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Application of Oxidation-Reduction Potential and pH To Investigate a Ferric Oxide Waste Disposal Pond and a Lead Processing Waste Site

By Alexander May and Joseph B. Peterson

UNITED STATES DEPARTMENT OF THE INTERIOR



BUREAU OF MINES

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

BUREAU OF MINES

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CONTENTS

Page

Abstract	1
Introduction	2
Procedure	3
Oxidation-reduction potential and pH measurements	3
Standard solutions	3
Ferric oxide waste disposal pond samples	3
Lead processing waste site samples	4
Computational program	4
Test results	4
Standard solutions	4
Ferric oxide waste disposal pond	6
Lead processing waste site	6
Computational program	6
Discussion	11
Reduction potential versus dilution	11
Reduction potential versus temperature	11
Reduction potential versus pH	12
Computational program	13
Conclusions	14
Acknowledgments	14
References	14
Appendix A.—Equations for reduction potentials versus temperature	16
Appendix B.—Reactions and equations for reduction potentials	17

ILLUSTRATIONS

1. Reduction potentials of potassium ferricyanide and potassium ferrocyanide solution, 1:1 mole ratio, 0.002 molar, from 5 to 80 °C	5
2. Reduction potentials versus pH of sludge and of supernatant from ferric oxide waste disposal pond ...	8
3. Reduction potentials of supernatant from ferric oxide waste disposal pond from 5 to 70 °C	8
4. Reduction potentials of well samples from lead processing waste site from 5 to 70 °C	9
5. Reduction potentials of stream samples from lead processing waste site from 5 to 70 °C	9
6. Lead sulfate solubility, as lead, in sulfuric acid from program and from literature	10
7. Program-calculated lead species present in well water sample GJ-3, as percentage of total lead present	10

TABLES

1. Reduction potentials of potassium ferricyanide and potassium ferrocyanide solution, 1:1 mole ratio, from 0.0004 to 0.1 molar, at 25 °C	5
2. Reduction potentials of potassium ferricyanide and potassium ferrocyanide solution, 1:1 mole ratio, 0.002 molar, from 5 to 80 °C	5
3. Reduction potentials of supernatant liquid from ferric oxide waste disposal pond from 5 to 70 °C	6
4. Typical chemical analyses of well waters and stream waters from lead processing waste site	7
5. Observed reduction potentials of well and stream samples from lead processing waste site from 5 to 70 °C	7
6. Program-calculated lead species present in well water sample GJ-3 at pH 6.7	7
7. Observed and calculated thermodynamic values at 25 °C for potassium ferricyanide and potassium ferrocyanide standard solutions, ferric oxide waste disposal pond sample, and lead processing waste site samples	12

TABLES—Continued

	<i>Page</i>
A-1. Equations for reduction potential versus temperature for standard solutions, ferric oxide waste disposal samples, and lead processing waste site samples	16
B-1. Reactions that define iron species equilibria boundaries for figure 2	17
B-2. Calculated reduction potentials for reactions B-1 through B-5	17
B-3. Calculated pH for reactions B-6 through B-8	17
B-4. Reactions used to calculate thermodynamic functions for table 7	17

UNIT OF MEASURE ABBREVIATIONS USED IN THIS REPORT

°C	degree Celsius	m	meter
<i>F</i>	Faraday's constant coulombs per gram equivalent weight)	mg/L	milligram per liter
g	gram	mL	milliliter
ha	hectare	mV	millivolt
J/(mol•K)	joule per mole (gram molecular weight) per kelvin	mV/°C	millivolt per degree Celsius
kJ/mol	kilojoule per mole (gram molecular weight)	pct	percent
		V	volt

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APPLICATION OF OXIDATION-REDUCTION POTENTIAL AND pH TO INVESTIGATE A FERRIC OXIDE WASTE DISPOSAL POND AND A LEAD PROCESSING WASTE SITE

By Alexander May¹ and Joseph B. Peterson²

ABSTRACT

The U.S. Bureau of Mines investigated the application of oxidation-reduction potential (ORP) and pH measurements to environmental studies of mining and mineral processing wastes, and developed a computer program to estimate the concentrations of species of lead present in samples from a lead processing waste site. The methods and techniques for the ORP-pH measurements were investigated using known standard solutions made in the laboratory, samples from a ferric oxide waste disposal pond at a rutile production plant, and samples of well water and stream water from the lead processing waste site. ORP values were measured from 5 to 80 °C, from pH 1 to pH 12, and at various ratios of oxidant to reductant.

The ORP-pH values can help identify valence values and species of ions present, including those of major, minor, and trace concentrations, and also indicate possible reactions at various pH values. The ORP measurements versus temperature yield data from which thermodynamic values can be calculated. The application and limitations of these measurements are discussed, and a brief discussion of the computational program to identify species of lead is presented.

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INTRODUCTION

The U.S. Bureau of Mines (USBM) mission is to help ensure the Nation an adequate supply of minerals at acceptable economic, environmental, and social costs. Management of mineral wastes requires the Bureau's special attention because domestic mineral industries are being challenged by increasing pressures for a cleaner environment. Mining and processing wastes may contain heavy toxic metals, some wastes are radioactive, and some produce corrosive effluents. The major effects of such wastes on the environment are contamination of water supplies through leaching of metals and toxic materials, contamination of the air by gases, smoke, or dust carrying toxic materials, and direct contamination of people and animals by possible contact with toxic materials. USBM input into mining management and regulations is essential because of the Bureau's mission, knowledge of mining, and environmental experience. The latter includes prior work that characterized the radium content of phosphogypsum stockpiles in Florida and determined that radium was not leached from these wastes (1-2).³ The USBM has also performed extensive investigations of other phosphate wastes (3), acid mine wastes (4-5), mining and mineral wastes (6), and a phosphate slag stockpile of the Tennessee Valley Authority (TVA) (7).

For this current study, samples were obtained from Kerr-McGee Co., a producer of rutile from ilmenite, in Mobile, AL. The waste material from this operation is contained in a ferric oxide waste disposal pond; the sludge is primarily ferric oxide and the supernatant is primarily weak hydrochloric acid. Samples from this site were used only to test the application of oxidation-reduction potential (ORP) and pH measurements to an actual waste.

The USBM also entered into a memorandum of agreement with Interstate Lead Co., a secondary lead producer, at Leeds, AL, to investigate possible lead contamination. Waste material from Interstate Lead Co. had been used as a landfill at an off-site location. Stream and well waters from the landfill site, referred to in this report as the "lead processing waste site," were investigated, and the species of lead present were estimated.

A major gap in the literature of contamination by mining and mineral processing wastes is that of identification of the chemical species present. Knowledge of the chemical species present is very important in order to predict the toxicity and result of pollutants on the environment. The importance of chemical species and their determination and interactions in freshwater, marine, and terrestrial systems are thoroughly discussed in an extensive report from a 1984 symposium in Berlin, Germany, devoted entirely to "Speciation" in environmental processes (8).

Major crystalline components (greater than approximately 5 pct) of a solid waste can be determined by X-ray diffraction. Species of elements present in appreciable quantities in solutions have been identified by electrometric methods (9-10), Raman and infrared spectra (11), ion chromatographic determination of separated complexes (12), and selective extraction procedures (8). Some methods for identifying species are applicable to determining species in trace amounts, in the parts per billion concentration range, but any procedure to isolate or concentrate a species may change the form of the species initially present.

In this report we have assumed that the components in the systems investigated were in equilibrium, and that trace elements and their species had the same ORP and pH as the overall system. The ORP of some samples investigated remained constant within ± 0.6 pct over a 4-month period, indicating that equilibrium had been attained.

Pourbaix (13) published a very comprehensive atlas of diagrams of ORP versus pH for 90 elements. Krumbein and Garrels (14) classified natural sediments in terms of ORP and pH. Bass-Becking and others (15) examined 6,200 pairs of published data and concluded that at least 4,000 of these were not reliable. Faulty measurements and lack of understanding of the data led many to abandon ORP-pH measurements. Brookins published many ORP-pH diagrams of transuranic and actinide elements and of bismuth associated with the Oklo Natural Reactor, Gabon (16-17). Many assumptions were made about the system involved. Dragun's book in 1988 (18) contains a discussion of ORP-pH measurements and includes many ORP-pH diagrams. Collins (19), at the USBM's former Bartlesville Petroleum Research Center, described apparatus for the ORP-pH method applied to oilfield waters, but did not report results from its use. Champ and others proposed a sequence of reactions based on ORP thermodynamic principles and implied that the sequence could be used as a basis for geochemical exploration and for waste management (20). Even though the literature contains many examples, very few measurements of ORP-pH have been used to predict species found in mining and mineral processing wastes.

The formation of species that involve neither ORP nor pH, for example, $\text{Pb}^{+2} + \text{SO}_4^{-2} \rightarrow \text{PbSO}_4$, would not be directly evident from the ORP-pH measurements or diagrams. Species of major, minor, and trace elements in natural systems, with or without ORP-pH involvements, can be identified by computation of the equilibrium composition of the system. Numerous computations and computer programs such as PHREEQE and WATEQ4F have been written for this purpose (8, 12, 21-24).

³Italic numbers in parentheses refer to items in the list of references preceding the appendixes.

This report is concerned with determining the usefulness and limitations of ORP-pH measurements applied to investigations of mining and mineral processing wastes and with determining species of lead present in samples from the lead processing waste site. The methods and techniques for the ORP-pH measurements were investigated using known standard solutions made in the

laboratory, samples from the ferric oxide waste disposal pond site, and samples from the lead processing waste site. Reliable and reproducible data were obtained under conditions applicable to waste systems, and the application and limitations of these measurements are discussed. A brief discussion of a computational program to identify species of lead is presented.

PROCEDURE

OXIDATION-REDUCTION POTENTIAL AND pH MEASUREMENTS

The apparatus for the ORP-pH measurements consisted of an Omega pH-millivolt meter, model PHB-52, with a pH range of 0 to 14, a millivolt range of $\pm 1,999$, and resolutions of 0.01 pH, 0.1 °C, and 1 mV. The unit was ac or battery operated for use in the laboratory or field. An Orion Research Microprocessor Ionalyzer/901, capable of resolutions 10 times those of the Omega instrument, was also used. A platinum redox electrode, Orion 97-78-00, and an Omega model ORE-1311-U silver-silver chloride reference electrode, containing saturated potassium chloride, were interfaced with the pH-millivolt meter. The electrode potentials were referenced to the standard hydrogen electrode as reduction potentials, in accordance with recommendations of the Union of Pure and Applied Science (25-26). The reduction potential of the silver-silver chloride electrode was given as 199 mV at 25 °C (27) by the manufacturer of the electrode. However, Covington (28), in a research study, gave a potential of 198.1 mV at 25 °C and 165.7 mV at 60 °C, which were the values used in this report. A Lauda RM6 constant-temperature bath-circulator, with a range of -15 to 120 °C ± 0.01 °C, was used to maintain constant temperatures as needed. Reagent-grade chemicals and demineralized water were used, and the samples were analyzed for total concentrations of major, minor, and trace elements by inductively coupled plasma spectrography, atomic absorption spectroscopy, titration, and ion-chromatographic methods.

ORP and pH measurement procedures were developed to decrease the risk of faulty readings. The procedures involved iterative methods of data collection required to ensure consistent representative results. The potentials listed in this report are reduction potentials, which were the measured potentials of the platinum electrode against the silver-silver chloride reference electrode, plus the potentials of the silver-silver chloride electrode at the temperatures of measurement. The reduction potential of a silver-silver chloride electrode containing 0.1 molar potassium chloride is nearly a linear function of temperature (29); the temperature coefficient of the saturated potassium chloride electrode was not found in the literature.

Therefore, the potential (E) of the silver-silver chloride saturated potassium chloride electrode at any temperature (t) from 5 to 80 °C inclusive was calculated as a linear function of the two potentials cited above from reference 28. The results were

$$E = 198.1 - 0.9257 (t - 25) \text{ mV} . \quad (1)$$

STANDARD SOLUTIONS

Equimolar amounts of potassium ferrocyanide and potassium ferricyanide were used to prepare a series of nine standard solutions. The concentrations of the solutions varied from 0.0004 molar to 0.10 molar. The solutions were placed in the Lauda constant-temperature bath, and the ORP and pH of each solution were measured as a function of temperature from 5 to 80 °C in 5 °C increments. The system temperature was allowed to equilibrate before the pH and ORP measurements were taken. This series of measurements was repeated to verify reproducibility. Similar measurements were taken on potassium ferricyanide and potassium ferrocyanide solutions whose concentrations were not equimolar. Although the results of the tests on concentrations that were not equimolar are not included in this report, they confirmed the theory and the reliability of the methods used.

Other measurements taken included ORP as a function of pH. These measurements were made by adjusting the pH of the solution to 1.0 with concentrated sulfuric acid. The pH was increased by adding incremental amounts of 0.1 normal sodium hydroxide. After each addition, the solution was allowed to equilibrate and measurements of ORP and pH were recorded if the pH reading increased by more than 0.5 unit with the incremental dose.

FERRIC OXIDE WASTE DISPOSAL POND SAMPLES

Grab samples were obtained directly from the ferric oxide waste disposal pond. This pond was approximately 6 ha (15 acres) in area, 6 m (20 feet) deep, and inactive at the time of sampling. The same procedures for the ORP-pH measurements were followed for the field

FERRIC OXIDE WASTE DISPOSAL POND

The supernatant liquid from the Kerr-McGee ferric oxide waste disposal pond in Mobile, AL, is a dilute solution of hydrochloric acid, about 0.3 pct HCl, containing 12 pct Fe, 3.8 pct Mn, 2.8 pct Na, 0.05 pct Ca, 0.05 pct Al, and 0.04 pct Mg. At the existing conditions of this site, the measured pH values and reduction potentials of the sludge and supernatant liquid were the same. The average reduction potential was 683.8 mV and the pH was 1.09 at 25 °C. This potential was very stable and varied only 9 mV over a 4-month period. Comparison of this ORP-pH data point with the calculated ORP-pH diagram for the major component, iron, indicated that the predominant potential-determining chemical species present were the ferrous and ferric ions. When the sludge and the supernatant liquid were each treated with sodium hydroxide to adjust the pH, the reduction potentials of the supernatant liquid became slightly greater than those of the sludge, as illustrated in figure 2.

Figure 2 also contains an ORP-pH diagram for iron calculated from free energy data by Wagman and others (30) by the methods given in detail by Pourbaix (13). The standard state of the Wagman data is unit molality at 25 °C, and the calculations assume a 1:1 ratio between the activities of the oxidized and reduced species, also at 25 °C. Potentials are related to changes in the mole ratios or activities by

$$0.059 \log \frac{(\text{conc ox}) (\text{activity coeff ox})}{(\text{conc red}) (\text{activity coeff red})}$$

Thus, a 10-fold change in ratios of concentrations or activity coefficients results in a change of 0.059 V in the potential, which was experimentally observed. Comparison of observed ORP-pH data with calculated ORP-pH values is valid, keeping in mind that the lines for the calculated equilibria may be shifted about 0.1 V or 1 pH unit, but still retain their relative positions.

The reactions, B-1 through B-8 inclusive, and their associated reduction potentials and pH's for each calculated line in figure 2 are given in appendix B. The reduction potentials of the supernatant solution versus temperature are given in table 3 and illustrated in figure 3.

Table 3.—Reduction potentials of supernatant liquid from ferric oxide waste disposal pond from 5 to 70 °C

Temperature, °C	Reduction potential, mV	
	Observed	Calculated ¹
5	669.5	669.1
10	671.6	672.9
15	675.8	676.3
20	680.1	679.5
25	683.8	682.4
30	685.5	685.0
35	687.1	687.3
40	689.1	689.2
50	691.5	692.3
60	693.2	694.1
70	695.6	694.7

¹Equation A-2.

LEAD PROCESSING WASTE SITE

Table 4 gives the chemical analyses typical of the well and stream samples from the lead processing waste site. The elements and species listed make up about 99.9 pct of the total composition of the samples. The analyses of the well samples and of the stream samples for lead were by graphite furnace atomic absorption.

Table 5 gives the reduction potentials from 5 to 70 °C of the well and stream samples. Figure 4 illustrates these potentials for the well samples, and figure 5 illustrates these potentials for the stream samples. The potentials of the stream samples were approximately between those of well samples GJ-1 and GJ-2.

COMPUTATIONAL PROGRAM

Figure 6 shows the comparison between the literature values (33) and the program-calculated values for lead sulfate solubility in sulfuric acid. Table 6 gives the program-calculated molar concentrations of species of lead present in sample GJ-3 at pH 6.7, the pH of the sample as it naturally existed, the amount of each species as percent of total lead, and the logarithm of these percentages. Figure 7 illustrates these percentages from pH 1 to pH 14. Results similar to those shown in table 6 and in figure 7 were obtained for the other well water and stream samples.

Table 4.—Typical chemical analyses of well waters and stream waters from lead processing waste site¹

	Well water samples			Stream water samples	
	GJ-1	GJ-2	GJ-3	Upstream	Downstream
Cations, mg/L:					
Aluminum	17.0	6.7	12.0	0.4	0.3
Calcium	241.0	52.6	369.0	1.1	4.2
Iron	10.4	1.3	27.2	0.15	0.14
Lead	0.030	0.007	0.023	0.006	0.004
Magnesium . . .	45.6	13.8	92.2	0.9	1.4
Manganese . . .	1.13	0.21	4.99	0.03	0.03
Sodium	71.8	28.9	333.0	0.9	4.5
Anions, mg/L:					
Bicarbonate . . .	293.1	203.0	324.3	6.1	5.9
Chloride	21.4	22.3	171.0	1.1	2.1
Fluoride	0.12	0.17	0.09	0.28	0.35
Nitrate	0.45	0.36	0.72	0.84	0.73
Sulfate	619.0	31.0	1704.0	3.1	21.3
E, mV	444.7	428.5	482.5	443.4	448.7
pH	7.6	7.7	6.7	5.2	5.6

E Oxidation reduction potential.

¹Analytical values determined to the units shown.

Table 5.—Observed reduction potentials (in millivolts) of well and stream samples from lead processing waste site from 5 to 70 °C

Temperature, °C	Well water samples			Stream water samples	
	GJ-1	GJ-2	GJ-3	Upstream	Downstream
5	485	458	507	467	469
10	468	451	498	461	463
15	459	442	487	457	460
20	451	434	477	448	454
25	446	431	478	441	447
30	431	423	477	436	442
35	426	399	468	430	434
40	415	387	456	418	424
50	392	383	433	396	403
60	355	358	386	379	386
70	ND	297	344	344	347

ND Not determined.

Table 6.—Program-calculated lead species present¹ in well water sample GJ-3 at pH 6.7

Species	Concentration, molar	Percent of total lead	Logarithm of percent of total lead
Total Pb	1.110×10^{-07}	100.00	+2.000
Pb ⁺²	2.452×10^{-08}	22.09	+1.344
PbCl ⁺¹	4.745×10^{-09}	4.27	+0.631
PbCl ₂	3.598×10^{-11}	0.03	-1.489
PbCl ₃ ⁻¹	7.475×10^{-14}	0	-4.172
PbCO ₃	$<1.000 \times 10^{-38}$	0	<-29
PbSO ₄	$<1.000 \times 10^{-38}$	0	<-29
Pb(OH) ⁺¹	8.170×10^{-08}	73.60	+1.867
HPbO ₂ ⁻¹ ·H ₂ O . .	2.631×10^{-16}	0	-6.625
Pb ₃ (OH) ₄ ⁺² . . .	1.283×10^{-19}	0	-9.937
Pb ₄ (OH) ₄ ⁺⁴ . . .	$<1.000 \times 10^{-38}$	0	-29
PbO	$<1.000 \times 10^{-38}$	0	<-29
H ₂ PbO ₂	0.364×10^{-12}	0	-2.405

¹The minimum concentration reported by the program is 1.000×10^{-38} molar.

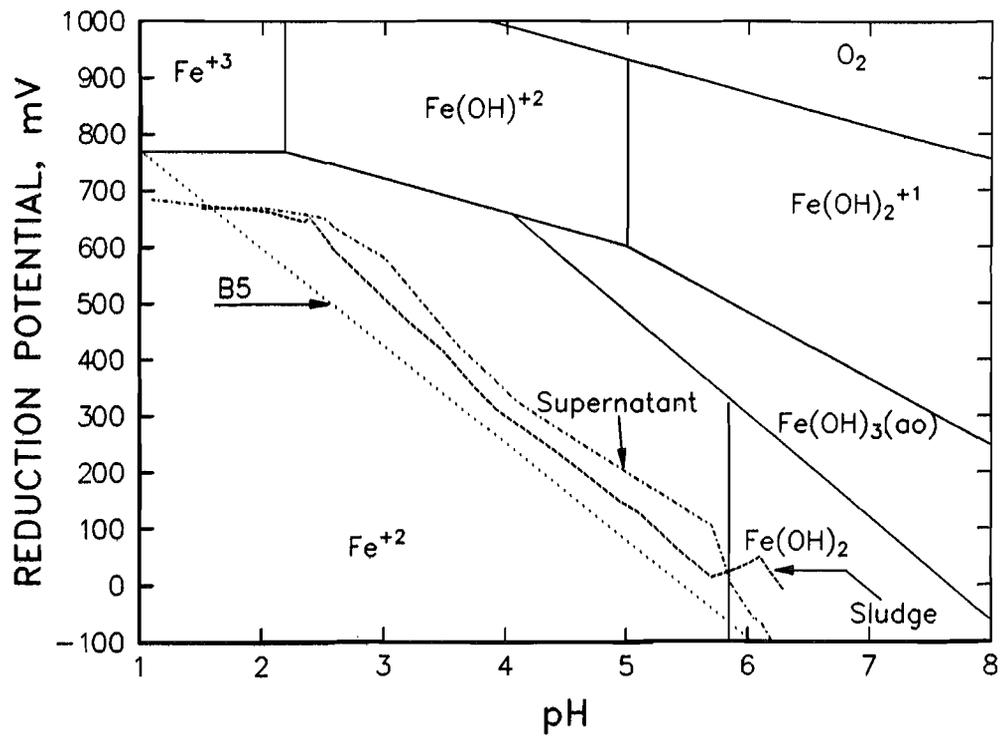


Figure 2.—Reduction potentials versus pH of sludge and of supernatant from ferric oxide waste disposal pond. ORP-pH diagram for iron species.

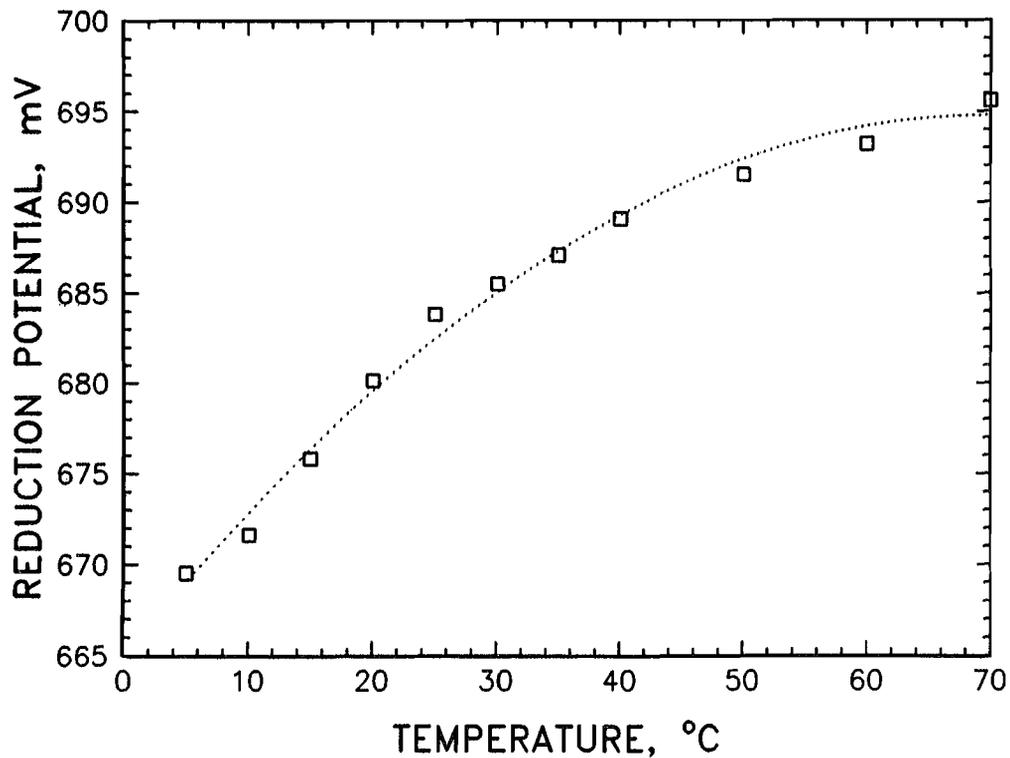


Figure 3.—Reduction potentials of supernatant from ferric oxide waste disposal pond from 5 to 70 °C.

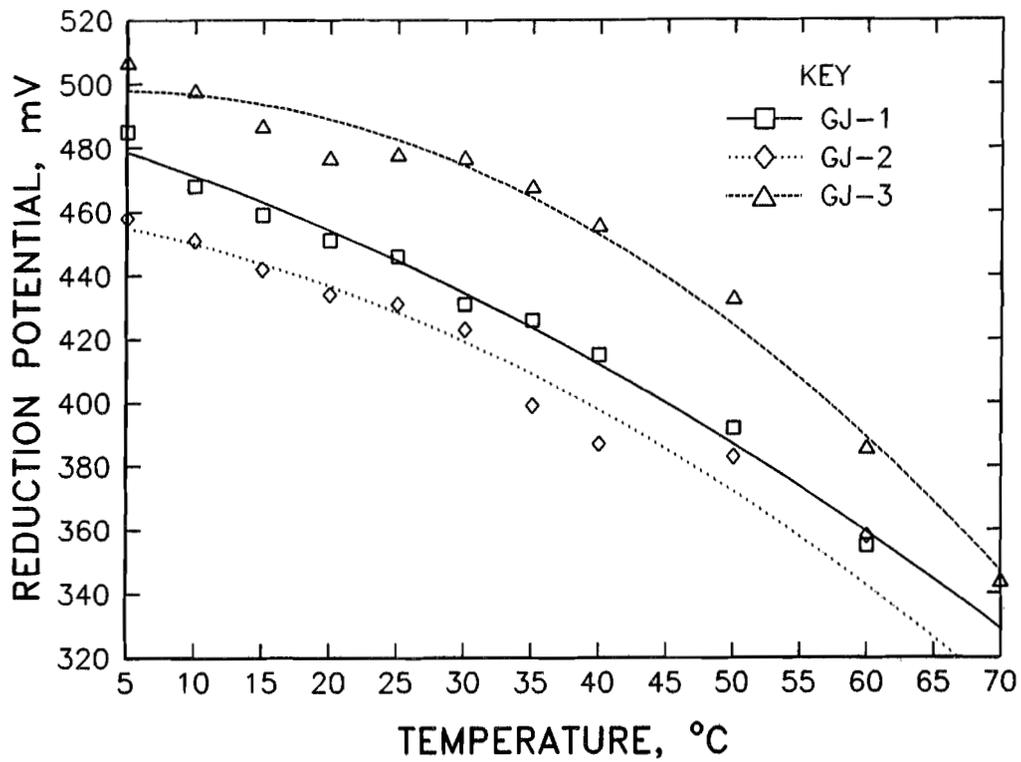


Figure 4.—Reduction potentials of well samples from lead processing waste site from 5 to 70 °C.

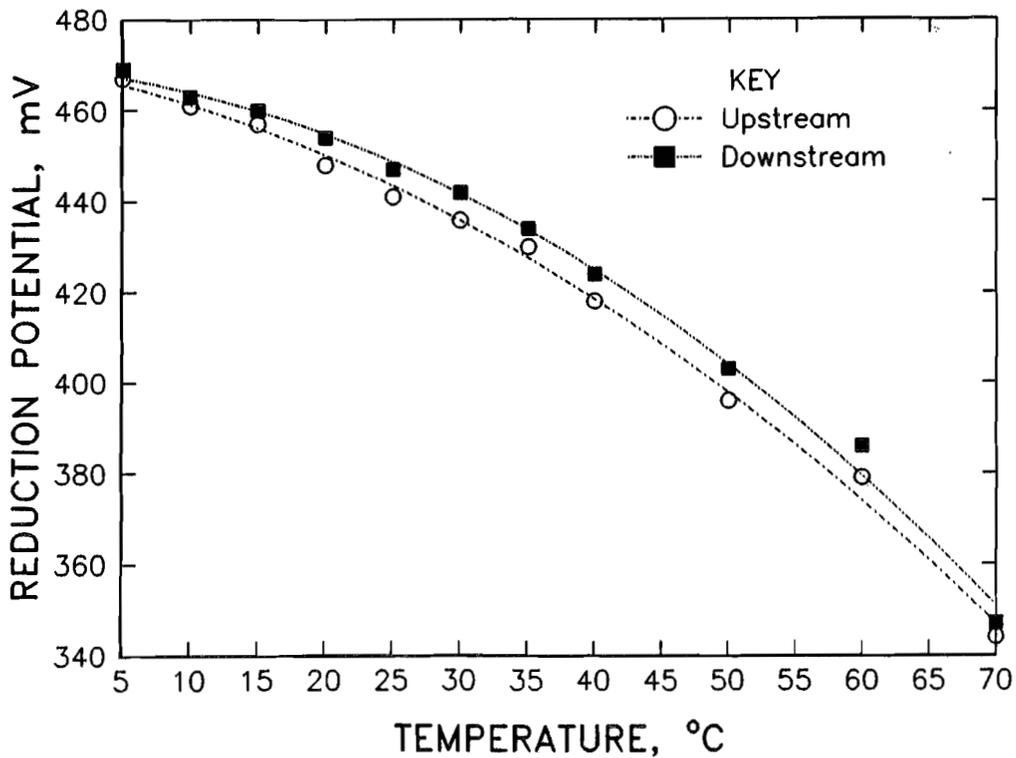


Figure 5.—Reduction potentials of stream samples from lead processing waste site from 5 to 70 °C.

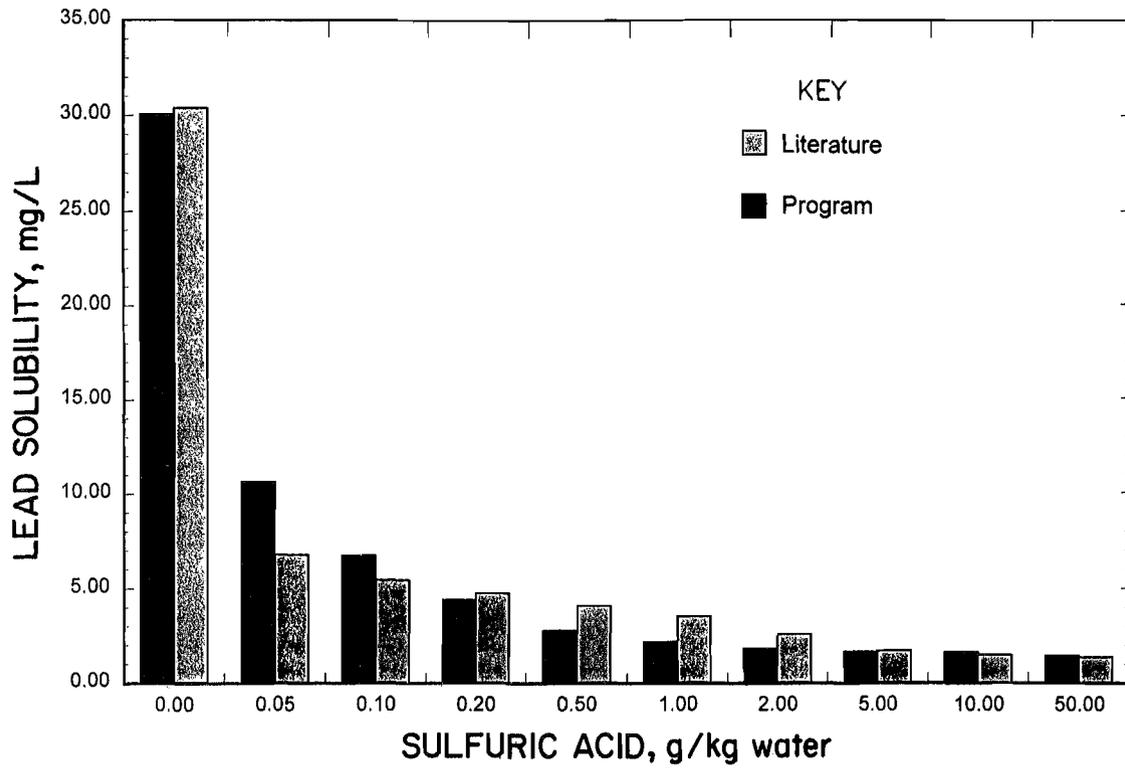


Figure 6.—Lead sulfate solubility, as lead, in sulfuric acid from program and from literature.

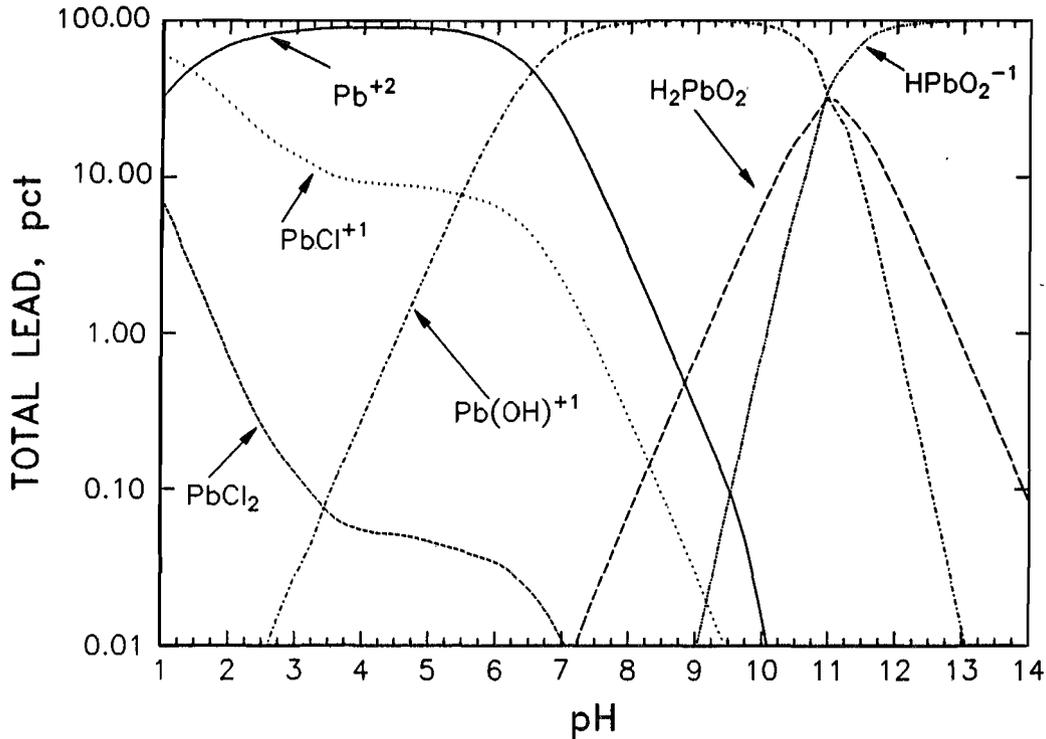


Figure 7.—Program-calculated lead species present in well water sample GJ-3, as percentage of total lead present.

DISCUSSION

REDUCTION POTENTIAL VERSUS DILUTION

The USBM investigated the usefulness and limitations of ORP-pH measurements applied to environmental studies of mining and mineral processing wastes. Therefore, the observed reduction potentials of solutions were determined in open beakers exposed to normal atmospheric conditions. The observed potentials of dilutions of potassium ferricyanide and ferrocyanide are shown in table 1. The paired t-test statistic for the agreement between the observed and reference data was 2.928 with a two-tailed probability of 0.0118, which showed poor agreement between the data. However the observed data of table 1 fit equation 3, obtained by least squares polynomial regression of the data:

$$E = 378.0 + 70.0 u^{0.5} - 22.7 u, \quad (3)$$

where u is ionic strength. When u was 0, the observed standard potential was 378.0 mV. Kolthoff and Tomsicek (32) reported a value of 356.0 mV from measurements of samples in nitrogen atmospheres. These authors state that solutions more dilute than 0.004 molar gave higher potentials in air than in a nitrogen atmosphere. The USBM results agree with this. Since the investigation was to seek practical applications of ORP-pH to mining wastes, and not to determine standard potentials, no measurements were made in nitrogen atmospheres. Measurements of potentials on dilutions of samples can yield information to calculate partial molar thermodynamic functions, which would help identify reactions involved in mixtures of components in solution. However, difficulty was encountered in obtaining consistent results at low concentrations for the standard solutions. Many environmental samples, especially surface waters, are already very dilute systems (15). It was concluded that measurements of potentials on dilution of environmental samples would not be a practical application of ORP-pH measurements to most mining and mineral processing wastes.

REDUCTION POTENTIAL VERSUS TEMPERATURE

As noted previously in the "Test Results" section, the reduction potentials versus temperature were measured for a solution of potassium ferricyanide and potassium ferrocyanide in a 1:1 mole ratio of 0.002 molar concentration (table 2); a ferric oxide waste disposal pond sample (table 3); and five lead processing waste site samples: well samples GJ-1, GJ-2, and GJ-3, and two stream samples,

upstream and downstream (table 5). These data were fitted by polynomial least squares regression to equations of potential, E , as functions of temperature, t . These equations, A1 through A7, are given in appendix A. The paired t-test statistic for the agreement between the observed and calculated data in table 2 was 18.41, with a probability of 0.0000. Statistically, the theoretical data and the observed data were different. Figure 1 shows how they differ. The paired t-test statistic for the observed and calculated data in table 3 was 1.03, with a probability of 0.3255. There is a 32.6-pct chance that the two data are the same, and this is reflected in figure 3. The same statistic and probability for data in table 5 were as follows:

GJ-1 versus GJ-2:	-5.23, 0.0005
GJ-1 versus GJ-3:	13.37, 0.0000
GJ-2 versus GJ-3:	14.36, 0.0000
Upstream versus downstream:	8.02, 0.0000.

The well waters differ from each other, and the upstream samples differ from the downstream samples. Figures 4 and 5 show these results. These are expected results because the locations of the well and stream samples differ.

On substituting 25 °C into equations A-1 through A-7, and into their first derivative with respect to temperature, the values of the formal potentials, E , and temperature coefficients, $\Delta E/\Delta t$ (at 25 °C), are obtained. These were used to calculate the free energy, ΔG , entropy, ΔS , and enthalpy, ΔH , from equations 4, 5, and 6:

$$\text{Free energy: } \Delta G = -nFE, \quad (4)$$

$$\text{Entropy: } \Delta S = nF(\Delta E/\Delta t), \quad (5)$$

$$\text{Enthalpy: } \Delta H = \Delta G + T\Delta S, \quad (6)$$

where n = number of electrons involved in reaction,

F = Faraday's constant = 96,487 coulombs per gram equivalent weight,

E = potential, mV,

and T = absolute temperature, K.

Table 7 contains values of E and $\Delta E/\Delta t$, ΔG , ΔS , and ΔH derived from the observed data, values of ΔG ,

ΔS , and ΔH calculated from NIST data (29), and E and $\Delta E/\Delta t$ derived from these values of ΔG and ΔS . The values reported in table 7 under the heading "Calculated" are calculated from the thermodynamic data corresponding to the reactions given in appendix B, equations B-1, B-9, B-10, B-11, and B-12.

The values of E , $\Delta E/\Delta t$, ΔG , ΔS , and ΔH (table 7) for the standard solution agree very well with the values calculated from equation B-9. The values of the ferric oxide waste disposal pond sample correspond to those calculated from equation B-1, with contributions from those calculated from equation B-10. The values of the well samples, GJ-1, GJ-2, and GJ-3, and the stream samples correspond to those calculated from equation B-10, with some contributions from those calculated from equation B-12. The reaction, equation B-11, may have only a minor influence on the test results because the calculated thermodynamic values from equation B-11 differ considerably from the observed values.

The results of these tests indicate that reduction potential measurements at different temperatures can aid in identifying reactions involved in an aqueous system. The

observed values of ΔG and ΔH were close to theoretical values calculated from possible reactions involved. Thus, these measurements give excellent estimates of the actual thermodynamics involved in a given reaction. This would be very useful information in development of a process for treatment of mining and mineral processing wastes.

REDUCTION POTENTIAL VERSUS pH

Figure 2 illustrates observed reduction potentials of the ferric oxide waste disposal pond sludge and supernatant samples versus pH, along with calculated boundaries between oxidation states of species. In the disposal pond sludge and supernatant, the reduction potential was 689 mV and the pH was 1.08. This would correspond to an equilibrium between Fe^{+2} and Fe^{+3} . The observed ORP-pH values are actually on boundaries between species, but the positions of the ORP-pH data points differ from calculation of the boundaries because of ionic strengths, activities, side reactions, and kinetic effects not used in the calculated boundaries. The observed data indicated the possible following equilibria.

Table 7.—Observed and calculated thermodynamic values at 25 °C for potassium ferricyanide and potassium ferrocyanide standard solutions, ferric oxide waste disposal pond sample, and lead processing waste site samples

Sample or equation	E, mV	$\Delta E/\Delta t$, mV/°C	ΔG , kJ/mol	ΔS , J/(mol•K)	ΔH , kJ/mol
OBSERVED ¹					
Standard solution	406.0	-2.498	-39.2	-241.0	-111.1
Ferric oxide solution	682.4	0.546	-65.8	52.7	-50.1
Well water samples:					
GJ-1	444.7	-1.968	-42.9	-189.9	-99.5
GJ-2	428.5	-1.738	-41.3	-167.7	-91.3
GJ-3	482.5	-1.462	-46.5	-141.1	-88.6
Stream water samples:					
Upstream	443.4	-1.426	-42.8	-137.6	-83.8
Downstream	448.7	-1.304	-43.3	-125.8	-80.8
CALCULATED ²					
Equation B-1	769.0	1.170	-74.2	112.9	-40.6
Equation B-9	390.8	-2.494	-37.7	-240.6	-109.4
Equation B-10	502.3	-1.772	-48.5	-171.0	-99.4
Equation B-11	228.8	-0.168	-118.6	-16.3	-142.9
Equation B-12	400.9	-0.474	-38.7	-97.0	-87.1

E Potential.
 $\Delta E/\Delta t$ Temperature coefficient.
 ΔG Free energy.
 ΔH Enthalpy.
 ΔS Entropy.

¹Derived from regression of observed data, equations A-1 through A-7, and equations 3, 4, and 5.

²Except for reaction B-1, calculated from formal potential of 390.8 mV (26) and NIST data (24).

From approximately pH 1 to pH 2.5 there is an equilibrium between Fe^{+2} and Fe^{+3} ions. From approximately pH 2.5 to pH 3.8 there is an equilibrium between Fe^{+2} and $\text{Fe}(\text{OH})^{+2}$ ions. In the $\text{Fe}(\text{OH})^{+2}$ ion the iron is in the +3 oxidation state. From approximately pH 3.8 to pH 5.7 there is an equilibrium between Fe^{+2} and soluble $\text{Fe}(\text{OH})_3$. From approximately pH 5.7 to pH 6.2 there is an equilibrium between Fe^{+2} and insoluble ferrous hydroxide, $\text{Fe}(\text{OH})_2$. Another line on the calculated ORP-pH diagram, marked "B5," represents the equilibrium between Fe^{+2} and insoluble $\text{Fe}(\text{OH})_3(\text{cr})$, equation B-5. The area of insoluble $\text{Fe}(\text{OH})_3(\text{cr})$, not indicated on figure 2, would be at ORP-pH values above and to the right of line B5. The observed data that would correspond to line B5 would be the data points from approximately pH 2.5 to pH 5.7. The potentials of the sludge sample were closer to the Fe^{+2} - $\text{Fe}(\text{OH})_3(\text{cr})$ line than those of the supernatant sample. These pH values also correspond to those above which $\text{Fe}(\text{OH})_3(\text{cr})$ precipitates, pH 2.3, and $\text{Fe}(\text{OH})_2$ precipitates, pH 5.5 (34).

The reduction potentials versus pH for sample GJ-3 from the lead processing waste site reflect equilibria among Fe^{+2} , $\text{Fe}(\text{OH})^{+2}$, and $\text{Fe}(\text{OH})_2^{+1}$. The ORP-pH diagram for this sample is similar to that of figure 2, but is not illustrated in a separate figure. The position of the ORP-pH values are shifted to higher pH values than those shown in figure 2.

As mentioned previously, an objective of this investigation is to explain the role, usefulness, and limitations of ORP-pH measurements in mining and mineral processing wastes investigations. The ORP-versus-pH measurements help define the system under investigation by providing experimental boundaries between possible species present. One important application of these measurements is determining the ORP and pH of the system as it normally exists in the environment. It is reasonable to assume that the components of the environmental samples investigated were in equilibrium, since the potentials of the samples remained constant for several months. Thus, the trace components have the same ORP-pH value as that of the major components, and possible species present of the major, minor, and trace components can be identified through the ORP-pH of the system. The ORP of the lead in the downstream sample was 448.7 mV and its pH was 5.6, the same as that of the bulk sample. This definitely excludes Pb^{+4} ions and indicates Pb^{+2} in equilibrium with its hydroxides or other species as discussed in the section on the computational program.

COMPUTATIONAL PROGRAM

Results obtained through the computational program are not accessible through ORP-pH measurements because ORP-pH data do not quantify species present. ORP-pH measurements reflect the important, potential-controlling reactions, which are assumed to be at equilibria among the major constituents present and not at equilibria among minor or trace elements present. Also, some reactions do not involve potential or pH changes. The program does not "prove" the existence of species present, but indicates concentrations of species that are likely to be present, which satisfy dozens of thermodynamic relationships. The program requires ionization and stability constants and solubility products of reactions of major, minor, and trace components, all of which are needed to establish equilibria in a system. It also requires summations of species to account for total concentrations of elements from an analysis. The selection of constants, reactions, and species to consider in the program was based on the chemistry involved and on species listed in the NIST data (30). The program results generally agree with analytical and literature data and are chemically reasonable. Calculated pH values from the program are very sensitive to analytical input data, and the program needs to recognize and compensate for unreasonable input data.

The lead solubilities in sulfuric acid (figure 6) agree well with literature values (33), verifying the accuracy of the program-calculated results. The results obtained by the program, as reflected in table 6 and figure 7, could not be readily obtained by other means. The total concentration of lead in the well sample GJ-3 was only 0.023 mg/L (1.11×10^{-7} molar), yet the concentrations of 13 species have been estimated down to 2×10^{-33} mg/L (1×10^{-38} molar).

The program was designed especially for lead. It could be expanded to consider other elements, but considering the time and effort involved, the authors decided to use the program WATEQ4F (24) for future work. Geochemical programs would be especially useful to determine concentrations of toxic species, such as chromate versus chromic ions. The application of ORP-pH measurements coupled with computational programs could have wide applications to mining and mineral processing waste investigations.

CONCLUSIONS

Rapid, potential-controlling reactions determine the reduction potentials and pH of aqueous systems. In this report we have assumed that the potential and pH environment of the total system is also that of major, minor, and trace elements present. This assumes that all species of elements present are in thermodynamic equilibria. This assumption is valid because ionic reactions in aqueous systems are rapid, and measurements of potential and pH of some of the samples showed that their values were constant over several months. Replication of measurements also gave consistent results, which would not have been true if a nonequilibrium, changing condition existed.

1. The ORP-pH values are useful to identify species of ions present, and thermodynamic values derived from

these measurements can help identify possible reactions at various pH values.

2. The ORP measurements versus temperature yield data from which good estimates can be made of free energy, entropy, and enthalpy involved in aqueous oxidation-reduction reactions. This information would be very useful in development of a treatment process to clean up a mining or mineral processing waste site.

3. Reactions of oxygen, when present from air or in solution, with water and with ions in solution contribute to the potentials of the samples.

4. The computational program can estimate species of ions present and their concentrations in samples. The presence of 13 species of lead in a sample containing 0.023 mg/L of lead was estimated from pH 1 to pH 14 by the program.

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APPENDIX A.—EQUATIONS FOR REDUCTION POTENTIALS VERSUS TEMPERATURE

Table A-1.—Equations for reduction potential versus temperature for standard solutions, ferric oxide waste disposal samples, and lead processing waste site samples

Sample	Equation ¹	Number
Standard solution	$E = 468.4 - 2.498(t)$	A-1
Ferric oxide solution	$E = 665.0 + 0.849(t) - 0.00605(t^2)$	A-2
Well water samples:		
GJ-1	$E = 485.5 + 1.299(t) - 0.01339(t^2)$	A-3
GJ-2	$E = 459.1 + 0.713(t) - 0.02050(t^2)$	A-4
GJ-3	$E = 497.4 + 0.261(t) - 0.03446(t^2)$	A-5
Stream water samples:		
Upstream	$E = 469.1 + 0.628(t) - 0.01597(t^2)$	A-6
Downstream	$E = 469.2 + 0.336(t) - 0.01936(t^2)$	A-7
Ferricyanide and ferrocyanide	$E = 453.15 - 2.494(t)$	A-8

¹E = potential, mV; t = temperature, °C.

Equation A-1 was derived by least squares regression of the observed reduction potentials in table 2 (in the main text). Equation A-2 was derived by least squares regression of the observed reduction potentials in table 3. Equations A-3 through A-7 were derived by least squares regression of the observed reduction potentials in table 5. Thus, results from equations A-1 through A-7 represent "smoothed" observed data.

Equation A-8 was derived as follows: Reference 31 gives a reduction potential of 390.8 mV for the reduction of a 0.002 molar solution of potassium ferricyanide to

potassium ferrocyanide at 25.0 °C. Reference 29 gives entropies of hydrogen (gas and ferricyanide and ferrocyanide ions, from which the change in entropy on reduction of ferricyanide to ferrocyanide was calculated, as $-240.642 \text{ J}/(\text{mol}\cdot\text{K})$. This value divided by 96.5 ($F/1000$) gives the temperature coefficient for this reduction, which was $-2.4936 \text{ mV}/^\circ\text{C}$. Thus the "theoretical" equation for the reduction of ferricyanide to ferrocyanide versus temperature is

$$E_t = 390.8 + (t - 25) (-2.4936) = 453.15 - 2.4936 t.$$

APPENDIX B.—REACTIONS AND EQUATIONS FOR REDUCTION POTENTIALS

Table B-1.—Reactions that define iron species equilibria boundaries for figure 2

Equilibrium equation ¹	Number
$\text{Fe}^{+3}(\text{ao}) + 1/2\text{H}_2 \rightarrow \text{Fe}^{+2}(\text{ao}) + \text{H}^{+1}$	B-1
$\text{FeOH}^{+2}(\text{ao}) + \text{H}^{+}(\text{ao}) + \text{e}^{-} \rightarrow \text{Fe}^{+2}(\text{ao}) + \text{H}_2\text{O}(\text{l})$	B-2
$\text{Fe}(\text{OH})_2^{+1}(\text{ao}) + 2\text{H}^{+}(\text{ao}) + \text{e}^{-} \rightarrow \text{Fe}^{+2}(\text{ao}) + 2\text{H}_2\text{O}(\text{l})$	B-3
$\text{Fe}(\text{OH})_3(\text{ao}) + 3\text{H}^{+}(\text{ao}) + \text{e}^{-} \rightarrow \text{Fe}^{+2}(\text{ao}) + 3\text{H}_2\text{O}(\text{l})$	B-4
$\text{Fe}(\text{OH})_3(\text{cr}) + 3\text{H}^{+}(\text{ao}) + \text{e}^{-} \rightarrow \text{Fe}^{+2}(\text{ao}) + 3\text{H}_2\text{O}(\text{l})$	B-5
$\text{Fe}(\text{OH})_2(\text{ao}) + 2\text{H}^{+}(\text{ao}) \rightarrow \text{Fe}^{+2}(\text{ao}) + 2\text{H}_2\text{O}(\text{l})$	B-6
$\text{FeOH}^{+2}(\text{ao}) + \text{H}^{+}(\text{ao}) \rightarrow \text{Fe}^{+3}(\text{ao}) + \text{H}_2\text{O}(\text{l})$	B-7
$\text{Fe}(\text{OH})_2^{+1}(\text{ao}) + \text{H}^{+}(\text{ao}) \rightarrow \text{Fe}(\text{OH})^{+2}(\text{ao}) + \text{H}_2\text{O}(\text{l})$	B-8

¹(ao) denotes an un-ionized substance, or an ion for which no further ionization is considered; (l) denotes a liquid; and (cr) denotes a crystalline solid.

Table B-2.—Calculated reduction potentials for reactions B-1 through B-5

Equation	E, mV
B-1	769
B-2	898 - (59.2)(pH)
B-3	1194 - (2)(59.2)(pH)
B-4	1357 - (3)(59.2)(pH)
B-5	971 - (3)(59.2)(pH)

Table B-3.—Calculated pH for reactions B-6 through B-8

Equation	pH
B-6	5.84
B-7	2.18
B-8	5.00

Table B-4.—Reactions used to calculate thermodynamic functions for table 7

Equilibrium equation ¹	Number
$\text{Fe}^{+3}(\text{ao}) + 1/2\text{H}_2 \rightarrow \text{Fe}^{+2}(\text{ao}) + \text{H}^{+1}$	B-1
$\text{Fe}(\text{CN})_6^{-3} + 1/2\text{H}_2 \rightarrow \text{Fe}(\text{CN})_6^{-4} + \text{H}^{+}$	B-9
$1/4 \text{O}_2 + \text{H}^{+1} + \text{Fe}^{+2} \rightarrow \text{Fe}^{+3} + 1/2\text{H}_2\text{O}$..	B-10
$1/4 \text{O}_2 + \text{H}^{+1} + \text{e}^{-} \rightarrow 1/2\text{H}_2\text{O}$	B-11
$1/4 \text{O}_2 + 1/2\text{H}_2\text{O} + \text{e}^{-} \rightarrow \text{OH}^{-}$	B-12

¹(ao) denotes an un-ionized substance, or an ion for which no further ionization is considered.