

LABORATORY DETERMINATION OF PARAMETERS INFLUENCING METAL DISSOLUTION FROM SULFIDIC WASTE ROCK¹

by

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Abstract. Researchers from the U.S. Bureau of Mines have been conducting a series of laboratory studies to examine the general characteristics of metal dissolution from mine wastes, as well as possible chemical control strategies. The studies reported upon in this paper involved samples of sulfidic waste rock obtained from a gold-mining operation. Experimental methods included columns, perforated baskets, and Buchner funnels, coupled with humidity and controlled-atmosphere chambers.

Results indicated that concentrations of soluble metals were one to two orders of magnitude higher in the leachate obtained during the initial two or three leachings than in leachates collected later. During the initial seven leachings, samples stored and leached under nitrogen produced the same metal leachate concentrations as samples stored and leached in laboratory air. The biocide sodium benzoate had little effect on the initial phase of dissolution, although another biocide, sodium lauryl sulfate, did reduce initial metal mobility. This effect appears to be related to the surfactant properties of the sodium lauryl sulfate on the stored contaminants and not to a decrease in biological activity.

During the second phase of leachings, the use of biocides and/or the exclusion of oxygen reduced metal dissolution and sulfate production. Results indicated that two reaction pathways, biologic and oxidation by air, contributed nearly equally to metal dissolution and sulfate formation.

Additional Key Words: waste rock, inert atmosphere, wet/dry cycle, leaching, biocide.

Introduction

Acid rock drainage, or ARD, is a result of natural oxidation of sulfide minerals in rock that has been exposed to air and water. Rock excavated to gain access to an ore body (waste rock) is often a major source of ARD. The mechanisms of acid formation and the severity of the

problem have recently been reviewed by Steffen, Robertson, and Kirsten, Inc. (1989) and will not be discussed herein.

Ongoing investigations at U.S. Bureau of Mines laboratories have established some of the natural conditions that influence the formation of acid and the mobility of metals during weather-

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ing of metal mine mill tailings (Doepker, 1991). The question is, "are those laboratory tailings study results directly comparable to similar studies of the formation of ARD from sulfide-containing waste rock?"

Experimental Methods and Protocols

Samples of sulfidic waste rock were obtained from a Nevada gold-mining operation. These samples had been previously crushed to fragments less than 5 cm in diameter and contained over 7 pct sulfur. Portions of these samples were leached under various conditions and methods. The details of these conditions and methods as parts of a series of studies are discussed below.

Series I

Series I was designed to examine some experimental parameters that may influence the precision of the protocol and the methods used to determine dissolution parameters and to explore the effects of biocides on dissolution. Two leaching columns were constructed from 0.61-m lengths of 7.6-cm-inside-diameter (ID) polyvinyl chloride (PVC) pipe equipped with cemented couplings and bushings in which perforated Nalgene plates had been installed. A 9-cm in diameter G6 (Fisher Scientific) borosilicate glass-fiber filter was placed on the perforated plate before the bushings were installed. One and one-half kilograms of waste rock fragments less than 1 cm in diameter was added to each column. The days between leachings (leach cycle) were varied between 1 and 21 days. These two leaching columns were identical to those frequently used in previous studies with tailings (Doepker, 1991).

The first leaching of both columns was carried out with 500 cm³ of synthetic rain (SR), which was formulated on the basis of the chemical composition for western rain as described by Bainbridge et al. (1980). The pH of the SR was adjusted to 5.5 and used

throughout. Approximately 350 cm³ of leachate was obtained. The difference between the volume of leachant and the volume of leachate defined the field capacity of the waste columns. The two columns were then leached with 150 cm³ of SR, 1 g/L sodium lauryl sulfate (SLS) with a pH of 6.5, or 1 g/L sodium benzoate (NaBz) with a pH of 6.5 to determine the effects of a biocide on leachate acidity and metal concentrations (Kleinmann, 1981; Kleinmann and Erickson, 1983; Erickson et al., 1985; Rastogi and Sobek, 1986; and Watzlaf, 1986). After 25 leachings, the leachant volume was increased to 175 cm³ for an additional 15 leachings. Detailed leaching protocol is reported in table 1.

Three kilograms of waste rock was placed into three perforated, polypropylene dipping baskets 20.3 cm in diameter by 20.3 cm high. Four kilograms of waste rock was placed into two other baskets. Baskets 1 and 5 received bulk samples, while basket 2 received a sample from which most of the <0.5-cm material had been removed. Samples for baskets 3 and 4 were partially sieved to reduce the amount of material under 0.1 cm and over 2.5 cm in size. The purpose of the partial segregation of the waste rock by size was to estimate the effect of rock-fragment size on leached metal concentrations and to address one of the problems associated with obtaining representative waste rock samples. All dipping baskets were placed into 20 L, Nalgene, heavy-duty cylindrical tanks and covered. A summary of the weights and sizes used in the five baskets is presented in table 2.

Leachings were carried out with 250 cm³ of selected leachants (SR, SLS, or NaBz) with leaching cycles ranging from 1 to 21 days (table 1). Covers remained on the tanks at all times except when leachant was dripped onto the sample through a 7.7-cm in diameter perforated filter funnel.

Leachates were obtained by tilting the dipping bucket at an angle of approximately 30° over the tanks and collecting the complete sample.

Table 1. Listing of Series I test protocols.

TEST 1.										
Leach No.	1	2	3	4	5	6	7	8	9	
Leach cycle (a)	START	2	4	6	2	1	11	2	5	
(days)										
	Leachant/Volume (cm ³)									
column 1	SR/500b	SR/150	SR/150	SR/150	SR/150	SR/150	SR/150	SR/150	SR/300	
column 2	SR/500	SR/150	SR/150	SR/150	SR/150	SR/150	SR/150	SR/150	SR/300	
basket 1	SR/500	SR/250	SR/250	SR/250	SR/250	SR/250	SR/250	SR/250	SR/500	
basket 2	SR/500	SR/250	SR/250	SR/250	SR/250	SR/250	SR/250	SR/250	SR/500	
basket 3	SR/500	SR/250	SR/250	SR/250	SR/250	SR/250	SR/250	SR/250	SR/500	
basket 4	SR/500	SR/250	SR/250	SR/250	SR/250	SR/250	SR/250	SR/250	SR/500	
basket 5	SR/500	SR/250	SR/250	SR/250	SR/250	SR/250	SR/250	SR/250	SR/500	

TEST 2.											
Leach No.	10	11	12	13	14	15	16	17	18	19	20
Leach cycle	4	7	10	10	14	7	14	8	9	11	7
(days)											
	Leachant/Volume (cm ³)										
column 1	SR/150	SR/150	SR/150	SR/150	SR/150	SR/150	SR/150	SR/150	SR/150	SR/150	SR/150
column 2	SLS/150c	SLS/150	SLS/150	SLS/150	SLS/150	SLS/150	SLS/150	SLS/150	SLS/150	SLS/150	SLS/150
basket 1	SLS/250	SLS/250	SLS/250	SLS/250	SLS/250	SLS/250	SLS/250	SLS/250	SLS/250	SLS/250	SLS/250
basket 2	SLS/250	SLS/250	SLS/250	SLS/250	SLS/250	SLS/250	SLS/250	SLS/250	SLS/250	SLS/250	SLS/250
basket 3	SR/250	SR/250	SR/250	SR/250	SR/250	SR/250	SR/250	SR/250	SR/250	SR/250	SR/250
basket 4	SR/250	SR/250	SR/250	SR/250	SR/250	SR/250	SR/250	SR/250	SR/250	SR/250	SR/250
basket 5	SLS/250	SLS/250	SLS/250	SLS/250	SLS/250	SLS/250	SLS/250	SLS/250	SLS/250	SLS/250	SLS/250

TEST 3.													
Leach No.	21	22	23	24	25	26	27	28	29	30	31	32	33
Leach cycle	7	7	7	7	14	15	14	17	14	14	21	10	14
(days)													
	Leachant/Volume (cm ³)												
column 1	NaBz/150d	NaBz/150	NaBz/150	NaBz/150	NaBz/150	NaBz/175	NaBz/175	NaBz/175	NaBz/175	NaBz/175	NaBz/175	NaBz/175	NaBz/175
column 2	SR/150	SR/150	SR/150	SR/150	SR/150	SR/175	SR/175	SR/175	SR/175	SR/175	SR/175	SR/175	SR/175
basket 1	SR/250	SR/250	SR/250	SR/250	SR/250	SR/250	SR/250	SR/250	SR/250	SR/250	SR/250	SR/250	SR/250
basket 2	SR/250	SR/250	SR/250	SR/250	SR/250	SR/250	SR/250	SR/250	SR/250	SR/250	SR/250	SR/250	SR/250
basket 3	NaBz/250	NaBz/250	NaBz/250	NaBz/250	NaBz/250	NaBz/250	NaBz/250	NaBz/250	NaBz/250	NaBz/250	NaBz/250	NaBz/250	NaBz/250
basket 4	NaBz/250	NaBz/250	NaBz/250	NaBz/250	NaBz/250	NaBz/250	NaBz/250	NaBz/250	NaBz/250	NaBz/250	NaBz/250	NaBz/250	NaBz/250
basket 5	SR/250	SR/250	SR/250	SR/250	SR/250	SR/250	SR/250	SR/250	SR/250	SR/250	SR/250	SR/250	SR/250

- a. Days between leachings.
- b. Synthetic Rain
- c. Sodium lauryl sulfate
- d. Sodium benzoate

Table 2. Waste rock weights and sizes in dipping baskets

	Dipping Baskets				
	1	2	3	4	5
Weight, kg . . .	3.0	3.0	3.0	4.0	4.0
Size, cm . . .	Bulk, -5	>0.5	-2.5 + 0.1	2.5 + 0.1	Bulk, -5

Series II

Three kilograms of waste rock was placed into each of four dipping baskets. Three baskets were placed into a nitrogen chamber while the fourth was kept in the laboratory atmosphere. The purpose of this test was to help establish the

amount of dissolvable secondary minerals stored in the sample at the start of the tests and to distinguish this amount from the amount mobilized through oxidation between leachings. Leachants (250 cm³ of SR or NaBz) were dripped onto the sample as described above. After the initial seven leachings (test 1), all baskets were re-

moved from the nitrogen chamber and placed into a closed tank. After six leachings, the covers of two baskets, 1 and 4, were discarded, and the volume of leachant was increased to 350 cm³ to compensate for increased evaporation. The leaching cycle time ranged between 2 and 25 days. A listing of the Series II protocol is presented in table 3.

Series III

This test series was directed to studying the effects of three variables (humidity, that is, loss of stored water, biocides, and an inert atmosphere) on the dissolution of species from a sample of waste rock.

Table 3. Listing of Series II test protocols

TEST 1.													
Leach No.	1	2	3	4	5	6	7						
Leach cycle(a)	START	2	3	7	4	3	7						
Basket 1.-----													
Atmosphere	Nitrogen	Nitrogen	Nitrogen	Nitrogen	Nitrogen	Nitrogen	Nitrogen						
L-ant/vol.	bSRc/250	SR/250	SR/250	SR/250	SR/250	SR/250	SR/250						
Basket 2.-----													
Atmosphere	Nitrogen	Nitrogen	Nitrogen	Nitrogen	Nitrogen	Nitrogen	Nitrogen						
L-ant/vol	SR/250	SR/250	SR/250	SR/250	SR/250	SR/250	SR/250						
Basket 3.-----													
Atmosphere	Nitrogen	Nitrogen	Nitrogen	Nitrogen	Nitrogen	Nitrogen	Nitrogen						
L-ant/vol	SLSd/250	SLS/250	SLS/250	SLS/250	SLS/250	SLS/250	SLS/250						
Basket 4.-----													
Atmosphere	LAB.AIR	LAB.AIR	LAB.AIR	LAB.AIR	LAB.AIR	LAB.AIR	LAB.AIR						
L-ant/vol	SR/250	SR/250	SR/250	SR/250	SR/250	SR/250	SR/250						
TEST 2. LAB AIR													
Leach No.	8	9	10	11	12	13	14	15					
Leach cycle	4	3	7	11	11	9	11	7					
Basket 1.-----													
Conditions	CLOSED	CLOSED	CLOSED	CLOSED	CLOSED	CLOSED	OPEN	OPEN					
L-ant/vol	SR/250	SR/250	SR/250	SR/250	SR/250	SR/250	SR/350	SR/350					
Basket 2.-----													
Conditions	CLOSED	CLOSED	CLOSED	CLOSED	CLOSED	CLOSED	CLOSED	CLOSED					
L-ant/vol	SR/250	SR/250	SR/250	SR/250	SR/250	SR/250	SR/250	SR/250					
Basket 3.-----													
Conditions	CLOSED	CLOSED	CLOSED	CLOSED	CLOSED	CLOSED	CLOSED	CLOSED					
L-ant/vol	SLS/250	SLS/250	SLS/250	SLS/250	SLS/250	SLS/250	SLS/250	SLS/250					
Basket 4.-----													
Conditions	CLOSED	CLOSED	CLOSED	CLOSED	CLOSED	CLOSED	OPEN	OPEN					
L-ant/vol	SR/250	SR/250	SR/250	SR/250	SR/250	SR/250	SR/350	SR/350					
TEST 2. LAB AIR													
Leach No.	8	17	18	19	20	21	22	23	24	25	26	27	28
Leach cycle	8	7	7	7	14	15	14	17	14	14	25	10	14
Basket 1.-----													
Conditions	OPEN	OPEN	OPEN	OPEN	OPEN	OPEN	OPEN	OPEN	OPEN	OPEN	OPEN	OPEN	OPEN
L-ant/vol	SR/250	SR/350	SR/350	SR/350	SR/350	SR/350	SR/350	SR/350	SR/350	SR/350	SR/350	SR/350	SR/350
Basket 2.-----													
Conditions	CLOSED	CLOSED	CLOSED	CLOSED	CLOSED	CLOSED	CLOSED	CLOSED	CLOSED	CLOSED	CLOSED	CLOSED	CLOSED
L-ant/vol	NaBzf/250	NaBz/250	NaBz/250	NaBz/250	NaBz/250	NaBz/250	NaBz/250	NaBz/250	NaBz/250	NaBz/250	NaBz/250	NaBz/250	NaBz/250
Basket 3.-----													
Conditions	CLOSED	CLOSED	CLOSED	CLOSED	CLOSED	CLOSED	CLOSED	CLOSED	CLOSED	CLOSED	CLOSED	CLOSED	CLOSED
L-ant/vol	SR/250	SR/250	SR/250	SR/250	SR/250	SR/250	SR/250	SR/250	SR/250	SR/250	SR/250	SR/250	SR/250
Basket 4.-----													
Conditions	OPEN	OPEN	OPEN	OPEN	OPEN	OPEN	OPEN	OPEN	OPEN	OPEN	OPEN	OPEN	OPEN
L-ant/vol	SR/350	SR/350	SR/350	SR/350	SR/350	SR/350	SR/350	SR/350	SR/350	SR/350	SR/350	SR/350	SR/350

a. Days between leaching b. Leachant used and its volume(cc) c. synthetic rain d. Sodium lauryl sulfate
e. Lids on (closed) or off (open) f. Sodium benzoate

In the first test of series III, the effects of relative humidity on the storage of waste rock were examined. Five 11-cm Nalgene polypropylene suction funnels were used. Whatman No. 3, 11-cm filter paper was placed into a funnel along with 250 g of segregated waste rock (particle size <0.75 cm). One sample (funnel 1) was placed into the nitrogen chamber at >90 pct relative humidity and then into an air chamber held at saturation. The other four funnels were stored in air chambers at 10, 30, 60, and 80 pct relative humidity. The funnels were removed from the chambers during leaching with 125 cm^3 of SR. The samples were allowed to drain freely for approximately 24 hours, during which time the funnels were covered with plastic wrap to reduce evaporation. The funnels containing the waste rock were then reintroduced into the humidity chambers. Funnel 1 remained in a nitrogen chamber at all times for nine consecutive leachings, after which it was given the same treatment as the others and was stored in a chamber in which the humidity was maintained near saturation. The leaching cycles are given in table 4.

A second set of four 12.6-cm^3 porcelain suction funnels received 250 g of the same waste rock (particle size <0.75 cm). Two of these funnels were placed in the nitrogen chamber and two were opened to the laboratory atmosphere. One of each subset was leached with NaBz and one with SR. After nine initial leachings (test 1) with 125 cm^3 of leachant under a nitrogen atmosphere, the two funnels were removed from the chamber, leached under laboratory conditions (test 2) seven times, and then placed back into the nitrogen chamber for an additional six leachings (test 3).

To examine the effect of leachant pH on leachate metal concentrations, 1 kg of the bulk waste rock (particle size <0.5 cm) was placed in three 10-cm ID acrylic columns. Whatman No. 3 filter paper was used on the perforated base of the columns. Leachants were 250 cm^3 of SR (pH = 5.4), 1 g/L disodium hydrogen phosphate (pH = 8.9), or 1 g/L sodium hydrogen carbonate (pH = 8.1). The columns were

opened to laboratory air between leachings for periods ranging between 3 and 25 days.

All collected leachate samples were measured for pH, conductivity, and volume; metal concentrations were determined with a Perkin-Elmer Plasma II ICP spectrometer. Anion analyses were conducted with a Dionex 4000i ion chromatograph (IC) equipped with an AS4A separation column.

Results and Discussion

The mine operator reported that the waste rock used in this study consisted of approximately 40 to 50 pct quartz, 10 to 20 pct illite, 10 to 20 pct calcite, 7 to 9 pct dolomite, and 5 to 6 pct montmorillonite. Minerals found in amounts less than 5 pct included siderite, kaolinite, jarosite, iron oxides, and pyrite. The results of chemical analyses of a fraction of the waste (particle size passing a 100-mesh screen) carried out in the laboratory are shown in table 5.

A strong acid assay, the maximum leachability assay (Bainbridge et al., 1980), shows that there is a greater contribution of sulfide minerals in the fines fraction. This would suggest that pyrite, galena, arsenopyrite, and other metal sulfides may be concentrated in smaller rock fragments.

Measurements of the concentrations of aluminum (Al), arsenic (As), barium (B), calcium (Ca), cadmium (Cd), cobalt (Co), chromium (Cr), copper (Cu), iron (Fe), magnesium (Mg), manganese (Mn), nickel (Ni), lead (Pb), sulfur (S), zinc (Zn), and sulfate (SO_4) in the acquired leachates were determined. ICP-determined S was found to be equal to one-third of the SO_4 as analyzed by the IC within an experimental uncertainty of 5 to 10 pct. For the sake of brevity, complete data tables have not been included, but graphs representing collected data for As, Cu, and S are presented. Some generalized observations for other elements will be made, however.

Table 4. Listing of Series III, Filter funnels test protocol, effect of inert atmosphere

TEST 1.									
Leach No.	1	2	3	4	5	6	7	8	9
Leach cycle(a)	START	3	4	7	7	7	7	7	14
Funnel 1.									
Atmosphere	Nitrogen	Nitrogen	Nitrogen	Nitrogen	Nitrogen	Nitrogen	Nitrogen	Nitrogen	Nitrogen
L-ant/vol	bNaBz/150	NaBz/125	NaBz/125	NaBz/125	NaBz/125	NaBz/125	NaBz/125	NaBz/125	NaBz/125
Funnel 2.									
Atmosphere	Nitrogen	Nitrogen	Nitrogen	Nitrogen	Nitrogen	Nitrogen	Nitrogen	Nitrogen	Nitrogen
L-ant/vol	SRd/150	SR/125	SR/125	SR/125	SR/125	SR/125	SR/125	SR/125	SR/125
Funnel 3.									
Atmosphere	Lab.air	Lab.air	Lab.air	Lab.air	Lab.air	Lab.air	Lab.air	Lab.air	Lab.air
L-ant/vol	SR/150	SR/125	SR/125	SR/125	SR/125	SR/125	SR/125	SR/125	SR/125
Funnel 4.									
Atmosphere	Lab.air	Lab.air	Lab.air	Lab.air	Lab.air	Lab.air	Lab.air	Lab.air	Lab.air
L-ant/vol	NaBz/150	NaBz/125	NaBz/125	NaBz/125	NaBz/125	NaBz/125	NaBz/125	NaBz/125	NaBz/125
TEST 2. LAB.AIR									
Leach No.	10	11	12	13	14	15	16		
Leach cycle	15	14	17	14	14	25	14		
Funnel 1.									
L-ant/vol	NaBz/125	NaBz/125	NaBz/125	NaBz/125	NaBz/125	NaBz/125	NaBz/125		
Funnel 2.									
L-ant/vol	SR/125	SR/125	SR/125	SR/125	SR/125	SR/125	SR/125		
Funnel 3.									
L-ant/vol	SR/125	SR/125	SR/125	SR/125	SR/125	SR/125	SR/125		
Funnel 4.									
L-ant/vol	NaBz/125	NaBz/125	NaBz/125	NaBz/125	NaBz/125	NaBz/125	NaBz/125		
TEST 3.									
Leach No.	17	18	19	20	21	22			
Leach cycle	10	12	13	13	13	13			
Funnel 1.									
Atmosphere	Nitrogen	Nitrogen	Nitrogen	Nitrogen	Nitrogen	Nitrogen			
L-ant/vol	NaBz/125	NaBz/125	NaBz/125	NaBz/125	NaBz/125	NaBz/125			
Funnel 2.									
Atmosphere	Nitrogen	Nitrogen	Nitrogen	Nitrogen	Nitrogen	Nitrogen			
L-ant/vol	SR/125	SR/125	SR/125	SR/125	SR/125	SR/125			
Funnel 3.									
Atmosphere	Lab.air	Lab.air	Lab.air	Lab.air	Lab.air	Lab.air			
L-ant/vol	SR/125	SR/125	SR/125	SR/125	SR/125	SR/125			
Funnel 4.									
Atmosphere	Lab.air	Lab.air	Lab.air	Lab.air	Lab.air	Lab.air			
L-ant/vol	NaBz/125	NaBz/125	NaBz/125	NaBz/125	NaBz/125	NaBz/125			

a. Days between leachings. b. Leachant used and volume (cm³).
 c. Sodium benzoate. d. Synthetic rain

Series I

The five baskets in Series I, test 1, were leached identically with SR. Figure 1 shows characteristic curves for Cr, Mn, and Zn as a function of leachant volume. Because the size of the rock and/or the weight of the sample differed in these baskets, these graphs can be used as an indicator of the influence of rock size on Cr, Mn, and Zn dissolution. In general, more metal dissolution occurred when the finer material was present, while sample amount was far

less important (note that the results from baskets 1 through 3 were obtained from 3-kg waste rock samples while those from baskets 4 and 5 were obtained from a 4-kg waste rock sample). Other species, such as As, Cu, and S, show similar curves (figure 2) for test 1 where SR leachant was used throughout. Considering the exaggerated size segregation followed in this test, it might be assumed that normal experimental handling procedures could lead to experimental precision well below the factor of two observed here. The order of baskets 1, 5, 4, 3,

Table 5. Maximum leach-ability assay for Nevada mine waste rock.

Element	Mg/kg
Ag	0
Al	578
As	800
Ba	65
B	181
Ca	2,180
Cd	26
Co	12
Cr	105
Cu	105
Fe	72,100
K	500
Mg	102
Mn	7
Na	68
Ni	21
Pb	19
P	30
Si	273
S	70,300
Zn	19

and 2 correspond to leachate concentrations from the highest to the lowest and is the inverse of leachate pH's of 1.54, 1.57, 1.63, 1.65, and 1.68, respectively.

Baskets 1, 2, and 5 were leached with SLS while baskets 3 and 4 were leached with SR in test 2. Figure 2 shows that the dissolution of As, Cu, and S was reduced through the addition of SLS when compared with the untreated sample. This suggests that biological activity may account for a portion of the dissolution. On the other hand, the dissolution of these species does not cease completely in the presence of SLS, indicating that a second mechanism is responsible for metal dissolution and SO₄ production. Previous results (Doepker and O'Connor, 1991a, b) suggested that biological pathways leading to metal release were negligible for columns of tailings.

In test 3, when the untreated samples (those leached with SR only) were treated with NaBz, dissolution decreased within a few leachings, while the SLS-treated samples secondarily

leached with synthetic rain (also test 3), exhibited a longer delay period before dissolution increased. This situation is consistent with a dissolution rate that depends somewhat on bacteria population density.

The leachate pH across the test 2 sequence was nearly constant at 1.72, 2.09, 1.87, 1.76, and 1.69 for baskets 1 through 5, respectively. In test 3, leachate pH's were 1.62, 1.98, 2.10, 1.97, and 1.63 for baskets 1 through 5, respectively. Baskets 1 and 5 (containing the bulk sample) produced the lowest average pH leachates. The leachate pH of biocide-treated baskets averaged only about 0.2 pH unit higher than the baskets leached with SR.

Figure 3 shows the effect of biocides on the dissolution of species from columns of waste rock containing rock sizes < 1 cm. If the leaching cycle can be assumed to be proportional to reaction time, then the slope of the lines in test 2 will be proportional to the rate of dissolution. The rate of dissolution of As, Cu, and S (SO₄) was reduced by the presence of SLS by a factor of 3.6, 2.5, and 2.2, respectively. Test 3 of this series again shows decreased dissolution rates for As, Cu, and S when NaBz was used, but, because of the apparent induction periods, a quantitative estimate of the effect is speculative. The near-zero slope associated with As and Cu dissolution at least suggests that NaBz may be more effective than SLS. The influence of leachate pH appears to be small. As in the leaching of tailings, the leachate pH is generally governed by the mineral phases being leached and is nearly independent of the pH of the leachant.

The average leachate pH across the three test sequences for column 1 were 1.56, 1.41, and 1.71, while for column 2, the leachate pH's relative to test 1 through 3 were 1.55, 1.62, and 1.59, respectively. The pH differential between SR-leached and SLS-leached columns (test 2) was about 0.2.

Figures 1 through 3 also show that the first six to eight leachings produced nearly one-half the total material leached. Similar results have

been reported in the column leaching of tailings (Doepker, 1991; Doepker and O'Connor, 1991a, b) with the exception that the apparent storage of mobile metal is often reduced in tailings. This

would suggest either a relatively large mobile metal storage capacity or an oxidation rate greater than might be expected on the basis of surface area available.

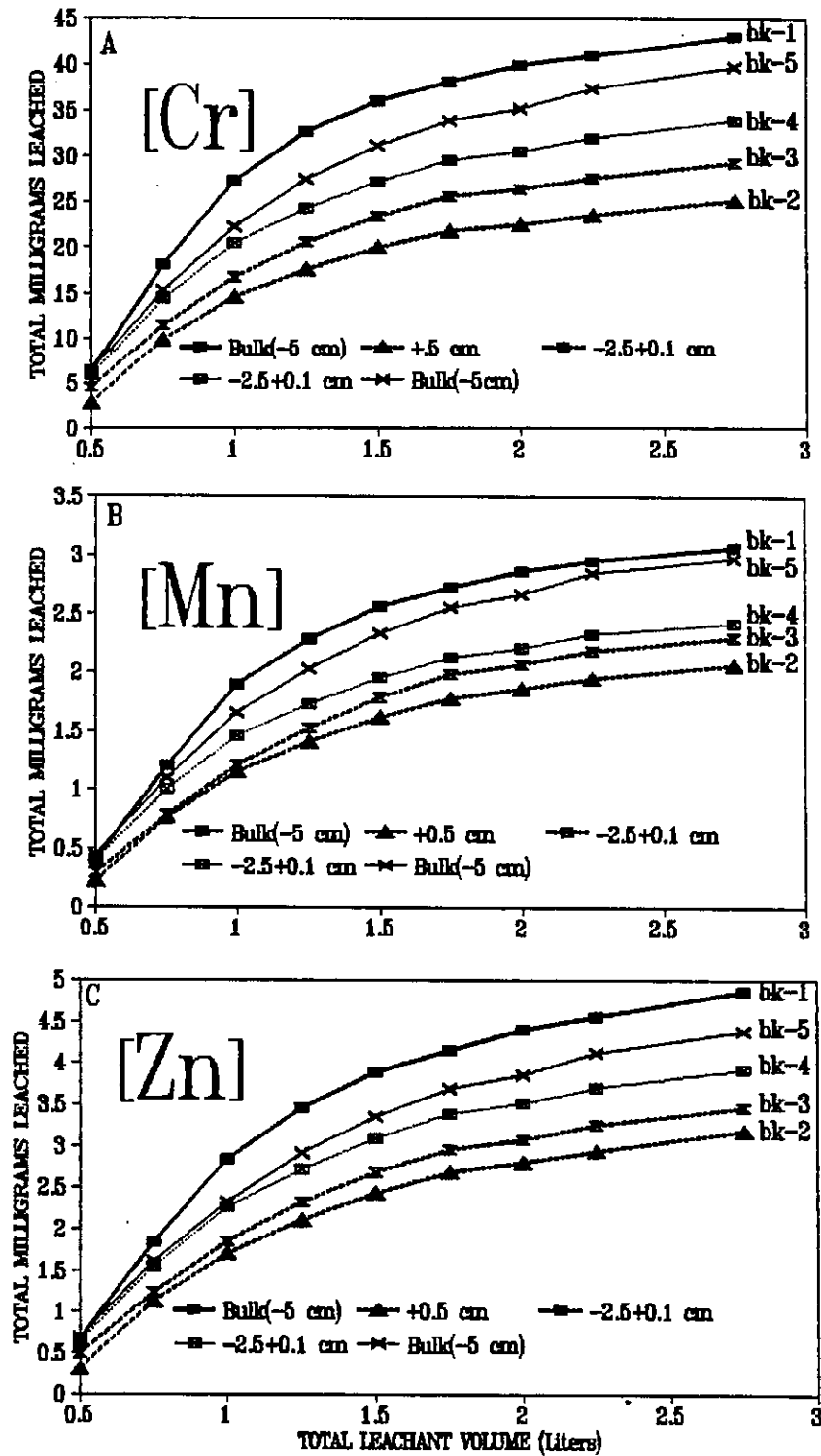


Figure 1. Series I, test 1: Influence of rock size and sample weight on the dissolution of A, Cr; B, Mn; and C, Zn.

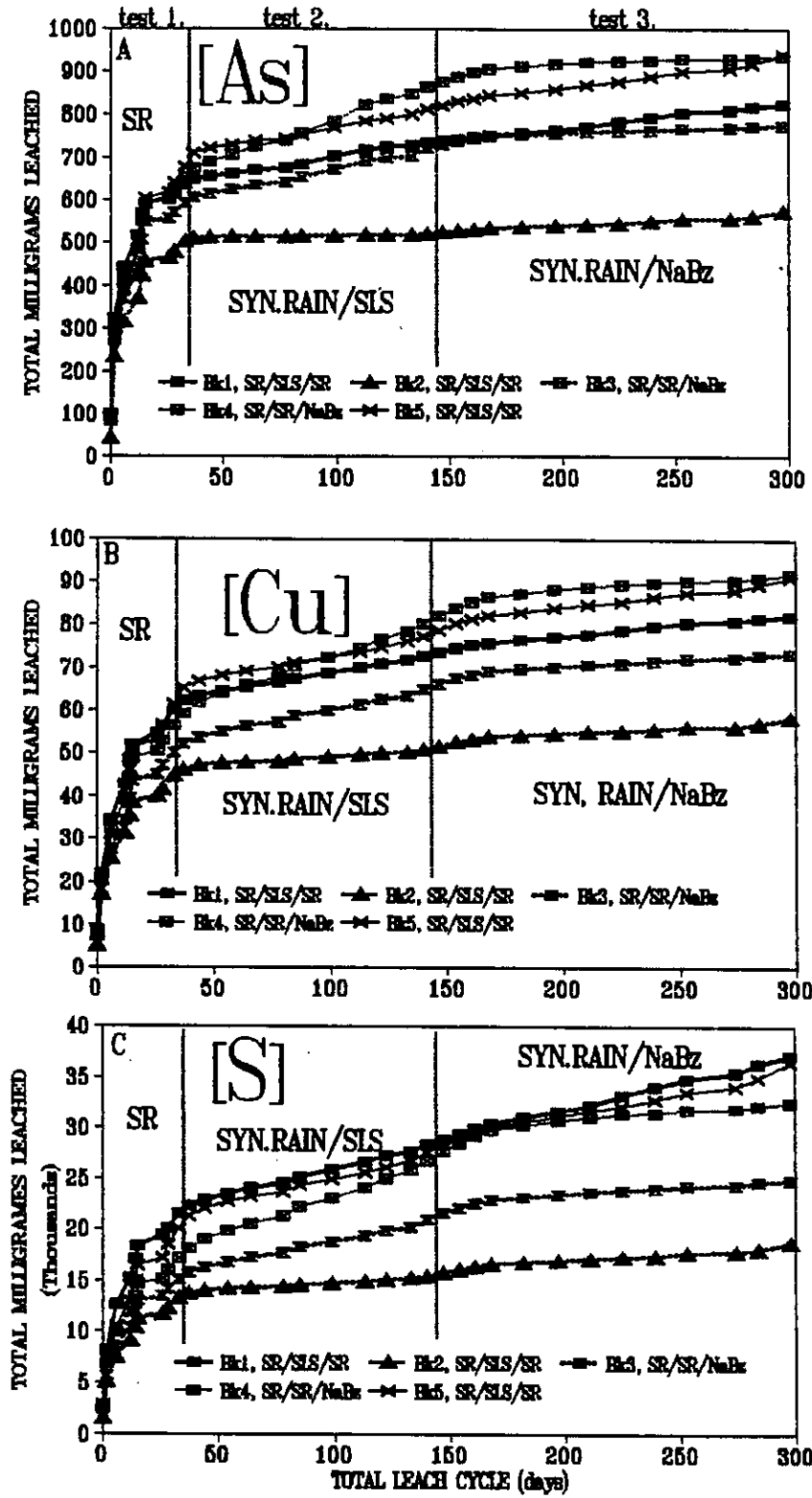


Figure 2. Series I: Milligrams leached from biocide-treated and untreated waste rock. A, As, B, Cu, and C, S.

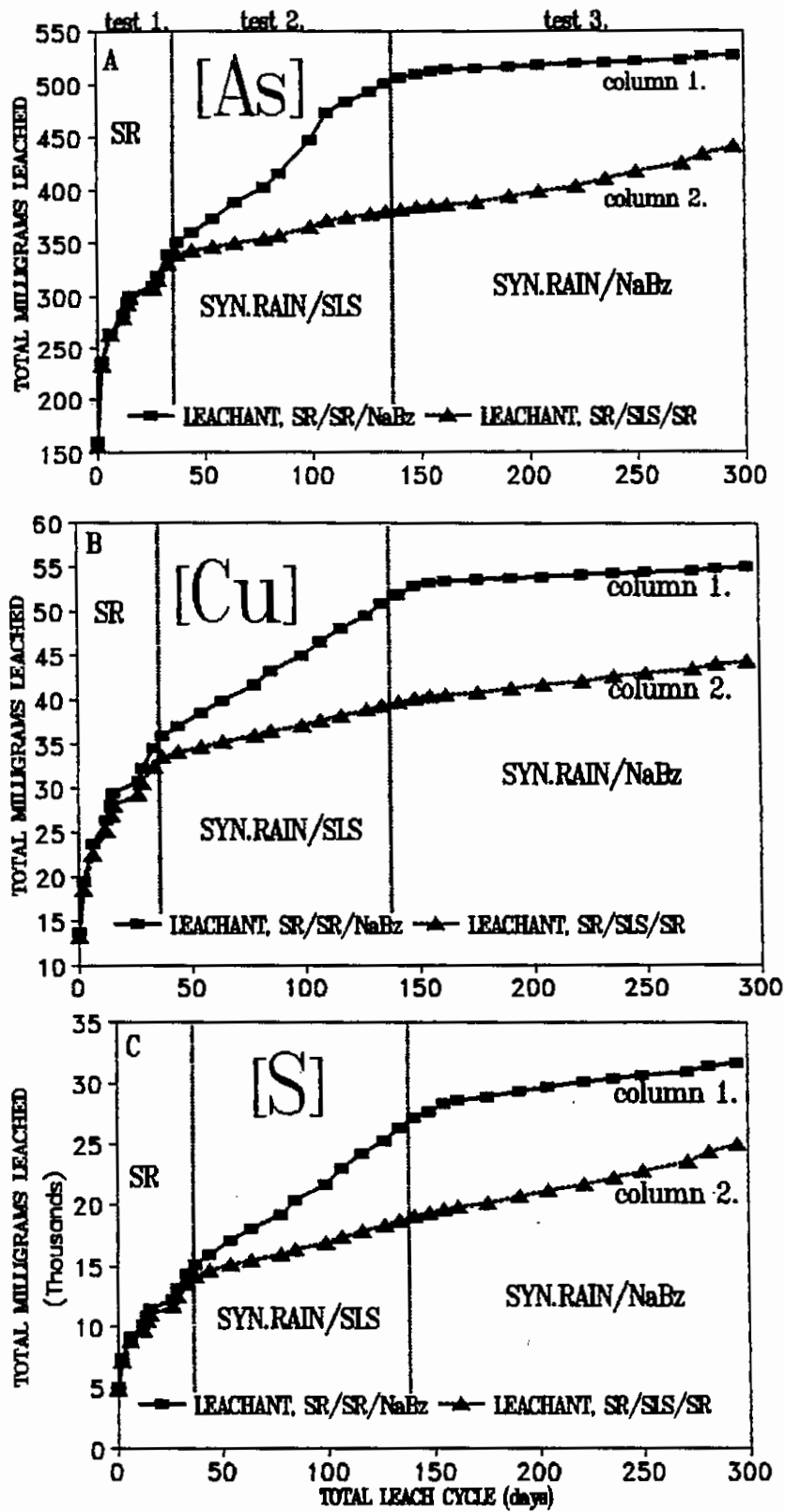


Figure 3. Series I: The effect of biocide treatment on the dissolution from columns of waste rock. A, As, B, Cu, and C, S.

Series II

In series II, atmospheric oxygen was excluded from the initial leachings. Figure 4 is a comparison of the results for Cd, Fe, and Mn under a nitrogen atmosphere and under laboratory air. Two observations are that

1. The average Cd, Fe, and Mn leachate concentrations of the two samples leached under a nitrogen atmosphere were nearly identical to those of the sample leached in air. This again suggested that the high concentrations observed during the first few leachings were primarily caused by storage of soluble secondary minerals (Kwong and Ferguson, 1990; Kwong, 1991).

2. SLS inhibited the initial dissolution process; that is, it delayed the dissolution of the stored secondary minerals. The average pH of the leachates in test 1 were 1.47, 1.42, 1.60, and 1.43 for baskets 1 through 4, respectively, and in test 2 were 1.74, 1.67, 1.86, and 1.69 for baskets 1 through 4. (Baskets 1 and 2 were averaged in figure 4.)

Since SLS is a strong surfactant in addition to being a biocide, a surface effect may be delaying the dissolution pathway. On the other hand, the antibacterial nature of SLS does appear to account for reduced metal dissolution under normal laboratory air (test 2).

Figure 5 demonstrates results for As, Cu, and S. Again, if it is assumed that the leaching cycle is proportional to reaction time, then relative rates may be estimated for the effects of SLS and NaBz. The ratios of rates for SR to SLS (test 2) are approximately 1.7:1 for As, 1.4:1 for Cu, and 1.8:1 for S. A similar evaluation of the effect of SLS and/or NaBz on the metal concentrations in leachates from tailings would suggest a much smaller contribution resulting from biological activity than is present in the tailings. Similar treatment of the data from test 3 reveals that the relative rates of SR to NaBz (basket 3 versus basket 2) are 2:1 for As, 1.8:1 for Cu, and 1.3:1 for S.

However, concentrations from the open baskets leached with SR were a factor of 2 less than concentrations from baskets leached with NaBz. Also, the average pH for the two open baskets was 0.25 pH units higher than the pH for the basket treated with NaBz (basket 2) and 0.35 higher than for the closed basket (3) leached with SR. At present, there is no plausible explanation for the higher pH observed in the open baskets.

It became apparent during this study that in order to quantify the effect of specific environments, the whole of the sample must be subjected to that specific environment. This, of course, may not be the case in relatively small columns or baskets that contain large amounts of a sample or are deeper than a few centimeters. The environment at the surface of such a sample may well be different from the environment of the interior of the sample.

Series III

To reduce the effects of environmental heterogeneity throughout the sample, small samples (250 g) were placed into 11- and 12.6-cm suction filters and leached under freely dripping conditions as described earlier.

Figure 6 compares the leachate concentrations of As, Cu, and S from filters leached in a nitrogen atmosphere to filters leached in air and to samples leached with SR or NaBz. The dissolution of stored As, Cu, and S was nearly complete after three or four leachings. The initial leachate concentrations for As ranged from 335 to 427 mg/L, for Cu from 51 to 38 mg/L, and for S from 17,500 to 21,500 mg/L. After nine leachings, these values were reduced to a level that depended on the composition of the atmosphere (whether nitrogen or air) and on the presence of NaBz. Under nitrogen, As concentrations with and without a biocide were 0.5 and 2.9 mg/L, respectively. In air, As concentrations were 17.6 mg/L with SR and 1.4 mg/L with NaBz. Similar effects were observed for the heavy metals Al, Cd, Co, Cr, Cu, Fe, Mn,

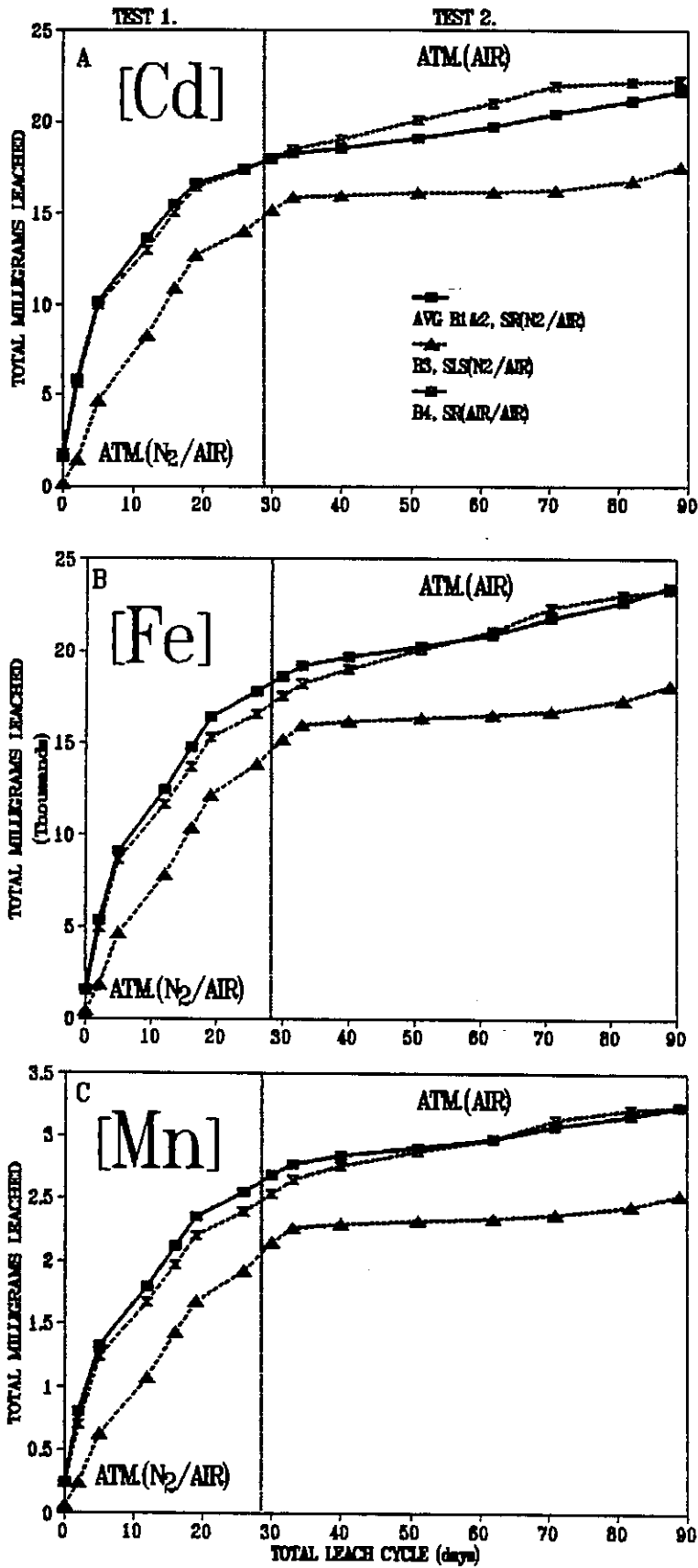


Figure 4. Series II, tests 1 and 2: Milligrams leached as influenced by atmosphere and biocide application. A, Cd, B, Fe, and C, Mn.

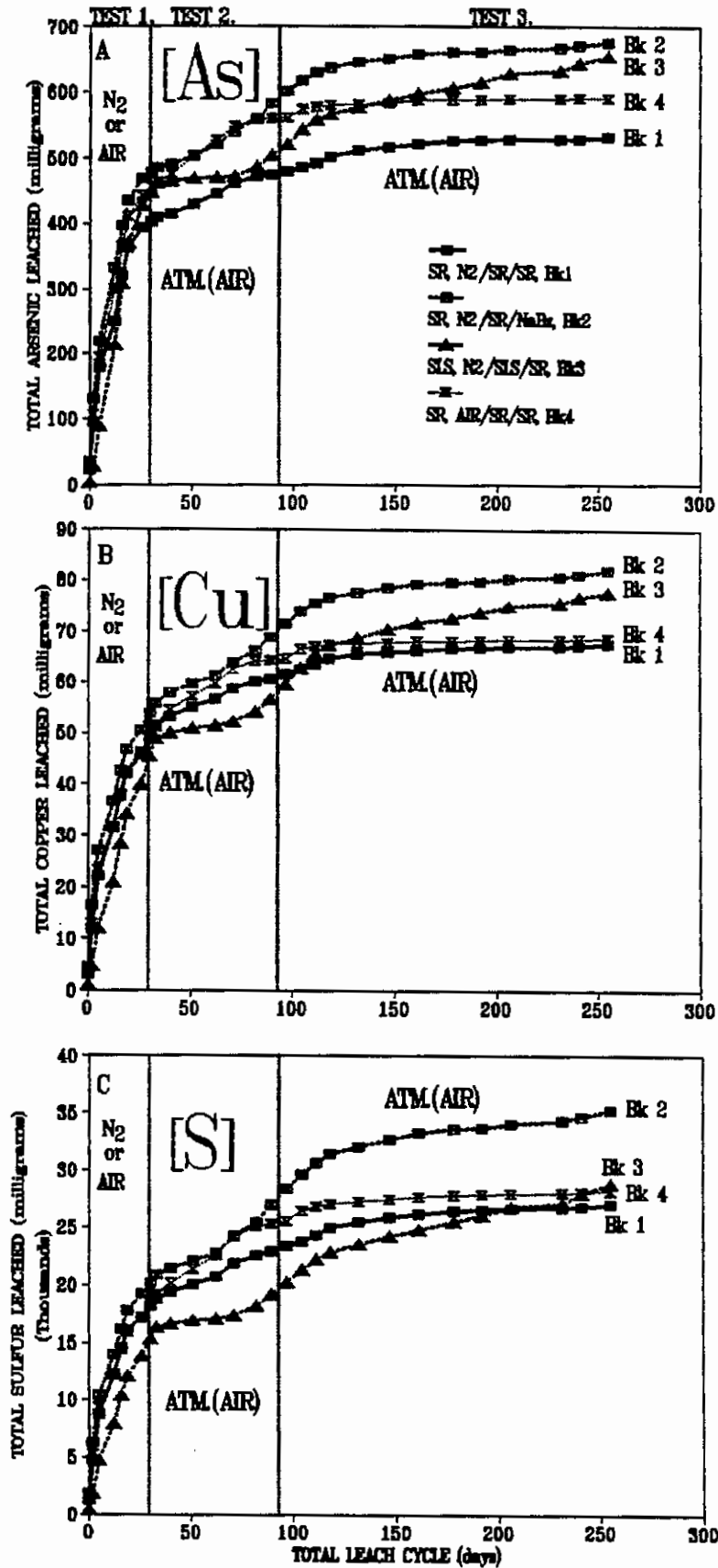


Figure 5. Series II: Milligrams leached as influenced by atmosphere and biocide application. A, As, B, Cu, and C, S.

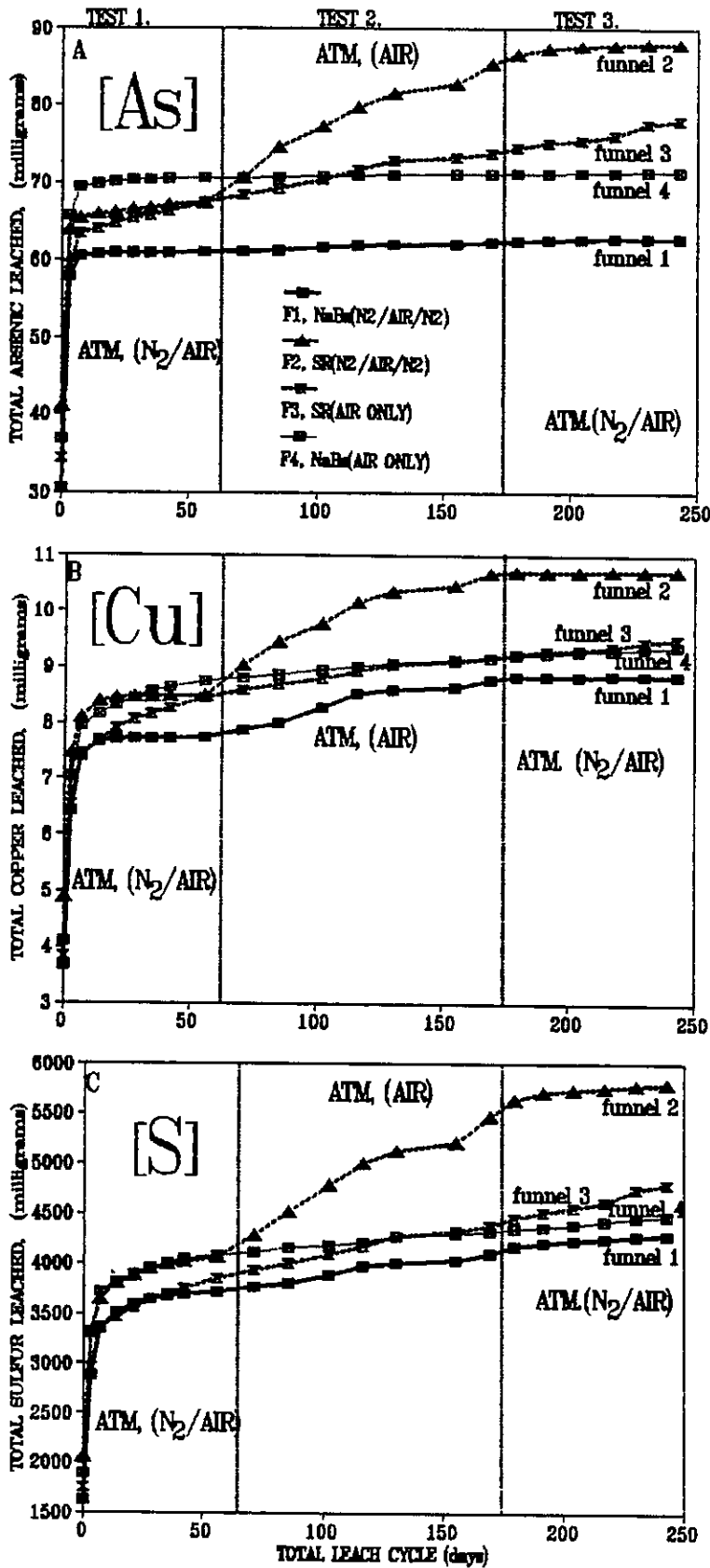


Figure 6. Series III: The effect of atmosphere and biocide treatment on leachate concentrations from waste rock contained in filter funnels. A, As, B, Cu, and C, S.

Ni, Pb, and Zn. Considering the slopes of the curves in figure 6, it appears that most of the As mobility may have been generated by a biological pathway, while Cu and S release may be attributed to both a biological and a chemical pathway, possibly air oxidation.

The role of water and water vapor in biological and air oxidation processes was examined in part through the use of five filters. Unfortunately, there was no clear-cut relationship between relative humidity and species mobility, as seen in figure 7. The rates of dissolution may be inferred through the slopes of the curves presented for As, Cu, and S. Although the total amount of a released element differs, the parallel nature of the curves would indicate that the rates of release were similar. The failure of this test may be totally the result of the experimental conditions because it was not possible to control the humidity during leaching. There was also a time lag of 2 to 4 days before the samples could be maintained at constant humidities. The maximum rate of biological oxidation and air oxidation as they relate to water content may be different, with air oxidation rates highest at the lower end of the humidity range (low pore water, high pore oxygen) and bio-oxidation rates highest at the upper end of the humidity range (high pore water, high dissolved oxygen). Attempts to resolve this dilemma are underway.

The three columns leached with SR (pH = 5.2), 1 g/L disodium phosphate (pH = 8.8), or sodium hydrogen carbonate (pH = 8.1) gave initial leachate pH's that ranged in value from 1.6 to 1.8 pH units. After 20 leachings with 250 cm³ of leachant each, the leachate pH was unaffected; that is, it ranged from 1.5 to 1.7. The concentrations illustrated in figure 8 showed little differentiation and almost identical slopes for the two base-leached columns and the column leached with SR. The oxidation by air of sulfide minerals in tailings requires the evaporation of at least a fraction of the pore water in order to obtain reasonable gas-solid interactions and oxidative reaction rates. Saturation of tailings reduces oxygen availability and oxidation

reaction rates. The large (unsaturated) voids in waste rock may negate this requirement and thereby lead to apparent increased oxidation reaction rates. This would indicate that differences in leachant pH of one or two pH units will have little or no effect on the total dissolution process.

Summary and Conclusion

In general, the laboratory leaching characteristics of the waste rock samples as reported in series I suggested (1) considerable mobile contaminants were stored within the waste rock sample, (2) leachate constituent concentrations depend on sample size to a minor degree, and (3) mineral segregation by particle size may produce leachate concentrations that depend on sample particle size. It was further noted that biocide treatment with SLS and/or NaBz reduced dissolution, but the results suggested a second oxidative pathway parallel to the biological reaction channel.

Series II eliminated the biological and/or air oxidative role in the initial contaminant release from the waste rock, demonstrating the storage capacity of the waste rock. Results of this series also suggested that at least one-half of the mobile contaminants originating from well-flushed waste rock are a result of biological activity. Although SLS delayed initial contaminant release, this effect appeared to be related to its surfactant property and not to decreased biological activity.

The release of stored mobile constituents was completed within three leachings from shallow filter flasks (series III). Subsequent leachings with NaBz revealed that As release was nearly eliminated while other metals again showed leaching characteristics of two or more reaction channels. Columns of waste rock leached with pH 8.8 disodium hydrogen phosphate or pH 8.1 sodium hydrogen carbonate failed to produce reduced leachate concentrations to a significant extent.

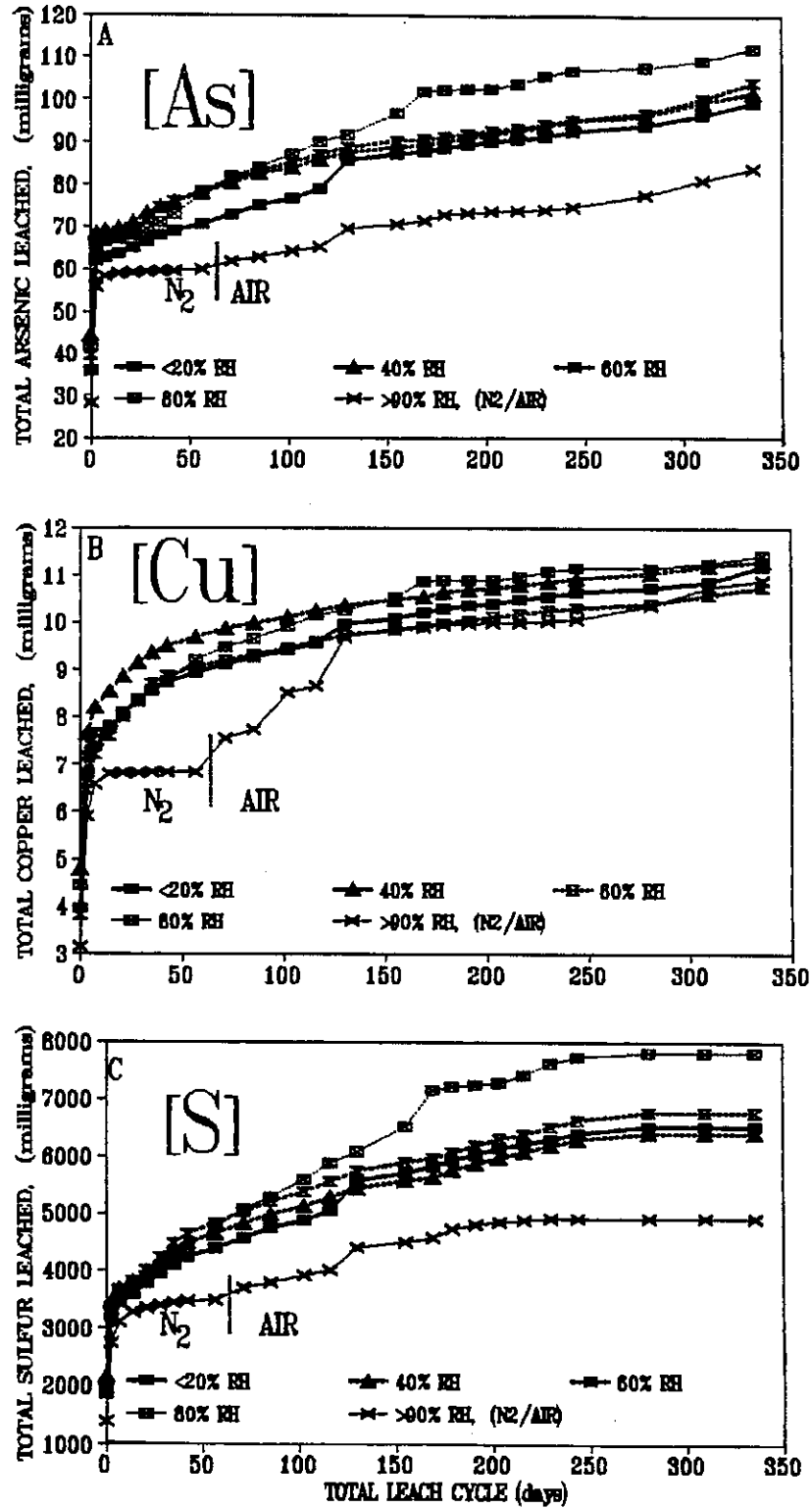


Figure 7. Series III: The influence of relative humidity on the dissolution from waste rock stored in filter funnels.
A, As, B, Cu, and C, S.

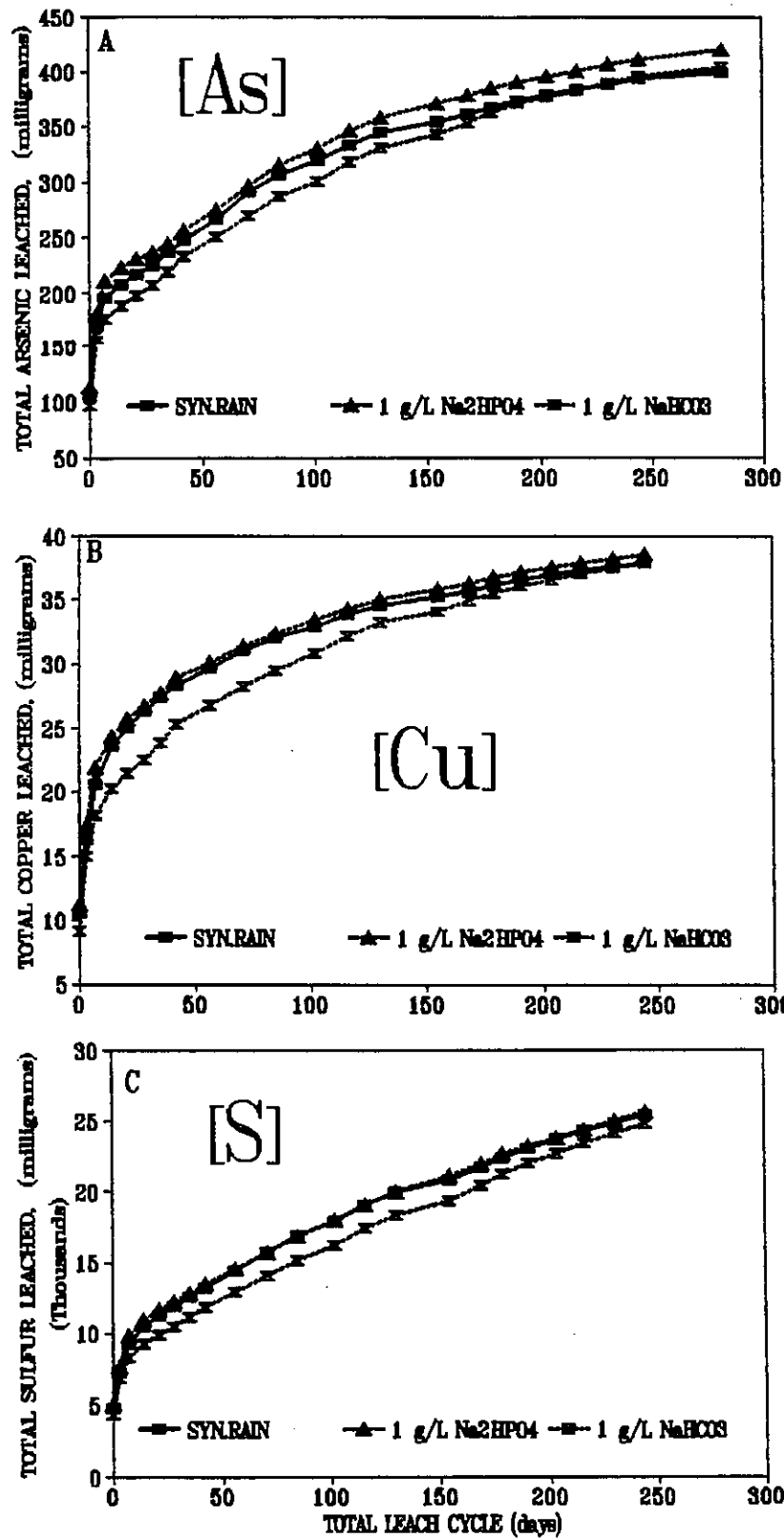


Figure 8. Series III: Comparisons of concentrations from columns of waste rock leached with SR, Na₂HPO₄, and Na₂HCO₃.
A, As, B, Cu, and C, S.

From this preliminary study, it became apparent that the dissolution characteristics of waste rock differ from those of mill tailings. The kinetic rate law for oxidation of waste rock and of tailings should be the same heterogeneous surface reaction, depending on reactive surface area and on oxygen partial pressure. The limiting reagent of the apparent reaction rate of oxidation in tailings may be the availability of oxygen. In waste rock, convection currents, the presence of large voids, and the ease of thermal pumping all tend to keep available oxygen above demand. The reduced reactive surface area of waste rock, as opposed to that of tailings, along with product build-up in zones that remain unflushed for considerable lengths of time, tends to limit the apparent oxidation rate.

It is also reasonable to suppose that biological pathways that increase overall reaction rates manyfold will be more important in waste rock because of the increased availability of oxygen. Thus, the loss of pore water, a critical condition in the oxidation of tailings, appears to be of little importance to the oxidation of waste rock because there are large voids that are not completely filled with pore water.

There is evidence that the effectiveness of biocides wanes after a period of time (see figure 5). This may not be caused by an increase in bioactivity but by the increased availability of reactive sites for air oxidation created through repeated flushings. Bio-oxidation must inhibit air oxidation since both reaction channels depend on a common reagent, i.e., oxygen.

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