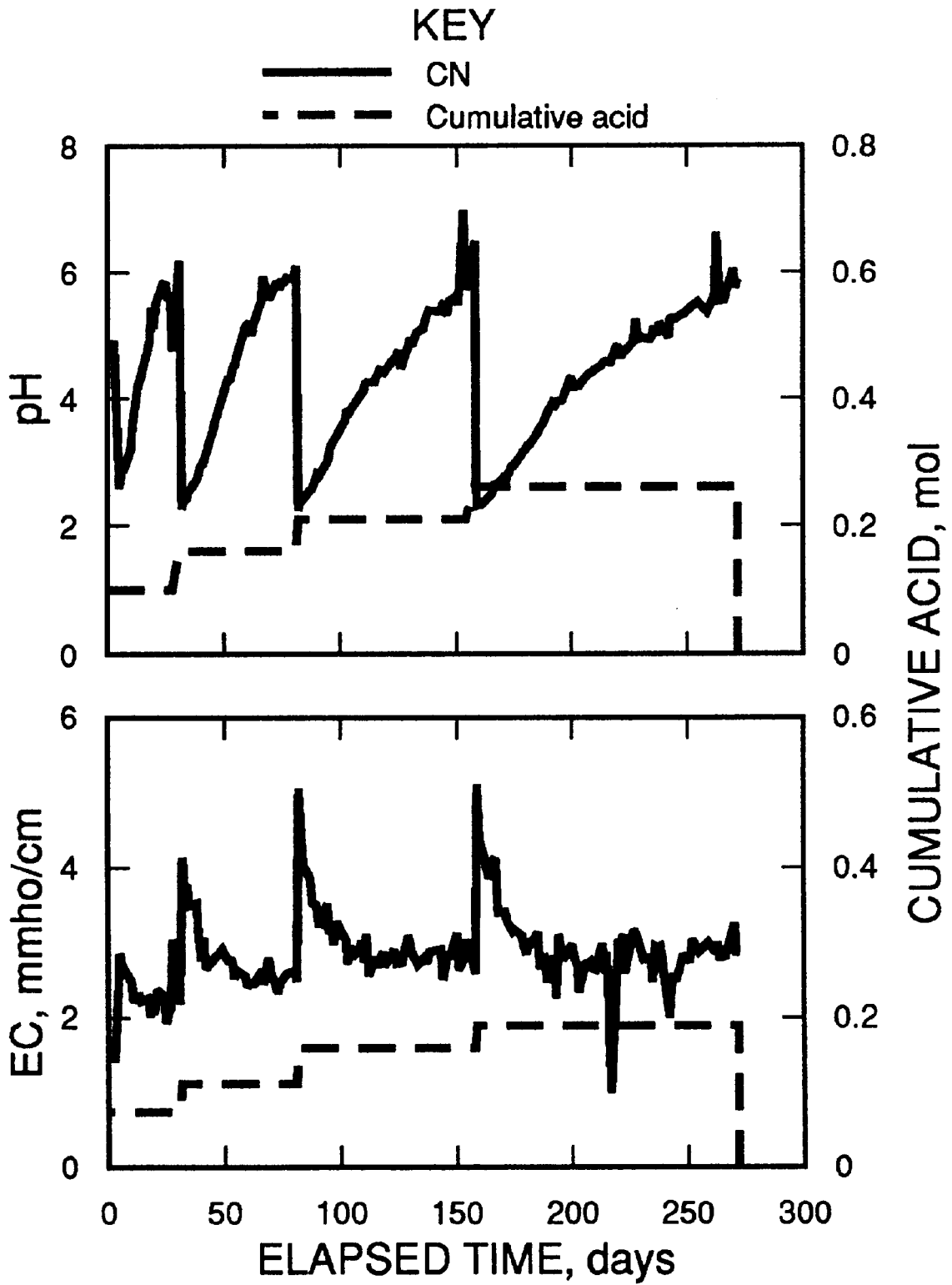
**Schematic of mine workings and test stope.**



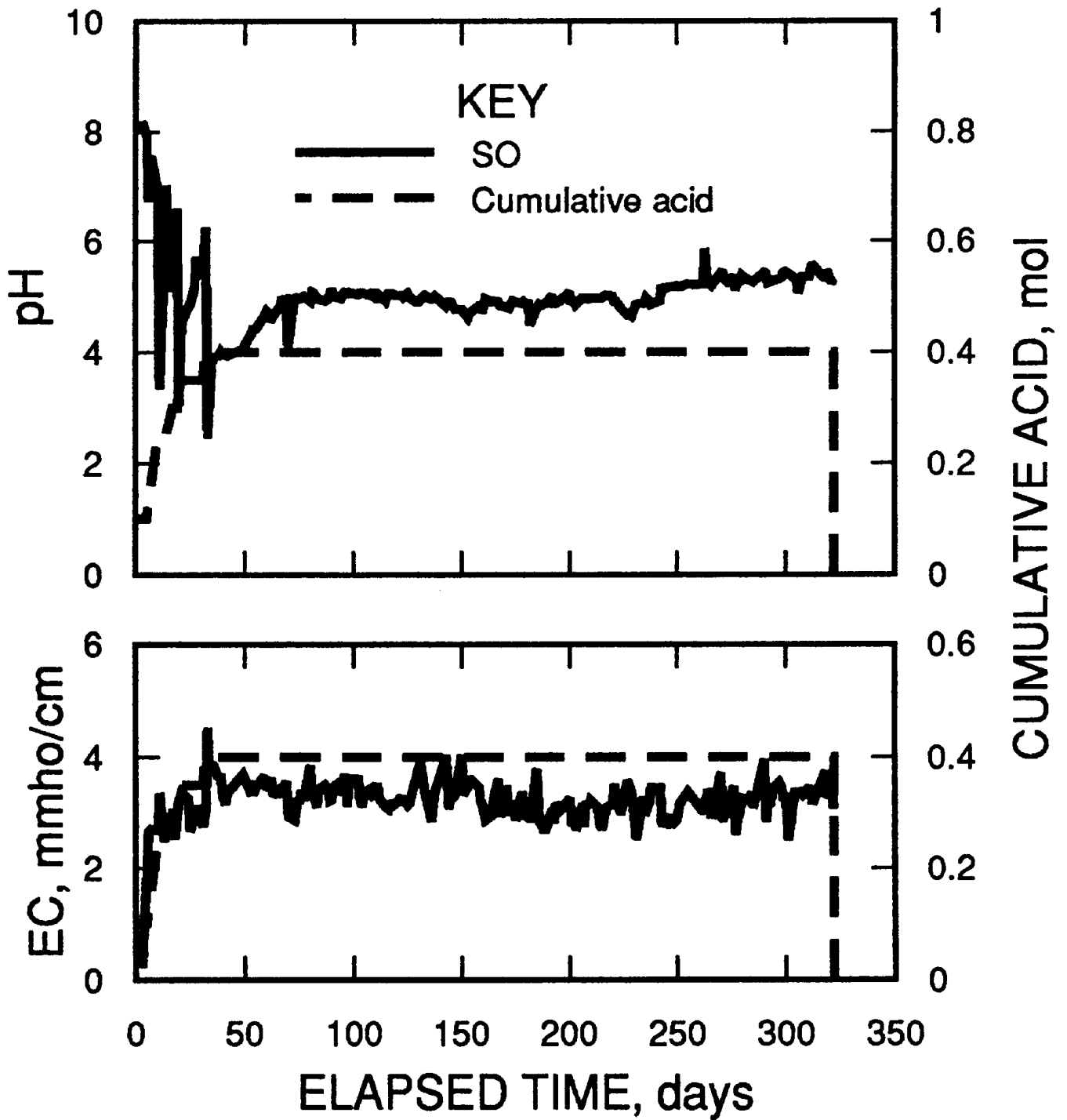
Figure 3



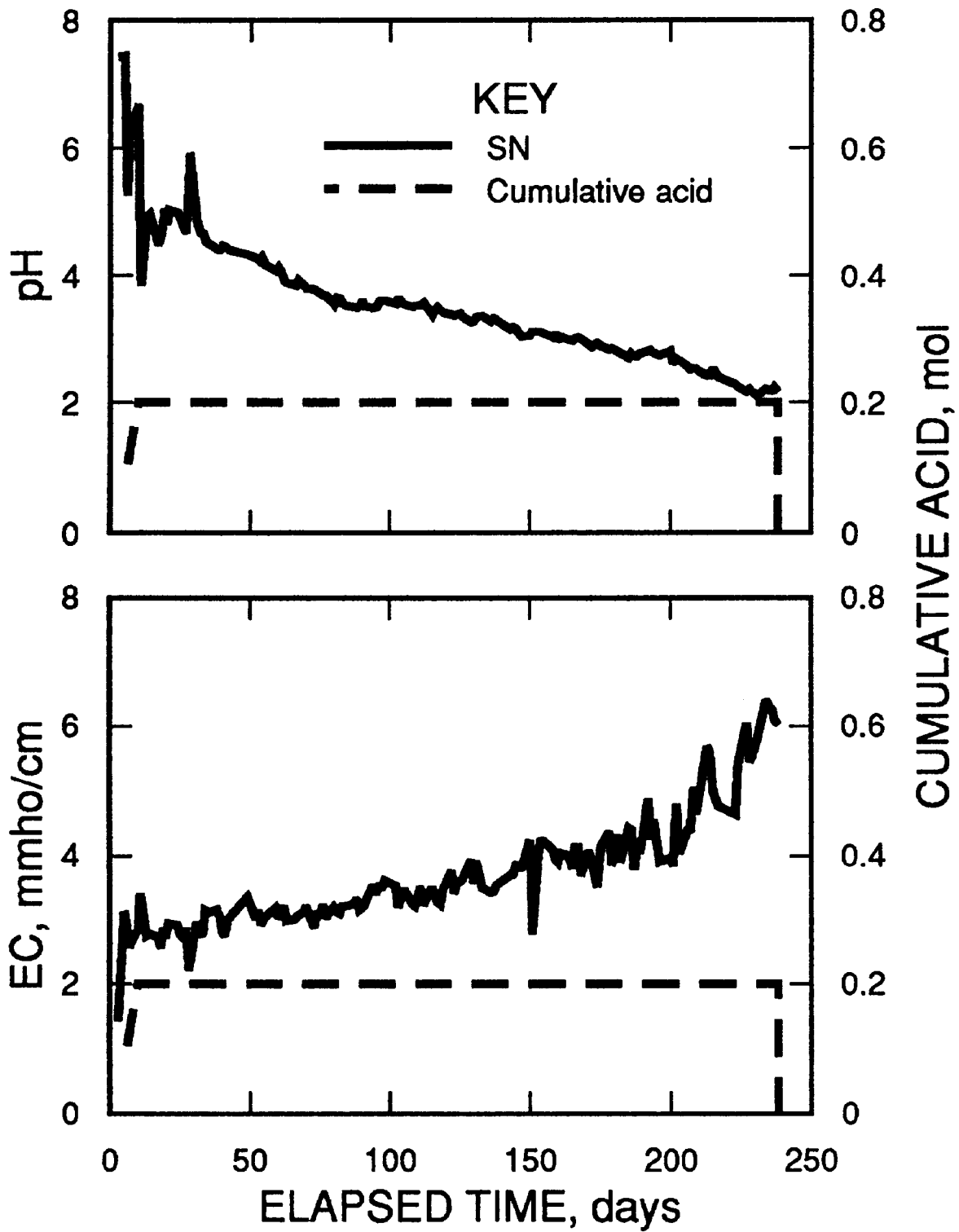
Particle-size distribution of tailings samples.

**Figure 4**

*pH of  $H_2SO_4$  wash leachate, sample CN.*

**Figure 5**

*pH of H<sub>2</sub>SO<sub>4</sub> wash leachate, sample SO.*

**Figure 6**

*pH of H<sub>2</sub>SO<sub>4</sub> wash leachate, sample SN.*

