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## **Role of Oxygen Transfer in Acid Mine Drainage Treatment**

By C. C. Hustwit, T. E. Ackman, and P. M. Erickson

UNITED STATES DEPARTMENT OF THE INTERIOR



BUREAU OF MINES

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**UNITED STATES DEPARTMENT OF THE INTERIOR  
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### UNIT OF MEASURE ABBREVIATIONS USED IN THIS REPORT

°C	degree Celsius	min <sup>-1</sup>	per minute
g	gram	mL	milliliter
gal	gallon	mol/L	mole per liter
gal/min	gallon per minute	(mol/L)/min	mole per liter per minute
h	hour		
lbf/in <sup>2</sup> (ga)	pound (force) per square inch, gauge	mol <sup>2</sup> /L <sup>2</sup>	square mole per square liter
mg/L	milligram per liter	mV	millivolt
(mg/L)/min	milligram per liter per minute	pct	percent
min	minute	s	second

# ROLE OF OXYGEN TRANSFER IN ACID MINE DRAINAGE TREATMENT

By C. C. Hustwit,<sup>1</sup> T. E. Ackman,<sup>2</sup> and P. M. Erickson<sup>3</sup>

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## ABSTRACT

The U.S. Bureau of Mines formulated a new mathematical model to characterize iron oxidation. The new model is intended to replace the currently used model, recommended by the Environmental Protection Agency (EPA), for most acid mine drainage (AMD) treatment applications. The new model was evaluated in a series of five synthetic AMD treatment tests. The initial ferrous iron concentrations ranged from 800 to 2,400 mg/L. In these tests, the Bureau model underpredicted the measured ferrous iron oxidation rates by a range of 3.24 to 8.03 pct. This was considered to be in close agreement after consideration of experimental error. The model proposed by the EPA was also evaluated using the same test data. The EPA model underpredicted the oxidation rates by a range of 77 to 100 pct in four tests and overpredicted by 19 pct in one test. The model formulated by the Bureau expresses that the rate of iron oxidation is a function of a treatment system's oxygen transfer efficiency and is independent of ferrous iron concentration when treated to near-neutral pH's. A new test method for evaluating oxygen transfer in flow-through reactors is also described.

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## INTRODUCTION

Acid mine drainage (AMD) is a common problem in the eastern coalfields of the United States. These drainages typically have high acidities and iron concentrations. The iron may be in the reduced, ferrous ( $\text{Fe}^{2+}$ ) form or in the oxidized, ferric ( $\text{Fe}^{3+}$ ) form.

Chemical treatment of AMD consists of three physico-chemical unit operations: neutralization, oxidation, and sludge separation. Addition of alkaline chemicals [e.g., sodium hydroxide ( $\text{NaOH}$ ), calcium oxide ( $\text{CaO}$ ), and calcium hydroxide ( $\text{Ca}(\text{OH})_2$ )] neutralizes acidity and/or precipitates some of the metals as hydroxides. Because  $\text{Fe}^{2+}$  oxidation proceeds more rapidly above pH  $\sim 3.5$ , neutralization is usually performed before or during the oxidation operation. Oxidation converts dissolved  $\text{Fe}^{2+}$  to  $\text{Fe}^{3+}$ , which hydrolyzes and forms the orange precipitate ferric hydroxide [ $\text{Fe}(\text{OH})_3$ ]. The final operation is liquid-sludge separation prior to discharge of the treated water to the receiving stream.

Equipment size and land needs for treatment plants are based on the calculated time requirements for the unit operations. These time requirements are dependent on water quality and the rates at which the chemical and physical processes are predicted to occur.

The chemical model currently used to predict the rate of  $\text{Fe}^{2+}$  oxidation expresses the rate as a function of  $\text{Fe}^{2+}$  and dissolved oxygen (DO) concentrations and pH (1-3).<sup>4</sup> Hereafter this model will be referred to as the "iron-dependent model." The kinetics of  $\text{Fe}^{2+}$  oxidation were determined through bench-scale studies using low  $\text{Fe}^{2+}$  concentrations ( $< 7$  mg/L) (2). In contrast, AMD can contain high concentrations of  $\text{Fe}^{2+}$ , often in excess of 100

to 1,000 mg/L. Typically, AMD treatment results in the depletion of DO in the water.

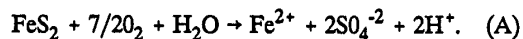
The depletion of DO can be crucial to the rate of  $\text{Fe}^{2+}$  oxidation and AMD treatment plant design. If the water contains, e.g., 63 mg/L of  $\text{Fe}^{2+}$ , complete oxidation demands about 9 mg/L of DO. Higher  $\text{Fe}^{2+}$  concentrations require that DO be replenished, typically by mechanical means, for oxidation to continue. Oxygen ( $\text{O}_2$ ) transfer, i.e., replenishment, is normally a slow process. Oxygen transfer can, therefore, become the rate-limiting step in AMD treatment when the rate of  $\text{O}_2$  replenishment cannot satisfy the  $\text{O}_2$  demand of  $\text{Fe}^{2+}$  for oxidation.

The issue of  $\text{O}_2$  replenishment became critical in the evaluation of the U.S. Bureau of Mines In-Line Aeration and Neutralization System (ILS, U.S. Patent 4,695,378). The ILS, which can be built in numerous design variations, simultaneously neutralizes and aerates AMD to replenish DO by venturi action in a flow-through reactor. In this report,  $\text{Fe}^{2+}$  oxidation rates measured in the ILS are described, and those rates are compared with rates estimated by both the iron-dependent model and a proposed alternative model that appears to predict oxidation rates more accurately under conditions of AMD treatment. The alternative model will be referred to as the "oxygen-dependent model" in this report. Development of the oxygen-dependent model required a new approach in determining  $\text{O}_2$  transfer efficiency applicable to flow-through reactors.

This work was done as part of the Bureau's program to reduce pollution from mining and clean up the Nation's contaminated waters and lands.

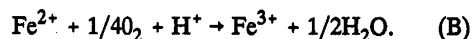
## BACKGROUND

When iron occurs in AMD, it is primarily due to the occurrence of pyrite ( $\text{FeS}_2$ ) in the coal seam and associated strata. The excavation of materials during the mining process results in the exposure of  $\text{FeS}_2$  to water and air. The overall reaction in which water and  $\text{O}_2$  oxidize  $\text{FeS}_2$  is



Initially, iron is in the reduced,  $\text{Fe}^{2+}$  form. As the water is exposed to  $\text{O}_2$ , however, a fraction of the iron will be oxidized to  $\text{Fe}^{3+}$  by chemical and/or biological means. The abiotic mechanism is dominant at near-neutral conditions. At low pH, acidophilic bacteria mediate the oxidation.

At most sites with AMD, a significant fraction of the iron remains in the  $\text{Fe}^{2+}$  form. Thus, the AMD treatment process typically consists of two chemical reactions. The first is an oxidation reaction in which  $\text{Fe}^{2+}$  is converted to  $\text{Fe}^{3+}$ :



This conversion is followed by a hydrolysis reaction that results in the precipitation of  $\text{Fe}^{3+}$ , principally as amorphous  $\text{Fe}(\text{OH})_3$ . This occurs according to



It is possible to remove iron as ferrous hydroxide [ $\text{Fe}(\text{OH})_2$ ] without oxidation, but this requires a very high pH. The minimum solubility of  $\text{Fe}^{2+}$  occurs at a pH of

<sup>4</sup>Italic numbers in parentheses refer to items in the list of references preceding the appendixes at the end of this report.

approximately 12.0 as shown in figure 1. Ferric iron reaches its minimum solubility at a pH of 8.0 (1). Therefore, a substantial chemical cost savings is possible if  $\text{Fe}^{2+}$  is oxidized during neutralization.  $\text{Fe}(\text{OH})_3$  is also preferred based on settling time, final sludge volume, and sludge stability (4).

The design of AMD treatment plants involves the sizing of flow equipment and basins or vessels. To perform such sizing, a chemical model (i.e., the iron-dependent model) is employed; the model uses flow rates, initial  $\text{Fe}^{2+}$  concentration, initial pH, and initial DO to predict reaction rates and consequently the required aeration times to achieve iron removal by precipitation. Concern that use of fixed values of initial  $\text{Fe}^{2+}$ , pH, and DO may not be an adequate and accurate basis for a model prompted this study. An alternative model was developed, which recognizes that  $\text{Fe}^{2+}$  concentration, pH, and especially DO can be time-dependent variables as opposed to fixed initial values.

The iron-dependent model indicates that for mine water above pH 3.5, the oxidation rate has a first-order dependency on  $[\text{Fe}^{2+}]$  and  $[\text{O}_2]$  and a second-order dependency on  $[\text{H}^+]$  (1-3, 5). This is indicated by the rate equation

$$\frac{-d[\text{Fe}^{2+}]}{dt} = \frac{k_{\text{Fe}} [\text{Fe}^{2+}] [\text{O}_2(\text{aq})]}{[\text{H}^+]^2}, \quad (1)$$

where  $k_{\text{Fe}} = 3 \times 10^{-12}$  (mol/L)/min, at 20° C,

$[\text{Fe}^{2+}] = \text{Fe}^{2+}$ , mol/L,

$[\text{O}_2(\text{aq})] = \text{O}_2$  aqueous phase, mol/L,

and  $[\text{H}^+] = \text{H}^+$ , mol/L.

Dilute  $\text{Fe}^{2+}$  solutions were used in developing this iron-dependent model (2-3, 5). At low concentrations, the activity of  $\text{Fe}^{2+}$  is approximately equal to its analytical concentration. Oxygen depletion does not normally occur in dilute  $\text{Fe}^{2+}$  solutions. For example, if the concentration of  $\text{Fe}^{2+}$  was 1 mg/L, only 0.14 mg/L of  $\text{O}_2$  would be consumed during oxidation. This amount is negligible in typical  $\text{O}_2$ -saturated solutions, which contain approximately 9 mg/L DO. In these studies the solution pH's were buffered.

A U.S. Environmental Protection Agency (EPA) design manual uses the iron-dependent rate equation to illustrate oxygenation and neutralization requirements for AMD treatment plants (1). Designs based on this equation should be effective for treating mildly contaminated mine drainage. However, the AMD treatment setting can be very different from the laboratory conditions used to

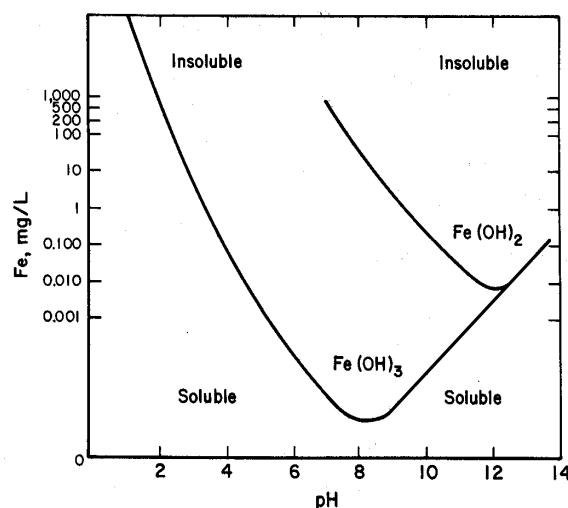


Figure 1.—Solubility curves for ferrous and ferric iron. [Source: U.S. Environmental Protection Agency (1)]

develop the iron-dependent model. Ferrous iron concentrations can range up to 1,000 mg/L or more in some cases. Any  $\text{Fe}^{2+}$  concentration above approximately 63 mg/L depletes  $\text{O}_2$  during oxidation without special design considerations. If plant designers fail to recognize that  $[\text{Fe}^{2+}]$ ,  $[\text{O}_2]$ , and  $[\text{H}^+]$  are time-dependent variables, then they may substitute saturation DO and the target effluent pH values into the iron-dependent model to solve for oxidation residence time. Later in this report the effects of these erroneous assumptions on design calculations are illustrated.

For  $\text{Fe}^{2+}$  oxidation to continue after  $\text{O}_2$  depletion, an additional physical reaction becomes part of the  $\text{Fe}^{2+}$  oxidation mechanism. That reaction is the mass transfer of  $\text{O}_2$  from the gas into the aqueous phase. This is expressed as



where  $\text{O}_{2(\text{g})} = \text{O}_2$  gas phase, mg/L,

and  $\text{O}_{2(\text{aq})} = \text{O}_2$  aqueous phase, mg/L.

Of the two reactions in the oxidation process, reactions B and D, it is generally believed that the  $\text{O}_2$  transfer reaction is slower (1, 4). This is due to  $\text{O}_2$ 's relative insolubility in water at ambient temperatures and pressures. The iron-dependent model adequately expresses the role of  $\text{O}_2$  in  $\text{Fe}^{2+}$  oxidation provided an ample amount of  $\text{O}_2$  is present. However, it does not model the proposed rate-limiting reaction in high- $\text{Fe}^{2+}$ -concentration AMD at near-neutral pH conditions, namely,  $\text{O}_2$  transfer.



An Fe<sup>2+</sup> oxidation model was developed based on the hypothesis that O<sub>2</sub> transfer is the rate-limiting step in Fe<sup>2+</sup> oxidation. It models the stoichiometrically predicted reactions involved in the treatment of high-Fe<sup>2+</sup>-concentration AMD: O<sub>2</sub> transfer and Fe<sup>2+</sup> oxidation, reactions D and B, respectively. The oxygen-dependent model contains two parts: (1) the O<sub>2</sub> transfer rate and (2) a stoichiometric constant relating Fe<sup>2+</sup> and O<sub>2</sub> in the oxidation reaction. The O<sub>2</sub> transfer rate from the literature (6) is

$$\frac{d[O_2]}{dt} = k_{O_2} ([O_2]_{sat} - [O_2]_t), \quad (2)$$

where  $k_{O_2}$  = O<sub>2</sub> transfer rate coefficient, min<sup>-1</sup>,

$[O_2]_{sat}$  = O<sub>2</sub> at saturation, mg/L,

and  $[O_2]_t$  = time-dependent concentration of O<sub>2</sub>, mg/L.

If O<sub>2</sub> transfer is much slower than Fe<sup>2+</sup> oxidation, then it becomes the rate-limiting step, and the rate of Fe<sup>2+</sup> oxidation can be expressed as

$$\frac{-d[Fe^{2+}]}{dt} = \frac{7 d[O_2]}{dt} = 7 k_{O_2} ([O_2]_{sat} - [O_2]_t), \quad (3)$$

where  $[Fe^{2+}]$  = Fe<sup>2+</sup> concentration, mg/L. The factor of 7 derives from the Fe<sup>2+</sup> oxidation stoichiometry, whereby 55.85 mg/L of Fe<sup>2+</sup> is oxidized by 8 mg/L O<sub>2</sub> (reaction B).

Since Fe<sup>2+</sup> rapidly consumes O<sub>2</sub> in circumneutral solutions and  $[O_2] \ll [O_2]_{sat}$ , equation 3 becomes

$$\frac{-d[Fe^{2+}]}{dt} = 7 k_{O_2} [O_2]_{sat}. \quad (4)$$

Integration of equation 4 at the boundary conditions yields

$$\frac{[Fe^{2+}]_t}{[Fe^{2+}]_0} = \exp\left(-\frac{7 k_{O_2} [O_2]_{sat} t}{[Fe^{2+}]_0}\right), \quad (5)$$

where  $[Fe^{2+}]_0$  = Fe<sup>2+</sup> at time = 0,

$[Fe^{2+}]_t$  = Fe<sup>2+</sup> at time = t,

and

$$[Fe^{2+}]_t = [Fe^{2+}]_0 - 7 k_{O_2} [O_2]_{sat} t. \quad (6)$$

If the hypothesis of O<sub>2</sub> transfer being the rate-limiting step in Fe<sup>2+</sup> oxidation is correct, then the measured O<sub>2</sub> transfer rate should predict the rate of Fe<sup>2+</sup> oxidation at circumneutral conditions.

## ACKNOWLEDGMENTS

The authors would like to acknowledge the contributions of Paul Yavorsky, physical scientist, and Sandra Borek, physical scientist, of the Bureau and Mark Wesolowski, chemist, of SSI Inc., Pittsburgh, PA. Mr. Yavorsky was responsible for the formulation of the proposed oxygen-dependent model based on O<sub>2</sub> transfer. Ms. Borek assisted in test preparations and water quality measurements. Mr. Wesolowski and his staff performed all analyses. In addition to monitoring water quality

analyses, he made significant recommendations regarding methods for the analysis of sulfite (SO<sub>3</sub><sup>2-</sup>) in the O<sub>2</sub> transfer test.

The authors would also like to thank Dave Hyman, Fred Sharp, John Kleinhenz, and John Odoski, of the Bureau, for their assistance in conducting the tests. Each provided valuable advice and were indispensable for their assistance during the tests.

## EXPERIMENTAL PLAN AND PROCEDURES

A study was conducted to evaluate the performance of the oxygen-dependent model in predicting Fe<sup>2+</sup> oxidation rates in a series of synthetic AMD tests. The iron-dependent model was also evaluated for its accuracy in predicting Fe<sup>2+</sup> oxidation rates for the same series of tests. The study consisted of three parts: (1) measurement of Fe<sup>2+</sup> oxidation rates in the ILS, (2) development of oxidation rate predictions using the oxygen-dependent model, and (3) development of oxidation rate predictions using

the current, iron-dependent model. An evaluation is presented of the accuracy of both models in predicting rates of Fe<sup>2+</sup> oxidation.

In the first part of the study, oxidation rates were measured in five treatments of synthetic AMD. These rates were subsequently used to measure the success of both the oxygen-dependent model and iron-dependent model in predicting Fe<sup>2+</sup> oxidation rates. The five nominal concentrations of Fe<sup>2+</sup> used, in milligrams per liter,

are as follows: 800 (in test ILS0800), 1,000 (in ILS1000), 1,200 (in ILS1200), 1,400 (in ILS1400), and 2,400 (in ILS2400). Figure 2 is a schematic of the ILS used in all tests. Ferrous iron concentrations were measured at the inlet and outlet of the ILS. The change in  $\text{Fe}^{2+}$  concentration across the system was then divided by the residence time within the ILS. The residence time was determined separately. Appendix A contains a detailed description of the test procedure.

The proposed oxygen-dependent model was used in the second part of the study to develop oxidation rate predictions for the five AMD tests. Use of the model required a measure of the ILS'  $\text{O}_2$  transfer capability (specifically, calculation of the  $\text{O}_2$  transfer rate coefficient). The  $\text{O}_2$  transfer rate coefficient ( $k_{\text{O}_2}$ ) is specific to a reactor and the ambient physical conditions of its use, including water temperature, pressure, and dissolved solids. An  $\text{O}_2$  transfer test was designed and conducted to determine  $k_{\text{O}_2}$  for the ILS under the same physical conditions used in the AMD tests. This test was patterned after the American Society of Civil Engineers' "A Standard for the Measurement of Oxygen Transfer in Clean Water" (6). The deoxygenating agent sodium sulfite ( $\text{Na}_2\text{SO}_3$ ) was dissolved in the water prior to the test. A sufficient quantity was used to remove all existing  $\text{O}_2$  from the water and any that would subsequently be introduced in the ILS. Decreases in  $\text{SO}_3^{2-}$  within the ILS could then be attributed to  $\text{O}_2$  introduced by the ILS. The water was treated in the ILS, and measurements were made to determine the initial and final concentrations of  $\text{SO}_3^{2-}$ . Oxygen transfer was calculated by converting the decrease in  $\text{SO}_3^{2-}$  to a stoichiometric equivalent amount of  $\text{O}_2$ . The rate was calculated by dividing this amount of  $\text{O}_2$  by the residence time. Finally, the rate constant was calculated by dividing the measured transfer rate by the  $\text{O}_2$  saturation

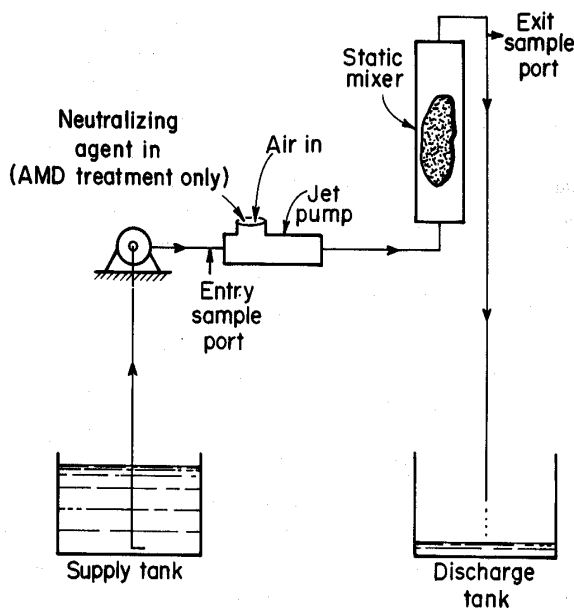


Figure 2.—Schematic of ILS.

concentration using equation 2 and solving for  $k_{\text{O}_2}$ . A detailed test procedure is contained in appendix B.

The third part of the experimental plan was to test the oxygen-dependent and iron-dependent models' ability to predict the oxidation rates observed in the synthetic AMD tests. This was strictly a mathematical operation since all necessary data had been developed in the preceding parts of the study. Initial  $\text{Fe}^{2+}$  concentrations, final pH, and  $\text{O}_2$  saturation concentrations were used in evaluating the models.

## PHASE 1 RESULTS: MEASURED IRON OXIDATION RATES

Synthetic AMD tests were conducted at nominal concentrations of 800 to 2,400 mg/L. In the  $\text{Fe}^{2+}$  oxidation tests, the ILS was operated at 50 lbf/in<sup>2</sup>(ga) with an AMD flow rate of 10 gal/min. Samples were drawn at the entry and discharge points and analyzed for pH, alkalinity, acidity,  $\text{Fe}^{2+}$ , Fe (total),  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Na}^+$ , and  $\text{SO}_4^{2-}$ . Dissolved  $\text{O}_2$  and temperature measurements were also made at both sampling locations. Water temperatures ranged from 25.4° to 30.4° C. Table 1 shows the chemical formulae used in the tests.

Table 1.—Formulary for synthetic AMD tests<sup>1</sup>

Test	$\text{Fe}_2\text{SO}_4$ , g	$\text{Na}_2\text{SO}_3$ , g
ILS0800 ..	7,516	134.3
ILS1000 ..	9,395	173.5
ILS1200 ..	11,274	127.8
ILS1400 ..	13,153	109.1
ILS2400 ..	24,427	104.5

<sup>1</sup>All tests were conducted using 500 gal of water and 0.95 g  $\text{CoCl}_2$ .

In a separate experiment, the residence time of water in the ILS was determined. Water was pumped through the ILS at the pressure and flow rates used in the  $\text{Fe}^{2+}$  oxidation tests. Contact time in the jet pump was believed to be negligible because of the high velocity of the water across the relatively short distance, so it was assumed that ILS residence time was approximately equal to that of the static mixer. Using a mixer constructed from transparent plastic allowed the residence time to be observed; a stop watch was used to measure the time. Five measurements of the residence time in the static mixer were averaged, providing an average time of 0.58 min (35 s).

Table 2 is a summary of water qualities. The complete data sets are presented in appendix C. Oxidation rates were calculated for each test by dividing the decrease in  $\text{Fe}^{2+}$  concentration by the residence time (table 3). The rates ranged from 575 to 668 (mg/L)/min. The synthetic AMD tests ranged from 783 to 2,474 mg/L  $\text{Fe}^{2+}$  and from mean pH values at discharge of 6.05 to 7.44, yet the oxidation rate range was very narrow. Figures 3A through C illustrate that the measured oxidation rate was independent of these factors under the conditions of the tests. These observations suggested that the iron-dependent model is not appropriate under these conditions.

Table 2.—Water quality in synthetic AMD tests

Test	Temp, °C	Inlet			Outlet			
		$\text{Fe}^{2+}$ (total), mg/L	$\text{Fe}^{2+}$ (free), <sup>1</sup> mg/L	DO, mg/L	pH	$\text{Fe}^{2+}$ (total), mg/L	DO, mg/L	pH
ILS0800 ..	25.4	783	560	0.20	5.80	448	0.11	6.05
ILS1000 ..	30.4	952	627	0.30	5.23	575	0.07	6.53
ILS1200 ..	26.8	1,119	750	0.63	5.03	760	0.11	7.44
ILS1400 ..	25.6	1,415	909	0.65	5.29	1,025	0.14	6.63
ILS2400 ..	27.3	2,474	1,450	1.01	4.71	2,126	0.14	6.91

DO Dissolved oxygen.

<sup>1</sup>The free  $\text{Fe}^{2+}$  concentration was estimated using the personal computer version of WATEQ4F obtained from the U.S. Geologic Survey, Reston, VA.

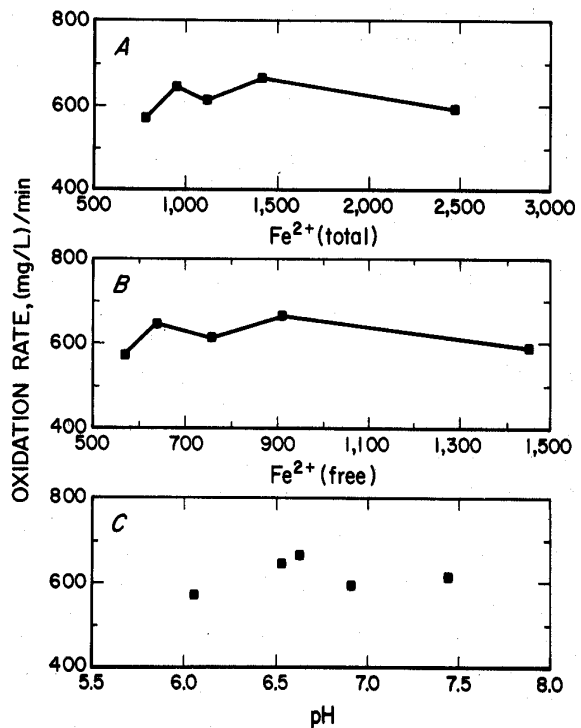


Figure 3.—Oxidation rate. A, Versus  $\text{Fe}^{2+}$  (total); B, versus  $\text{Fe}^{2+}$  (free); C, versus pH.

Table 3.—Measured oxidation rates from synthetic AMD tests<sup>1</sup>

(Measured oxidation rate equals change in  $[\text{Fe}^{2+}]$  divided by residence time)

Test	Change in $\text{Fe}^{2+}$ , mg/L	Measured oxidation rate, (mg/L)/min
ILS0800 ..	335	575
ILS1000 ..	377	646
ILS1200 ..	359	615
ILS1400 ..	390	668
ILS2400 ..	348	596

<sup>1</sup>Calculated at a residence time of 35 s.

## PHASE 2 RESULTS: OXYGEN-DEPENDENT MODEL DEVELOPMENT

The hydraulic parameters (i.e., pressures and flow rates) in the  $\text{O}_2$  transfer test were identical to those used during the  $\text{Fe}^{2+}$  oxidation tests. Deoxygenation of the water was accomplished by adding a solution containing 2,838.8 g of  $\text{Na}_2\text{SO}_3$  and 0.95 g of cobalt chloride ( $\text{CoCl}_2$ ) to 500 gal of tap water.  $\text{CoCl}_2$  is a catalytic agent that accelerates the oxidation of  $\text{SO}_3^{2-}$ . The amount of  $\text{Na}_2\text{SO}_3$

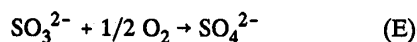
used was selected so as to be able to consume far more  $\text{O}_2$  than the ILS could transfer to the aqueous phase. Samples were drawn at the same locations and analyzed for  $\text{SO}_3^{2-}$  and  $\text{SO}_4^{2-}$ . Temperature and DO were also measured for each sample pair in the test. Appendix B contains a detailed description of the procedure for the  $\text{O}_2$  transfer test.

Table 4.—Calculation of oxygen transfer rate coefficient ( $k_{O_2}$ )

Sample pair	Temp, °C	SO <sub>4</sub> , mg/L			Equivalent O <sub>2</sub> transferred, mg/L	O <sub>2</sub> transfer rate, <sup>1</sup> (mg/L)/min	O <sub>2</sub> at saturation, mg/L	$k_{O_2}$ , min <sup>-1</sup>
		Inlet	Outlet	Change				
1 . . . . .	18.7	266	548	282	47.0	80.6	9.01	8.94
2 . . . . .	19.0	274	553	279	46.5	79.7	8.95	8.91
3 . . . . .	19.3	265	552	287	47.8	82.0	8.89	9.22
4 . . . . .	19.6	263	550	287	47.8	82.0	8.84	9.28
5 . . . . .	19.9	272	553	281	46.8	80.3	8.78	9.14
6 . . . . .	20.2	276	553	277	46.2	79.2	8.73	9.07
Average . . . . .								<sup>2</sup> 9.09

<sup>1</sup>Calculated at a residence time of 35 s.<sup>2</sup>Standard deviation = 0.14.

The increase in SO<sub>4</sub><sup>2-</sup> concentration in the ILS was used as a basis for calculating the O<sub>2</sub> transfer rate. The increase in SO<sub>4</sub><sup>2-</sup> can be directly attributed to the oxidation of SO<sub>3</sub><sup>2-</sup> within the system according to reaction E.



The increase in SO<sub>4</sub><sup>2-</sup> concentration was stoichiometrically converted into an equivalent amount of O<sub>2</sub> transferred. The amount of O<sub>2</sub> transferred was divided by the previously determined residence time to establish the O<sub>2</sub> transfer rate. The transfer rates ranged from 79.2 to 82.0 (mg/L)/min in six sample pairs as shown in table 4.

An O<sub>2</sub> transfer rate coefficient ( $k_{O_2}$ ) was calculated for each sample pair by dividing the transfer rate by the saturation concentration of O<sub>2</sub>. The values of  $k_{O_2}$  ranged from 8.91 to 9.28 min<sup>-1</sup>. The variation reflects the temperature differences and consequently the O<sub>2</sub> saturation concentrations of the sample pairs.

Table 5 presents the Bureau's oxidation rate predictions using the oxygen-dependent model. The value of O<sub>2</sub> at saturation for each test reflects the water temperature in each test. Oxidation rate predictions ranged from 458 to 507 (mg/L)/min.

Table 5.—Rate predictions of oxygen-dependent model<sup>1,2</sup>

Test	Temp, °C	O <sub>2</sub> at saturation rate, <sup>3</sup> mg/L	Predicted oxidation rate, (mg/L)/min
ILS0800 . . .	25.08	7.97	507
ILS1000 . . .	30.80	7.20	458
ILS1200 . . .	26.72	7.71	491
ILS1400 . . .	25.61	7.84	499
ILS2400 . . .	27.28	7.65	487

<sup>1</sup>O<sub>2</sub> transfer rate coefficient ( $k_{O_2}$ ) for 19.5° C = 9.09 min<sup>-1</sup>.<sup>2</sup>Constant = 7; see equation 4.<sup>3</sup>Source: Standard Methods for the Examination of Water and Wastewater, 16th ed. Am. Pub. Health Assoc., Washington, DC, 1985.

### PHASE 3 RESULTS: MODEL COMPARISON

The raw data presented in tables 3 and 5 show that the oxygen-dependent model underpredicts the measured Fe<sup>2+</sup> oxidation rate by a range of 12 to 29 pct for the five Fe<sup>2+</sup> oxidation tests. Iron oxidation rate predictions of the iron-dependent model are presented in table 6. In four of the tests this model underpredicted oxidation rates by 80 to 100 pct. In one test it underpredicted the rate by only 0.33 pct.

Probable sources of error in the Fe<sup>2+</sup> oxidation tests include the following: (1) chemical analysis error, (2) delay in arresting Fe<sup>2+</sup> oxidation during sample collection, (3) residual Fe<sup>2+</sup> oxidation in the analytical laboratory, and (4) changes in residence time due to pressure fluctuations during the tests. The first error source is random, and is typically ±2 pct according to measurements made on standard samples. Error due to delay in arresting reactions during sampling was estimated at 5 pct. Residual

oxidation in the analytical laboratory was estimated at 3 pct. Error due to fluctuations in residence time was estimated at 8 pct. Collectively, the maximum error from these factors was 15 pct in the direction of overestimating the Fe<sup>2+</sup> oxidation rate.

Application of this error correction to the Fe<sup>2+</sup> oxidation test data reduced the discrepancy between measured oxidation rates and the rate predicted by the oxygen-dependent model (fig. 4). The range of underprediction by the oxygen-dependent model, based on this correction, was reduced to 3.24 to 8.03 pct. The effect on the iron-dependent model was that in four of the tests the rate of underprediction was 77 to 100 pct. In the fifth test, the model overpredicted by 19 pct.

Another significant source of error in both models presented here was the lack of temperature control and its effect on reaction rate constants. Oxygen transfer tests

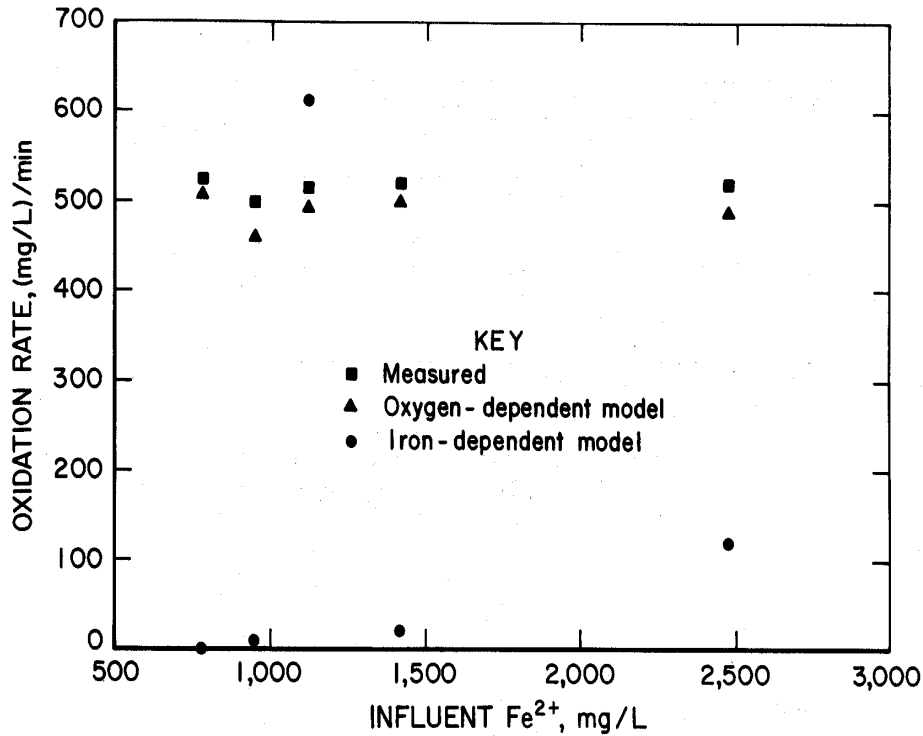


Figure 4.—Evaluation of models.

Table 6.—Rate predictions of Iron-dependent model<sup>1,2</sup>

Test	[Fe <sup>2+</sup> ], <sup>3</sup> mol/L	[O <sub>2</sub> ], <sup>4</sup> mol/L	pH	[H <sup>+</sup> ], <sup>5</sup> mol/L	[H <sup>+</sup> ] <sup>2</sup> , mol <sup>2</sup> /L <sup>2</sup>	Predicted oxidation rate, (mol/L)/min	Predicted oxidation rate, (mg/L)/min
ILS0800 . . . .	1.40E-02	2.49E-04	6.05	8.91E-07	7.94E-13	1.32E-05	7.73E-01
ILS1000 . . . .	1.70E-02	2.25E-04	6.53	2.95E-07	8.71E-14	1.32E-04	7.38E+00
ILS1200 . . . .	2.00E-02	2.41E-04	7.44	3.63E-08	1.32E-15	1.10E-02	6.13E+02
ILS1400 . . . .	2.53E-02	2.45E-04	6.63	2.34E-07	5.50E-14	3.38E-04	18.90E+01
ILS2400 . . . .	4.42E-02	2.41E-04	6.91	1.23E-07	1.51E-14	2.12E-03	1.18E+02

<sup>1</sup>Rate constant ( $k_{Fe}$ ) for 20° C = 3.00E-12 (mol/L)/min.

<sup>2</sup>See equation 1.

<sup>3</sup>Fe = initial Fe concentration.

<sup>4</sup>O<sub>2</sub> = O<sub>2</sub> concentration at saturation.

<sup>5</sup>H<sup>+</sup> concentration was calculated from pH.

used to measure  $k_{O_2}$  were conducted at 18.7° to 20.2° C. The literature value  $k_{Fe}$  was measured at 20° C. In contrast, synthetic AMD tests were conducted at 25.1° to 30.8° C. The elevated temperatures resulted from operation of a heat-generating recirculating pump connected to the AMD supply tank, and they could not be avoided with available equipment. Thus, the values of  $k_{O_2}$  and  $k_{Fe}$  are not corrected for the temperatures at which the Fe<sup>2+</sup>

oxidation tests were conducted. Reaction rate constants typically increase linearly with increasing temperature; it is reasonable to assume that both models would predict higher oxidation rates if the rate constants were corrected to the experimental temperature. This correction would require further study to calculate the reaction activation energy by the Arrhenius plot method.

## CONCLUSIONS AND RECOMMENDATIONS

The first finding of this study is that the iron-dependent model for  $\text{Fe}^{2+}$  oxidation does not extend to the high  $\text{Fe}^{2+}$  concentrations commonly encountered in AMD treatment. There are two primary considerations in applying the iron-dependent model: (1) the temperature correction for  $k_{\text{Fe}}$ , and (2) the values selected for pH, DO, and Fe. First, the  $k_{\text{Fe}}$  value, which was developed at 20° C, does not readily allow for temperature correction without duplicating the initial laboratory tests. Therefore, as is typically done in any industrial design, the  $k_{\text{Fe}}$  value from the literature is customarily used. Second, the iron-dependent model requires that constant pH, DO, and Fe values be used. This condition is now known not to be the case in typical AMD treatment. It is principally this aspect of the iron-dependent model—selection of the appropriate values—that may generate problems in application by treatment plant designers.

The second finding is that a model predicated on the hypothesis of  $\text{O}_2$  transfer as the rate-limiting step is probably correct. Evidence from this study strongly supports the oxygen-dependent model for the conditions that prevail in many mine drainage aeration operations. These conditions, as stated earlier, include near-neutral pH and  $\text{Fe}^{2+}$  in large excess over the amount of  $\text{O}_2$  supplied by transfer into the aqueous phase by the aeration device. Between concentrations of 783 and 2,474 mg/L, there was no observed oxidation rate dependence on  $\text{Fe}^{2+}$  concentration. A test not discussed in this report was conducted with an

initial  $\text{Fe}^{2+}$  concentration of 300 mg/L. In that test, the oxidation rate was iron dependent. There was no significant variation in the oxidation rate as the average  $\text{H}^+$  concentrations ranged from  $8.9 \times 10^{-7}$  to  $3.6 \times 10^{-8}$  mol/L (pH 6.05 to 7.44). Figure 4 clearly shows that the oxygen-dependent model qualitatively matched experimental data, while the iron-dependent model did not. Reasonable error sources were identified that could account for quantitative differences. No claims for the oxygen-dependent model can be made beyond the parameters of the tests presented.

The oxygen-dependent model is a significant departure from the iron-dependent model in use today. The iron-dependent model indicates that the easiest way to accelerate the treatment process is to increase the pH. Certainly this will result in the additional precipitation of metals. However, in the absence of adequate  $\text{O}_2$  transfer, much of the iron would remain in the reduced,  $\text{Fe}^{2+}$  state. Removal of iron as  $\text{Fe}^{2+}$  minimizes or eliminates the cost savings potential of including an oxidation step in the process.

The oxygen-dependent model suggests a different strategy in AMD treatment. Efforts in the design and operation of AMD treatment systems should focus on efficient mixing and maximum  $\text{O}_2$  transfer. These criteria should result in the optimum performance of chemical-neutralization-type treatment systems.

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## APPENDIX A.—LABORATORY PROCEDURES FOR SYNTHETIC AMD TESTS

1. The supply tank was filled prior to each test with 500 gal of tap water. The water was allowed to sit for 24 h.
2. The initial DO concentration and water temperature were measured. A membrane-type DO probe was used.
3. The water was then deoxygenated. A bucket of water was drawn from the tank. Based on the initial DO,  $\text{Na}_2\text{SO}_3$  was added to the water. The amount was calculated using the relationship that a half mole of  $\text{O}_2$  is consumed for each mole of  $\text{Na}_2\text{SO}_3$  present. Also, 0.95 g of  $\text{CoCl}_2$  was added.  $\text{CoCl}_2$  acts as a catalyst for the  $\text{SO}_2^{2-}$  oxidation reaction. It does not otherwise participate in the reaction. The  $\text{Na}_2\text{SO}_3$  was dissolved and the bucket was poured into the supply tank.
4. The water was mixed thoroughly and the DO was remeasured. If the DO was above 0 mg/L and equal to or less than 0.5 mg/L, the next step was performed. If the DO measured zero, the water was aerated by mechanical mixing until a measurable DO was recorded. In practice this was never required. If the DO was more than 0.5 mg/L, an additional amount of  $\text{Na}_2\text{SO}_3$  was dissolved and added. This was frequently necessary and probably was due to the reaction of a small amount of  $\text{SO}_3^{2-}$  with atmospheric  $\text{O}_2$  prior to being added to the water.
5. Ferrous sulfate ( $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ ) was the source of soluble iron for the tests. The amount required to establish the target concentration of  $\text{Fe}^{2+}$  was weighed out and added to a bucket of deoxygenated water. The iron salt was dissolved and the water was reintroduced to the tank. The water in the tank was thoroughly mixed.
6. A chemical feed pump with a reservoir tank was used to introduce an alkaline solution during the test. The reservoir tank was filled with 25 gal of tap water. This water was also deoxygenated to eliminate it as a source of DO. A bucket of water was drawn from the reservoir. To this water 0.05 g of  $\text{CoCl}_2$  was added. Based on a measurement of the initial DO in the water, an amount of  $\text{Na}_2\text{SO}_3$  was added. These salts were dissolved and the water was added back to the reservoir. The alkali used was NaOH 50 pct stock. An amount sufficient to neutralize the iron solution was measured out and added to the reservoir. While the water discharge was determined to be in the near-neutral range, it is probable that the pH within the ILS was substantially higher until complete mixing had occurred. The target flow rate for the alkaline solution was 1.0 gal/min. This rate was chosen to establish a 1:10 ratio of alkali to iron solution for the tests. Actual flow rates varied somewhat to achieve the desired pH in the outflow from the ILS.
7. Seven sets of four sample bottles each were prepared for the entry and discharge ports of the ILS. Each sample bottle was 250 mL. The first sample bottle in each set contained no preservative. The second contained 5 mL of concentrated hydrochloric acid (HCl). The third was filled with Ar and capped tightly. The last sample bottle contained no preservative or Ar. These last sample bottles were subsequently used to prepare filtered and acidified samples.
8. The system pump was turned on and the water pressure upstream from the jet pump was adjusted to 50 lbf/in<sup>2</sup>(ga). The chemical feed pump was set to the calculated flow rate and activated. After a minute delay, a grab sample was drawn from the discharge port. The pH of this sample was measured. The target discharge pH was 7.5. As necessary, the flow rate of the chemical feed pump was adjusted. In practice it was difficult to achieve the target pH. Adjustments were made to the extent that time permitted. In all cases a pH above 6.0 was achieved.
9. Samples were drawn from the entry and discharge ports simultaneously. All samples were analyzed for pH, alkalinity, acidity,  $\text{Fe}^{2+}$ , Fe (total),  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Na}^+$ , and  $\text{SO}_4^{2-}$ . Acidity and alkalinity determinations were made using EPA methods 305.1 and 310.1, respectively. Metals analyses, with the exception of  $\text{Fe}^{2+}$  analysis, were conducted using inductively coupled plasma (ICP) spectroscopy. Ferrous iron determinations were made by redox titration using potassium dichromate ( $\text{K}_2\text{Cr}_2\text{O}_7$ ) and a platinum electrode to the first derivative endpoint.  $\text{SO}_4^{2-}$  was analyzed by liquid chromatography.
10. At the completion of each set, two grab samples were taken. The first sample was analyzed for pH; the second was analyzed for DO and temperature.

## APPENDIX B.—LABORATORY PROCEDURES FOR OXYGEN TRANSFER TEST

1. The supply tank was filled with 500 gal of tap water and allowed to sit for 24 h.
2. The initial DO concentration and water temperature were measured.
3. The water was then deoxygenated. A bucket of water was drawn from the tank. Into this 0.95 g of  $\text{CoCl}_2$  was added and dissolved.  $\text{NaSO}_3$  was then added and dissolved in the bucket. The amount of  $\text{NaSO}_3$ , 2,838.8 g, was determined through trial and error to be in excess of that required to react with all initial DO plus that transferred by the ILS. The bucket of water was then added to the supply water and thoroughly mixed. DO was measured in the tank using a membrane-type probe to verify that there was no measurable amount of DO in the water.
4. Six 250-mL sample bottles were prepared for the entry and discharge locations, and 5 mL of formaldehyde-based preservative was added to each sample bottle.
5. The system pump was turned on and the pressure upstream from the jet pump was adjusted to 50 lbf/in<sup>2</sup>(ga).
6. Samples were simultaneously withdrawn at the entry and discharge points. The bottles were filled to the brim, tightly capped, and sealed with pliable film, through which  $\text{O}_2$  does not diffuse.  $\text{SO}_3^{2-}$  and  $\text{SO}_4^{2-}$  concentrations were determined analytically by the liquid chromatography method.
7. Throughout the test, water samples were drawn from the discharge sampling port and measured to ensure that there was no DO in the water. These samples were also used to measure the water temperature.



## APPENDIX C.—WATER QUALITY ANALYSES FOR SYNTHETIC AMD TESTS

Table C-1.—Water quality analysis for synthetic AMD test ILS0800, inlet samples

Sample .....	1	2	3	4	5	6	7	8
Field pH .....	5.85	NA	5.80	5.75	NA	NA	NA	NA
Lab pH .....	4.05	4.06	4.02	4.03	4.06	4.07	4.04	3.96
Alkalinity .. mg/L as CaCO <sub>3</sub> ..	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Acidity .... mg/L as CaCO <sub>3</sub> ..	1357	1356	1363	1370	1345	1346	1345	1346
Fe <sup>2+</sup> .....	794	781	791	780	788	767	777	778
Fe (total) .....	819	820	818	811	812	810	804	805
Filtered and acidified:								
Fe <sup>2+</sup> .....	NA	NA	NA	NA	NA	NA	NA	NA
Fe (total) .....	NA	NA	NA	NA	NA	NA	NA	NA
Ca <sup>2+</sup> .....	36.49	36.39	36.35	36.01	36.21	36.33	35.09	35.37
Mg <sup>2+</sup> .....	9.14	9.24	9.18	9.04	9.10	9.04	9.10	9.06
Na <sup>+</sup> .....	48.59	48.21	48.02	47.57	47.23	47.25	48.06	47.53
SO <sub>4</sub> <sup>2-</sup> .....	1500	1500	1500	1525	1500	1500	1500	1500
DO .....	0.2	NA	NA	NA	NA	NA	NA	NA
Temp .....	22.8	23.2	23.4	NA	23.8	23.8	24.1	25.1
Eh .....	358	358	366	368	363	358	363	369
Eh, temp .....	26.5	26.0	26.0	26.0	26.0	26.5	26.0	26.5
	9	10	11	12	13	14	Mean	SD
Field pH .....	NA	NA	NA	NA	NA	NA	5.80	NA
Lab pH .....	NA	3.96	3.97	4.06	4.06	3.89	4.02	NA
Alkalinity .. mg/L as CaCO <sub>3</sub> ..	0.0	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Acidity .... mg/L as CaCO <sub>3</sub> ..	1350	1351	1347	1351	1348	1355	1352	7
Fe <sup>2+</sup> .....	779	781	788	782	787	788	783	7
Fe (total) .....	816	819	825	833	829	827	818	8
Filtered and acidified:								
Fe <sup>2+</sup> .....	NA	NA	NA	NA	NA	NA	NA	NA
Fe (total) .....	NA	NA	NA	NA	NA	NA	NA	NA
Ca <sup>2+</sup> .....	35.74	35.78	36.43	36.15	35.86	35.99	36.01	0.40
Mg <sup>2+</sup> .....	9.18	9.14	9.22	9.30	9.22	9.22	9.16	0.08
Na <sup>+</sup> .....	48.63	49.00	48.84	49.04	49.49	49.12	48.33	0.71
SO <sub>4</sub> <sup>2-</sup> .....	1475	1475	1475	1475	1475	1475	1491	15
DO .....	NA	NA	NA	NA	NA	NA	0.20	NA
Temp .....	25.7	NA	26.2	26.6	NA	27.4	24.74	1.47
Eh .....	368	368	398	376	393	398	372	14
Eh, temp .....	26.5	26.5	27.0	27.0	27.0	27.0	26.46	0.40

DO Dissolved oxygen.  
 Eh Oxidation potential.  
 NA Not available.  
 SD Standard deviation.

Table C-2.—Water quality analysis for synthetic AMD test ILS0800, outlet samples

Sample .....	1	2	3	4	5	6	7	8
Field pH .....	5.95	6.33	6.22	7.22	0.00	10.99	5.99	6.90
Lab pH .....	5.76	5.72	6.10	6.68	7.06	10.92	5.68	6.16
Alkalinity .. mg/L as CaCO <sub>3</sub> ..	8.48	5.50	15.00	24.62	30.81	129.14	4.35	14.99
Acidity .... mg/L as CaCO <sub>3</sub> ..	133	138	40	5	5	0	432	65
Fe <sup>2+</sup> .....	442	439	460	421	418	411	477	471
Fe (total) .....	818	818	818	818	818	818	818	818
Filtered and acidified:								
Fe <sup>2+</sup> .....	109	91.90	0.00	0.00	1.33	0.45	0.00	0.00
Fe (total) .....	109	91.90	0.00	0.00	1.37	0.45	0.00	0.00
Ca <sup>2+</sup> .....	37.62	36.54	38.05	37.91	37.56	38.59	37.10	37.89
Mg <sup>2+</sup> .....	9.75	9.57	9.80	9.85	9.80	9.89	9.75	9.81
Na <sup>+</sup> .....	575	559	594	701	697	790	457	602
SO <sub>4</sub> <sup>2-</sup> .....	1423	1403	1413	1525	1508	1545	1524	1429
DO .....	0.20	0.10	0.10	0.10	0.10	0.10	0.10	0.10
Temp .....	24.00	24.00	24.00	24.20	24.20	24.60	25.00	25.80
Eh .....	148	138	129	278	376	338	128	128
Eh, temp .....	24.50	25.00	25.00	24.00	26.50	26.00	26.00	27.00
	9	10	11	12	13	14	Mean	SD
Field pH .....	0.00	7.00	7.03	7.01	7.01	7.00	6.05	NA
Lab pH .....	5.86	5.71	6.09	5.97	5.92	5.80	6.39	NA
Alkalinity .. mg/L as CaCO <sub>3</sub> ..	6.58	5.80	10.16	9.74	8.63	7.81	20.12	31.11
Acidity .... mg/L as CaCO <sub>3</sub> ..	81	87	30	42	38	70	83	105
Fe <sup>2+</sup> .....	443	453	467	453	451	465	448	20
Fe (total) .....	818	818	818	818	818	818	818	0
Filtered and acidified:								
Fe <sup>2+</sup> .....	40.98	0.00	22.05	0.00	30.70	34.84	23.63	34.59
Fe (total) .....	41.00	0.00	22.14	0.00	30.76	35.18	23.68	34.60
Ca <sup>2+</sup> .....	37.33	37.89	37.84	37.39	37.84	38.04	37.68	0.47
Mg <sup>2+</sup> .....	9.79	9.80	9.75	9.76	9.81	9.79	9.78	0.07
Na <sup>+</sup> .....	588	595	616	604	609	609	614	74
SO <sub>4</sub> <sup>2-</sup> .....	1409	1424	1378	1418	1412	1513	1452	55
DO .....	0.10	0.10	0.10	0.10	0.10	0.10	0.11	0.03
Temp .....	26.00	26.20	26.50	26.80	27.10	27.40	25.41	1.22
Eh .....	113	0	88	97	93	74	152	101
Eh, temp .....	27.00	27.00	27.00	27.00	27.50	27.50	26.21	1.11
DO	Dissolved oxygen.							
Eh	Oxidation potential.							
NA	Not available.							
SD	Standard deviation.							

Table C-3.—Water quality analysis for synthetic AMD test ILS1000

Sample .....	1	2	3	4	5	6	7	Mean	SD
Inlet:									
Field pH .....	5.55	NA	5.33	NA	NA	NA	5.00	5.23	NA
Lab pH .....	3.90	3.89	3.87	3.87	3.87	3.85	3.85	3.87	NA
Alkalinity .. mg/L as CaCO <sub>3</sub> ..	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Acidity .... mg/L as CaCO <sub>3</sub> ..	1655	1670	1670	1670	1680	1675	1680	1671	8
Fe <sup>2+</sup> ..... mg/L..	955	952	955	951	948	956	949	952	3
Fe (total) ..... mg/L..	982	971	977	963	990	971	950	972	12
Filtered and acidified:									
Fe <sup>2+</sup> ..... mg/L..	NA	NA	NA	NA	NA	NA	NA	NA	NA
Fe (total) ..... mg/L..	NA	NA	NA	NA	NA	NA	NA	NA	NA
Ca <sup>2+</sup> ..... mg/L..	21.34	21.13	21.17	21.46	21.50	21.74	21.34	21.38	0.19
Mg <sup>2+</sup> ..... mg/L..	5.24	5.16	4.96	5.16	5.24	5.08	5.04	5.13	0.10
Na <sup>+</sup> ..... mg/L..	47.04	45.64	45.88	46.29	46.86	46.57	46.05	46.33	0.48
SO <sub>4</sub> <sup>2-</sup> ..... mg/L..	1750	1800	1775	1775	1775	1750	1775	1771	16
DO ..... mg/L..	0.05	0.05	NA	0.5	0.6	NA	NA	0.30	0.25
Temp ..... °C..	28.20	NA	NA	31.50	32.00	33.00	NA	31.18	1.80
Eh ..... mV..	454	453	460	464	459	470	465	461	6
Eh, temp ..... °C..	25.90	27.00	26.90	26.90	27.00	27.00	27.00	26.81	0.38
Outlet:									
Field pH .....	10.97	NA	7.00	6.36	NA	6.34	6.33	6.53	NA
Lab pH .....	10.82	10.97	6.45	5.98	5.76	5.80	5.86	7.38	2.24
Alkalinity .. mg/L as CaCO <sub>3</sub> ..	82.92	89.14	0.00	0.00	0.00	0.00	0.00	24.58	38.90
Acidity .... mg/L as CaCO <sub>3</sub> ..	0	0	39	105	304	283	293	146	131
Fe <sup>2+</sup> ..... mg/L..	569	547	566	608	573	572	592	575	18
Fe (total) ..... mg/L..	972	972	972	972	972	972	972	972	0
Filtered and acidified:									
Fe <sup>2+</sup> ..... mg/L..	1.40	1.70	3.02	126	114	146	147	77.03	65.76
Fe (total) ..... mg/L..	1.45	1.76	3.76	132	116	152	152	79.77	68.05
Ca <sup>2+</sup> ..... mg/L..	23.94	23.70	23.89	23.02	23.08	23.04	22.78	23.35	0.44
Mg <sup>2+</sup> ..... mg/L..	5.92	5.87	5.85	5.59	5.61	5.57	5.60	5.71	0.14
Na <sup>+</sup> ..... mg/L..	858	872	859	655	631	627	627	733	113
SO <sub>4</sub> <sup>2-</sup> ..... mg/L..	1821	1821	1758	1556	1564	1621	1603	1678	110
DO ..... mg/L..	0.05	0.05	0.00	0.10	0.10	0.10	0.10	0.07	0.04
Temp ..... °C..	28.00	NA	30.00	30.50	31.00	31.00	32.00	30.42	1.24
Eh ..... mV..	NA	NA	NA	NA	NA	NA	109	109	0
Eh, temp ..... °C..	26.50	26.00	26.00	26.00	26.50	26.50	24.50	26.00	0.65

DO Dissolved oxygen.  
Eh Oxidation potential.  
NA Not available.  
SD Standard deviation.

Table C-4.—Water quality analysis for synthetic AMD test ILS1200

Sample .....	1	2	3	4	5	6	7	Mean	SD
Inlet:									
Field pH .....	5.00	NA	NA	5.00	NA	5.15	5.00	5.03	NA
Lab pH .....	4.02	4.08	4.07	4.02	4.06	4.00	4.09	4.05	NA
Alkalinity .. mg/L as CaCO <sub>3</sub> ..	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Acidity ... mg/L as CaCO <sub>3</sub> ..	1996	2010	2013	1980	2040	2035	2045	2017	22
Fe <sup>2+</sup> .....	1132	1129	1137	1123	1127	1133	1049	1119	29
Fe (total) .....	1132	1129	1137	1123	1127	1133	1110	1127	8
Filtered and acidified:									
Fe <sup>2+</sup> .....	1143	NA	1145	1129	1130	NA	1115	1132	10.82
Fe (total) .....	1155	NA	1145	1138	1130	NA	1115	1137	13.63
Ca <sup>2+</sup> .....	37.54	37.64	37.64	37.43	37.54	37.64	36.82	37.46	0.27
Mg <sup>2+</sup> .....	9.18	9.59	9.49	9.28	9.49	9.49	9.38	9.41	0.13
Na <sup>+</sup> .....	48.65	48.45	48.55	49.37	51.31	51.00	47.94	49.32	1.22
SO <sub>4</sub> <sup>2-</sup> .....	2140	2150	2100	2140	2150	2150	2100	2133	21
DO .....	0.55	0.60	0.70	0.80	0.00	0.80	0.95	0.63	0.29
Temp .....	25.40	NA	26.40	NA	26.80	27.00	27.80	26.68	0.79
Eh .....	383	378	390	400	396	407	410	395	11
Eh, temp .....	23.60	24.00	23.40	23.50	24.10	23.20	23.40	23.60	0.31
Outlet:									
Field pH .....	7.30	7.30	NA	7.50	NA	7.90	NA	7.44	NA
Lab pH .....	6.53	6.52	6.61	6.46	6.42	6.32	6.93	6.54	NA
Alkalinity .. mg/L as CaCO <sub>3</sub> ..	43.56	37.98	42.01	34.84	6.98	3.18	40.91	29.92	15.96
Acidity ... mg/L as CaCO <sub>3</sub> ..	5	5	5	5	10	16	11	8	4
Fe <sup>2+</sup> .....	771	781	750	764	751	747	754	760	12
Fe (total) .....	1127	1127	1127	1127	1127	1127	1127	1127	0
Filtered and acidified:									
Fe <sup>2+</sup> .....	22.93	18.16	24.43	18.67	3.97	0.44	105	27.65	32.70
Fe (total) .....	22.93	18.16	24.43	18.67	3.97	0.44	105	27.65	32.70
Ca <sup>2+</sup> .....	39.24	7.77	39.22	39.17	38.44	39.45	46.48	35.68	11.68
Mg <sup>2+</sup> .....	9.84	9.93	9.97	9.95	9.77	9.86	9.68	9.86	0.10
Na <sup>+</sup> .....	829	813	822	823	907	889	778	837	42
SO <sub>4</sub> <sup>2-</sup> .....	1784	1801	1795	1812	2013	1989	1788	1854	93
DO .....	0.15	0.20	0.10	0.05	NA	0.05	0.10	0.11	0.05
Temp .....	26.00	26.00	26.50	27.00	NA	27.20	27.80	26.75	0.65
Eh .....	138	136	118	148	168	158	88	136	25
Eh, temp .....	21.40	22.20	22.40	22.00	23.00	23.20	24.30	22.64	0.88

DO Dissolved oxygen.  
 Eh Oxidation potential.  
 NA Not available.  
 SD Standard deviation.

Table C-5.—Water quality analysis for synthetic AMD test ILS1400

Sample	1	2	3	4	5	6	7	Mean	SD
Inlet:									
Field pH	5.30	NA	5.30	NA	5.30	NA	5.25	5.29	NA
Lab pH	3.96	NA	3.98	NA	3.98	NA	3.93	3.96	NA
Alkalinity . . . mg/L as CaCO <sub>3</sub>	0.00	NA	0.00	NA	0.00	NA	0.00	0.00	0.00
Acidity . . . . mg/L as CaCO <sub>3</sub>	2458	NA	2464	NA	2465	NA	2480	2467	8
Fe <sup>2+</sup> . . . . . mg/L	1412	NA	1412	NA	1419	NA	1416	1414	8
Fe (total) . . . . . mg/L	1412	NA	1412	NA	1419	NA	1416	1414	3
Filtered and acidified:									
Fe <sup>2+</sup> . . . . . mg/L	1395	NA	1380	NA	1381	NA	1405	1390	11
Fe (total) . . . . . mg/L	1398	NA	1412	NA	1418	NA	1405	1408	7
Ca <sup>2+</sup> . . . . . mg/L	33.25	NA	32.54	NA	34.07	NA	34.88	33.69	0.88
Mg <sup>2+</sup> . . . . . mg/L	8.77	NA	8.36	NA	8.26	NA	8.47	8.47	0.19
Na <sup>+</sup> . . . . . mg/L	42.74	NA	41.31	NA	43.35	NA	43.25	42.66	0.81
SO <sub>4</sub> <sup>2-</sup> . . . . . mg/L	2525	NA	2500	NA	2550	NA	2550	2531	21
DO . . . . . mg/L	0.50	NA	0.60	NA	0.70	NA	0.80	0.65	0.11
Temp . . . . . °C	24.60	NA	25.20	NA	26.00	NA	26.80	25.65	0.83
Eh . . . . . mV	NA	NA	303	NA	324	NA	334	320	13
Eh, temp . . . . . °C	22.10	NA	22.10	NA	22.10	NA	22.30	22.15	0.09
Outlet:									
Field pH	6.60	6.65	NA	6.66	NA	6.63	NA	6.63	NA
Lab pH	6.06	6.10	5.56	6.06	5.86	5.56	5.54	5.82	NA
Alkalinity . . . mg/L as CaCO <sub>3</sub>	2.70	8.07	6.58	10.68	7.83	6.03	5.99	6.84	2.26
Acidity . . . . mg/L as CaCO <sub>3</sub>	373	417	477	582	481	487	537	479	64
Fe <sup>2+</sup> . . . . . mg/L	1012	1023	1031	1036	1036	1024	1014	1025	9
Fe (total) . . . . . mg/L	1414	1414	1414	1414	1414	1414	1414	1414	0
Filtered and acidified:									
Fe <sup>2+</sup> . . . . . mg/L	220	231	261	271	277	287	310	265	29.09
Fe (total) . . . . . mg/L	232	231	261	272	278	294	310	268	27.58
Ca <sup>2+</sup> . . . . . mg/L	36.90	36.60	36.33	35.42	35.52	35.31	34.85	35.85	0.70
Mg <sup>2+</sup> . . . . . mg/L	9.28	9.04	8.95	8.72	8.48	9.04	8.34	8.84	0.31
Na <sup>+</sup> . . . . . mg/L	888	860	854	847	835	826	807	845	24
SO <sub>4</sub> <sup>2-</sup> . . . . . mg/L	2212	2261	2264	2316	2227	2234	2245	2251	31
DO . . . . . mg/L	0.15	0.20	0.15	0.15	NA	0.10	0.10	0.14	0.03
Temp . . . . . °C	24.80	25.00	25.20	25.80	NA	26.10	26.50	25.57	0.61
Eh . . . . . mV	91	86	81	78	73	68	81	79	7
Eh, temp . . . . . °C	22.20	22.30	22.30	22.30	22.20	21.40	20.80	21.93	0.55

DO Dissolved oxygen.  
Eh Oxidation potential.  
NA Not available.  
SD Standard deviation.

Table C-6.—Water quality analysis for synthetic AMD test ILS2400, inlet samples

Sample .....	1	2	3	4	5	6	7	Mean	SD
Inlet:									
Field pH .....	4.79	4.80	4.80	4.70	4.70	4.64	4.60	4.71	NA
Lab pH .....	3.73	3.78	3.79	3.76	3.78	3.76	3.79	3.77	NA
Alkalinity ... mg/L as CaCO <sub>3</sub> ..	NA	NA	NA	NA	NA	NA	NA	NA	NA
Acidity .... mg/L as CaCO <sub>3</sub> ..	4230	4200	4170	4150	4140	4150	4220	4180	34
Fe <sup>2+</sup> .....	2429	2477	2490	2453	2446	2504	2521	2474	31
Fe (total) .....	2429	2477	2490	2453	2446	2504	2520	2474	31
Filtered and acidified:									
Fe <sup>2+</sup> .....	2386	NA	2434	NA	2468	NA	2429	2429	29.34
Fe (total) .....	2386	NA	2434	NA	2468	NA	2640	2482	95.74
Ca <sup>2+</sup> .....	50.20	50.20	49.80	51.84	51.94	52.14	52.24	51.20	0.99
Mg <sup>2+</sup> .....	13.67	13.78	13.57	13.37	14.08	13.47	13.88	13.69	0.23
Na <sup>+</sup> .....	57.96	58.27	56.94	57.65	57.45	58.88	57.86	57.86	0.57
SO <sub>4</sub> <sup>2-</sup> .....	4592	4592	4694	4592	4592	4592	4694	4621	46
DO .....	0.95	0.95	1.00	1.00	1.00	1.10	1.05	1.01	0.05
Temp .....	26.00	26.20	26.50	27.00	27.20	27.40	28.00	26.90	0.66
Eh .....	414	410	421	421	424	425	432	421	6.72
Eh, temp .....	25.60	25.70	24.60	25.30	26.30	25.00	26.60	25.59	0.65

DO Dissolved oxygen.  
Eh Oxidation potential.  
NA Not available.  
SD Standard deviation.

Table C-7.—Water quality analysis for synthetic AMD test ILS2400, outlet samples

Sample	1	2	3	4	5	6
Field pH	7.43	NA	7.34	7.17	7.07	7.00
Lab pH	5.39	5.63	5.61	5.65	5.52	5.51
Alkalinity . . . mg/L as CaCO <sub>3</sub>	2.14	3.29	3.45	3.45	3.14	3.50
Acidity . . . . mg/L as CaCO <sub>3</sub>	215	450	412	536	679	920
Fe <sup>2+</sup> . . . . . mg/L	2122	2071	2032	2034	2185	2142
Fe (total) . . . . . mg/L	2525	2525	2525	2525	2525	2525
Filtered and acidified:						
Fe <sup>2+</sup> . . . . . mg/L	206	303	366	316	509	602
Fe (total) . . . . . mg/L	206	303	372	316	509	602
Ca <sup>2+</sup> . . . . . mg/L	57.66	57.52	56.51	57.37	57.22	56.74
Mg <sup>2+</sup> . . . . . mg/L	15.00	15.06	15.10	15.54	14.98	14.90
Na <sup>+</sup> . . . . . mg/L	1769	1653	1706	1642	1546	1441
SO <sub>4</sub> <sup>2-</sup> . . . . . mg/L	4366	4269	4330	4217	4358	4305
DO . . . . . mg/L	0.20	0.10	NA	0.15	0.15	0.20
Temp . . . . . °C	26.20	26.50	NA	26.70	27.00	27.00
Eh . . . . . mV	69	55	-28	75	-31	-45
Eh, temp . . . . . °C	23.70	24.20	22.80	27.10	25.10	26.30
	7	8	9	10	Mean	SD
Field pH	6.97	6.73	6.75	6.53	6.91	NA
Lab pH	5.49	5.47	5.59	5.31	5.52	NA
Alkalinity . . . mg/L as CaCO <sub>3</sub>	4.23	4.25	4.03	3.55	3.50	0.58
Acidity . . . . mg/L as CaCO <sub>3</sub>	1084	1217	1310	1339	816	389
Fe <sup>2+</sup> . . . . . mg/L	2220	2196	2207	2056	2126	70
Fe (total) . . . . . mg/L	2525	2525	2525	2525	2525	0
Filtered and acidified:						
Fe <sup>2+</sup> . . . . . mg/L	718	726	789	790	532	211
Fe (total) . . . . . mg/L	718	726	789	790	533	210
Ca <sup>2+</sup> . . . . . mg/L	56.49	55.84	56.11	55.33	56.68	0.73
Mg <sup>2+</sup> . . . . . mg/L	14.94	14.43	14.73	14.34	14.90	0.32
Na <sup>+</sup> . . . . . mg/L	1370	1316	1298	1266	1501	176
SO <sub>4</sub> <sup>2-</sup> . . . . . mg/L	4380	4219	4273	4256	4297	57
DO . . . . . mg/L	0.15	0.10	0.10	0.10	0.14	0.04
Temp . . . . . °C	27.50	27.90	28.20	28.50	27.28	0.75
Eh . . . . . mV	-83	-43	-64	-32	-13	54
Eh, temp . . . . . °C	23.60	25.40	27.20	26.50	25.19	1.49
DO	Dissolved oxygen.					
Eh	Oxidation potential.					
NA	Not available.					
SD	Standard deviation.					