Negative pH and extremely Acidic mine waters from Iron Mountain, California

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Current Status: Oxidation of sulfide minerals in mine workings and mine wastes can result in the formation of extremely acidic waters and elevated concentrations of dissolved metals. The Richmond Mine at Iron Mountain, California was declared a U.S. E.P.A. Superfund site, because of the extremely high concentrations of metals (100's g/L) and acid (pH between 0 and -3.6) observed in waters derived from the mine workings. This project was initiated to quantify the geochemical mechanisms leading to the formation of these extreme concentrations, and methods to quantify the mine water pH for calculating mineral saturation indices and for developing remediation plans for the site.

Next Steps: Future research efforts will be directed toward evaluating mechanisms limiting the solubility of metals in hyperacidic mine drainage waters, methods for remediating these waters and a conceptual model applicable to hyperacidic mine waters in general.

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Negative pH and Extremely Acidic Mine Waters from Iron Mountain, California

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Extremely acidic mine waters with pH values as low as −3.6, total dissolved metal concentrations as high as 200 g/L, and sulfate concentrations as high as 760 g/L, have been encountered underground in the Richmond Mine at Iron Mountain, CA. These are the most acidic waters known. The pH measurements were obtained by using the Pitzer method to define pH for calibration of glass membrane electrodes. The calibration of pH below 0.5 with glass membrane electrodes becomes strongly nonlinear but is reproducible to a pH as low as −4. Numerous efflorescent minerals were found forming from these acid waters. These extreme acid waters were formed primarily by pyrite oxidation and concentration by evaporation with minor effects from aqueous ferrous iron oxidation and efflorescent mineral formation.

Introduction

The pH scale for aqueous solutions and natural waters is often given as 0−14 without any explanation. It is an arbitrary and convenient range because it places the value for neutrality of pure water at 25 °C (pH = 7.0) squarely in the middle. Values of pH less than 0.0 and greater than 14.0 not only are possible but also have been prepared frequently in chemical laboratories. A definition for pH, however, had not been accepted until the 1920s, and a definition of pH values below 1.0 had not been possible until the last 22 years. For practical purposes, pH has been defined as $-\log a_{H+}$, where $a_{H+} = \gamma_{H+} m_{H+}$, and the former National Bureau of Standards (NBS) established a set of conventions that limits measurements to $1 \le pH \le 13$ and to ionic strength, $I \le 0.1$ m dm^{-3} (*1*). The main limitations are the activity coefficient expression, the range of defined standard pH buffers, and interferences with the reversible response of the glass H^+-sensitive membrane electrode. We demonstrate in this paper that pH can be defined and measured below 0.0 and that waters of such low pH exist in nature.

The two dominant sources of extreme acidity in natural waters are magmatic gases that contribute HCl, HF, and H_2SO_4 (from oxidation of H_2S and SO_2) to vents, fumaroles, crater lakes, and hot springs in active geothermal areas (*2*) and the oxidation of pyrite which produces sulfuric acid (*3–5*). The most acidic pH values reported for environmental samples known to the authors are HCl−H_2SO_4 hot springs near Ebeko volcano with estimated pH as low as −1.7 (*6, 7*), the HCl−HF fumarolic condensates from Kilauea Iki estimated to have a pH = −0.3 (*8*), the lake waters from Poas crater, Costa Rica with an estimated pH of −0.89 (*9, 10*), and the acid crater lake of Kawah Ijen on the island of Java with estimated pH values in the range of 0.02−0.2 (*11*). Low values of pH for pore waters in sulfidic tailings and acid mine waters issuing from metal sulfide deposits have been reported in the range of 0.1−2.1 (*12–14*). Errors are suspected for some of the values below pH 0.5, however, because low pH standard buffers were rarely used for calibration and the methods of calibration are not described. In this report we present new data on acid mine waters from the undergroundworkings at Iron Mountain that have pH values as low as −3.6 with total dissolved solids concentrations as high as several hundred grams per liter. We document the methods of calibration and measurement and recommend them for use in ultra-acidic waters.

The opportunity to sample and analyze acid mine waters of extraordinarily low pH arose in 1990 after the U.S. Environmental Protection Agency had completed underground renovations in the Richmond Mine at Iron Mountain, a Superfund site near Redding, CA. Iron Mountain was mined for gold, silver, copper, zinc, and pyrite (in the production of sulfuric acid). It was the largest producer of copper in the State of California and the sixth largest copper producer in the U.S. Mining of the thick iron oxide (gossan) cap began about 1879 and underground mining for copper began about 1897. It was mined intermittently until 1962 when open-pit mining for pyrite ceased. The first EPA Record of Decision in 1986 recommended partial capping of the mountain to prevent rapidly infiltrating surface runoff from reaching the underground workings. The decision also recommended surface water diversions, and subsurface renovation was recommended to determine whether underground remediation was possible. The main ore bodies are massive sulfides consisting of 95% or more pyrite, with chalcopyrite, quartz, sphalerite, and lesser amounts of pyrrhotite and galena making up the remaining 5% of the ore (*15, 16*). The Richmond ore body is a single massive sulfide about 50 m high, 70 m wide, and almost 1 km long. The country rock is the Balaklala rhyolite, underlain by the Copley greenstone, both of Devonian age. Country rocks were hydrothermally altered at the time of mineralization and were subsequently altered by seawater to an assemblage of quartz, albite, chlorite, and muscovite (sericite) (*15, 16*). Acid mine waters draining the site have been observed since at least 1940; Richmond Mine portal effluent typically has pH values of about 0.5−1.0 and very high concentrations of SO_4 (20−108 g/L), Fe (13−19 g/L), Zn (0.7−2.6 g/L), Cu (0.12−0.65 g/L), As (34−59 mg/L), Cd (4−19 mg/L), and Tl (0.2−0.4 mg/L) (*14, 17*). In 1983, Iron Mountain was listed on the National Priority List under CERCLA regulations, and detailed site characterization and remedial investigations were begun. Treatment alternatives have been examined, and part of the

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TABLE 1. Molality, pH, and Activity Coefficients for Sulfuric Acid Standards

H_2SO_4 molality	pH[a]	γ_{H+}[a]	pH[b]	γ_{H+}[b]
0.146	0.86	0.76	0.87	0.74
0.734	0.09	0.89	0.18	0.73
1.497	−0.38	1.28	−0.18	0.81
2.319	−0.79	2.12	−0.46	0.99
2.918	−1.07	3.23	−0.64	1.20
3.657	−1.41	5.71	−0.85	1.58
4.485	−1.78	11.2	−1.08	2.24
5.413	−2.19	24.6	−1.32	3.37
7.622	−3.13	165.4	−1.87	8.96
9.850	−4.09	1200.	−2.37	22.96

[a] Values computed by PHRQPITZ (*25*) at 25 °C, using the MacInnes convention for scaling Pitzer single-ion activity coefficients. [b] Values computed by PHRQPITZ (*25*) at 25 °C, using unscaled Pitzer single-ion activity coefficients.

1986 Record of Decision was to conduct further subsurface investigations.

Experimental Section

The occurrence of Richmond Mine effluent waters with pH values less than 1 suggested that underground there may be seep waters with pH < 0 mixing with other waters with pH > 1. Hence, we were prepared to measure the pH of waters with negative pH before going into the field. Measurements of pH below 1.0 with a commercial glass membrane electrode may be subject to significant errors and uncertainties from several sources including the following: (1) inappropriate use of the conventional definition of pH, (2) strongly nonideal solution behavior, and (3) nonlinear and irreversible electrode response (which may include nonideal solution behavior, acid errors from asymmetry potential, residual liquid-junction potentials, and interfering reactions of sulfate with the reversible properties of the hydrated glass membrane (*1, 18*)).

Application of the Pitzer ion interaction theory to sulfuric acid (*19*) makes it possible to define pH values < 1 and to use a set of standardized sulfuric acid solutions as pH buffers for calibration purposes. The specific ion interaction theory, commonly referred to as the Pitzer equations for calculating activities and activity coefficients, considers aqueous ions to be mostly dissociated in solution instead of forming ion pairs and other complexes. Nonideal interactions between ions are accounted for by additive energy terms that are based on the virial series for intermolecular forces, analogous to that used for interacting gas particles in statistical mechanics (*20*). Both attractive and repulsive terms are considered, and mixing parameters allow for multicomponent interactions. Measurements of pH in H_2SO_4 solutions deviate less from ideal behavior than solutions of HCl, HNO_3, and H_3PO_4 acids (*21*). Galster (*22*) has noted that sulfuric acid shows the least tendency for acid errors among the strong acids (except phosphoric acid) and shows no sign of a leached layer in the glass membrane. Ferrous iron is the major cation in most acid mine waters. The addition of mixing parameters, for the $Fe(II)SO_4-H_2SO_4-H_2O$ system (*23*) to the Pitzer model, allows calculation of the pH of concentrated acidic ferrous-sulfate solutions of known molality.

Ten sulfuric acid standards were prepared (Table 1) for pH < 1.0 with molalities between 0.146 and 9.85 as determined by titration against anhydrous Na_2CO_3 as a primary standard. Molalities were checked by density determinations. The pH of these standard solutions was defined by the Pitzer method (*19, 24*), and the MacInnes convention was used for scaling individual ion activity coefficients using the computer program PHRQPITZ (*25*) (Figure 1). Defining individual ion activity coefficients

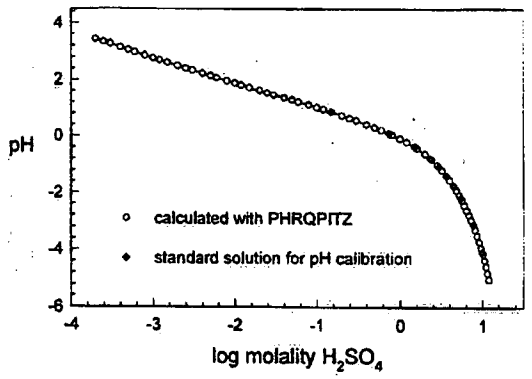

FIGURE 1. Curve for pH as a function of sulfuric acid concentration based on the Pitzer method using the PHRQPITZ code at 25 °C.

requires assumptions and choosing a theoretical approach. One attractive approach is simply to define pH as $-\log m_{H+}$ or to measure pH in terms of m_{H+} (*26, 27*) and thus avoid the ambiguities in the activity coefficient. Unfortunately, this approach harbors difficulties for acid mine waters because (1) analytical methods for protons tend to disturb the chemical equilibria, e.g., the acidity titration is neither very precise nor accurate owing to the irreproducible oxidation of iron and the hydrolysis and precipitation of metals that give poor inflection points, (2) determination of the "free" protons, as opposed to the "total" protons, will depend on a chemical model and its assumptions, a problem that becomes worse as the acidity increases, and (3) it would require a major departure from, and revision of, prior pH determinations and chemical modeling assumptions. A related approach would be to determine the pH by charge balance difference when the hydrogen ion is the major cation. This method would depend on a careful analysis but primarily suffers from being model-dependent. For example, sulfate (the major anion) is analytically determined as SO_4 but exists primarily in solution as HSO_4 (for pH < 2) complexed to varying degrees with metal cations. Another approach suggested by Knauss and others (*28, 29*) uses a liquid-junction-free cell containing specific ion electrodes to measure the activities of protons and chloride ions. This approach might be preferable for acid mine waters if there were a reliable sulfate, or bisulfate, ion-selective electrode, but none exists to the best of our knowledge.

Single-ion activity coefficient estimates for protons based on the Pitzer approach can be scaled with the MacInnes assumption (*25*) or left unscaled (*30*). We have used the MacInnes scaling because of its preference in brine calculations involving pH (*25, 31*), but we note that the pH determined will differ from unscaled pH values and that this difference increases with decreasing pH as seen in Table 1.

Two different electrodes were used for calibration: (1) an Orion Ross combination glass electrode with a 3.5 M KCl filling solution and (2) a Sargent-Welch combination glass electrode with a saturated (4.8 M) KCl filling solution. Temperature dependence was determined by measuring the electrode potentials of standards and samples at temperatures of 25, 35, 41, and 47 °C (Figure 2). In addition to the sulfuric acid standards, buffer standards of HCl–KCl (pH 1.0 and 2.0), potassium tetroxalate (pH 1.68), and potassium phthalate-HCl (pH 3.0) were used and found to be consistent and reproducible to within 0.02 pH units. Non-Nernstian response below pH 0.5 was observed for both electrodes. Acid errors were not an obvious problem as indicated by reproducible readings in the negative pH range although there was an initial adjustment necessary when changing to solutions of higher acid concentration. After completion of the field work, the response of the pH electrode assembly was assessed by

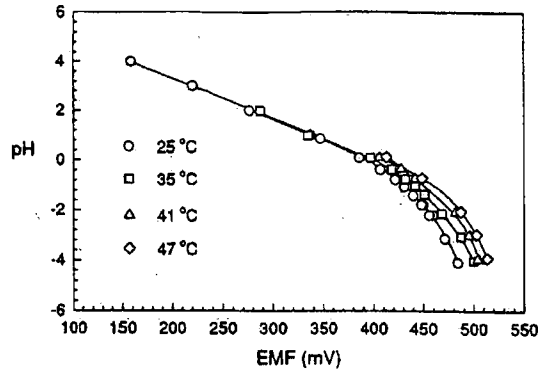

FIGURE 2. Calibration curves for Sargent-Welch combination electrode at four temperatures using pH as defined from Figure 1.

preparation of standard solutions containing known concentrations of pure H_2SO_4 and mixtures of H_2SO_4 and $FeSO_4$.

The Pitzer model (*20, 23–25*) was used to calculate the theoretical pH of the prepared standard solutions. If the unscaled Pitzer approach is used, pH values for sulfuric acid solutions begin to diverge from MacInnes scaled values at pH values below −0.5. For example, for a 5 molal sulfuric acid solution the MacInnes scaled pH would be −2, whereas the unscaled pH would be about −1.2.

Laboratory measurements were made to assess the effect of $FeSO_4$ addition on the response of the pH electrode to sulfuric acid solutions. Freshly prepared $FeSO_4 \cdot 7H_2O$ was added to normalized sulfuric acid solutions to cover a range in $FeSO_4$ concentration, the solutions were equilibrated, and the response measured while maintaining temperature, similar to the approach described by Blowes (*13*). The concentration of H_2SO_4 was varied from 0 to > 8 m, and the concentration of $FeSO_4$ was varied between 0 and > 2 m. The measured responses at 25 and 45 °C are presented in Figure 3A,B, a temperature range that spans most of the underground field conditions. Deviations of up to 20 mV were observed for samples ranging from 0 to > 2 m $FeSO_4$ for samples with approximately the same concentration of acid. This deviation in response can be attributed to either nonideal electrode effects or to interactions between ferrous iron, sulfate, or bisulfate ions. To account for the latter effect, the theoretical solution pH was calculated using PHRQPITZ (*25*). The known concentrations of $FeSO_4$ and H_2SO_4 were used as model input. The PHRQPITZ database was modified to include Pitzer ion interaction parameters to account for temperature-dependent interactions between Fe(II), HSO_4^-, and SO_4^{2-} (*23*). A comparison between the pH calculated using PHRQPITZ and the pH calculated using a sulfuric acid calibration curve and measured emf values indicates deviations in pH were < 0.5 pH units at 25 °C and < 0.3 pH units at 45 °C. The deviations were negative and were greatest for samples with the highest $FeSO_4$ and H_2SO_4 concentrations and the highest values of ionic strength, with the exception of positive deviations observed at very high H_2SO_4 concentrations (~8 m) and 45 °C. Therefore, we suggest pure sulfuric acid standards (Table 1) provide a good starting point for the measurement of pH in extremely acidic mine waters, such as those encountered in this study.

Residual liquid junction potentials were calculated for the experimental samples using the Henderson equation which was developed for weak electrolyte solutions (*1*). This equation provides information on the general trend in deviation expected for a residual liquid junction potential but may not provide an accurate estimate of magnitude. The calculated values indicate deviations in pH as a result of residual liquid junction potential approach +0.03 pH units for samples having pH > 0.5 and approach −0.2 pH units for the more acidic samples.

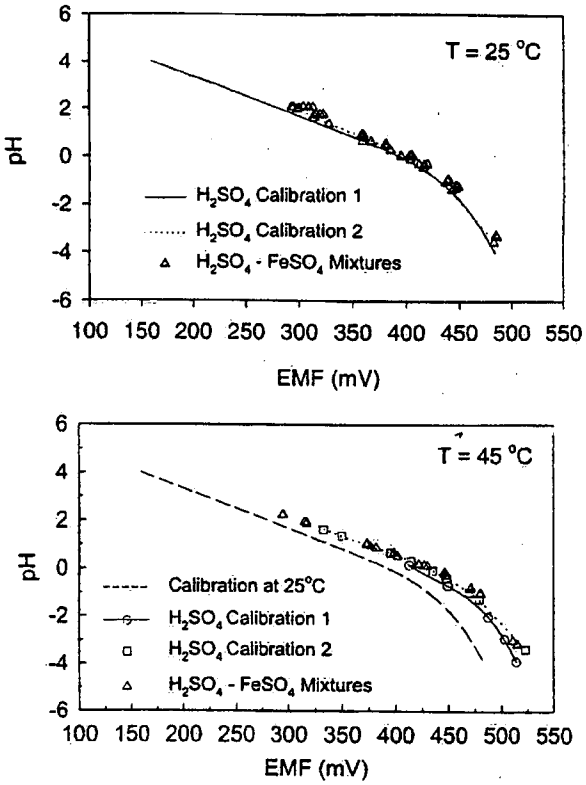

FIGURE 3. Electrode response for standards containing sulfuric acid and ferrous sulfate. (A) 25 °C and (B) 45 °C with sulfuric acid calibration curve at 25 °C (dashed line) and at 45 °C (solid line) shown as reference.

Water samples were collected as part of the subsurface reconnaissance at the Richmond Mine and were filtered on site by hand-pumping through 0.2 μm pore size membranes using polyethylene containers that hold 150 mL of solution, except for those with total dissolved solids greater than 200 g/L, which could not be filtered most likely due to instantaneous precipitation of metal–sulfate salts. Samples were diluted 1:10 with 0.1 M HCl for cation and Fe(II/total) determinations and 1:10 with distilled water for anion determinations. The field dilutions were essential because some undiluted samples precipitated a large mass of iron–sulfate crystals within minutes to hours after cooling to ambient temperatures and later chilling on ice. Four samples were collected in sterilized bottles for microbiological examination, which failed to find evidence of living *Thiobacillus ferrooxidans* in the waters of negative pH. *T. ferrooxidans* was cultured from a water sample with pH = 0.4 collected in October 1992 (I. Suzuki, written communication, 1993). The microbial results should not be considered a definitive statement that living microbes were not present, just that the conventional cultures were negative. Modifications in the culture medium may be required to successfully culture microbes from these extreme water compositions. Temperature, relative humidity, and pH were measured on site. Efflorescent minerals were collected in sealed plastic bags and in sealed glass jars. Several of the mineral specimens were later preserved in mineral oil.

Results and Discussion

Twelve acid mine waters were sampled in the underground workings of the Richmond Mine, ranging in pH from 1.5 to −3.6 (Table 2). The four samples with lowest pH values came from the following: (90WA109) drippings from a cluster of Zn–Cu melanterite [$(Fe^{II}_{.88}Zn_{.08}Cu_{.04})SO_4 \cdot 7H_2O$] stalactites in an open raise, (90WA110A) drippings in a large open stope,

TABLE 2. Acidic Mine Waters Found in the Richmond Mine, Iron Mountain, CA during September 1990[a]

sample code	pH	T(°C)	SO_4	Fe(total)	Fe(II)	Zn	Cu	Cd	Pb	As
90WA101	1.51	40.6	14	2.67	2.47	0.058	0.293	0.0004	0.0001	0.003
90WA102	0.52	29.9	NA	20.3	16.9	NA	NA	NA	NA	NA
90WA103	0.48	34.8	118	20.3	18.1	2.01	0.290	0.016	0.0036	0.056
90WA104	0.42	30.2	110	15.2	12.4	0.731	0.362	0.0048	0.0017	0.023
90WA105	0.42	33.4	130	22.3	20.4	2.26	0.218	0.018	0.0043	0.048
90WA106	0.52	37.8	118	21.2	19.4	2.04	0.301	0.016	0.0035	0.062
90WA107	0.46	47.1	130	20.6	18.8	2.28	0.209	0.018	0.0042	0.046
90WA108	−0.35	43.5	420	55.6	50.8	6.15	0.578	0.043	0.0043	0.169
90WA109	−0.7	38	360	86.2	79.7	7.65	2.34	0.048	0.0038	0.154
90WA110A	−2.5	42	760	124	34.5	23.5	4.76	0.211	0.012	0.340
90WA110B	−2.4	42	650	141	34.9	20.0	3.18	0.172	0.011	0.222
90WA110C	−3.6	46	NA	16.3	9.8	NA	NA	NA	NA	NA

[a] Concentrations are in grams per liter. NA = not analyzed.

(90WA110B) a pool of mine water collecting the drips of sample 90WA110A, associated with römerite [$Fe^{II}Fe^{III}_2(SO_4)_4 \cdot 14H_2O$] formation, and (90WA110C) a pool of mine water associated with rhomboclase [$(H_3O)Fe^{III}(SO_4)_2 \cdot 3H_2O$] formation. Abundant effloresences, stalactites, and stalagmites of these and other sulfate minerals were found throughout most of the accessible passages of the Richmond Mine (*32*). Minerals were identified by X-ray diffraction, optics, and microchemical tests and later confirmed by scanning electron microscopy-energy dispersive analysis (*33, 34*).

Chemical analyses for some of the major constituents in the mine waters are shown in Table 2. The pH values recorded here are the lowest yet reported anywhere that we know of for any acid mine water. The lowest pH of −3.6 is the lowest known for any water in the environment. The temperatures of these waters varied between 30 and 47 °C. The four lowest pH samples formed large crystalline masses of sulfate minerals upon cooling and therefore must have been at or above saturation with respect to these minerals when collected at the mine water temperatures. For example, water sample 90WA109 must have been near saturation with respect to Zn−Cu melanterite, because it was collected dripping from a large melanterite stalactite and an undiluted sample precipitated a large mass of melanterite crystals on cooling. Similarly, samples 90WA110A and B precipitated römerite and sample 90WA110C precipitated rhomboclase upon cooling. Heating and cooling of these samples has shown that the precipitation of melanterite is quickly reversible and can be used to determine the temperature dependence of the solubility and trace-element partitioning of that phase (*35*).

Mine waters of negative pH at Iron Mountain, CA, have been affected by at least four processes: (a) acid generation by pyrite oxidation, (b) concentration of H^+ and other ions by evaporation, (c) consumption of H^+ during oxidation of Fe(II) to Fe(III), and (d) acid production or consumption during efflorescent mineral formation.

Sulfuric acid is produced by the oxidation of pyrite according to the reaction

$$FeS_2 + 14Fe^{3+} + 8H_2O \rightarrow 15Fe^{2+} + 2SO_4^{2-} + 16H^+ \quad (1)$$

Considerable evaporation occurs in the underground mine waters at Iron Mountain due to the thermal energy released from reaction 1. Water temperatures as high as 47 °C were measured, and higher temperatures probably occur farther underground in inaccessible parts of the mine.

Process (c) consumes acidity at pH < 2 according to the reaction

$$Fe^{2+} + {}^1/_4O_2 + H^+ \rightarrow Fe^{3+} + {}^1/_2H_2O \quad (2)$$

because hydrolysis of Fe(III) is minimal.

The effect on solution pH from process (d) depends on the stoichiometry of the secondary sulfate salts formed. Melanterite, coquimbite, rhomboclase, copiapite, and jarosite have all been found to form as secondary salts at Iron Mountain. Formation of the simple salts melanterite and coquimbite by the reactions

$$Fe^{2+} + SO_4^{2-} + 7H_2O \rightarrow Fe^{II}SO_4 \cdot 7H_2O \quad (3)$$

$$2Fe^{3+} + 3SO_4^{2-} + 9H_2O \rightarrow Fe^{III}_2(SO_4)_3 \cdot 9H_2O \quad (4)$$

have no direct effect on pH but may have an indirect effect through changes in sulfate−bisulfate speciation. Formation of rhomboclase by the reaction

$$Fe^{3+} + 2SO_4^{2-} + H^+ + 4H_2O \rightarrow (H_3O)Fe^{III}(SO_4)_2 \cdot 3H_2O \quad (5)$$

will remove acidity from solution and store it in solid form. Copiapite and jarosite contain hydroxyl groups and therefore are considered basic salts, although the solutions from which they form are quite acidic; formation of these minerals releases acidity to solution by the reactions

$$Fe^{2+} + 4Fe^{3+} + 6SO_4^{2-} + 18H_2O \rightarrow Fe^{II}Fe^{III}_4(SO_4)_6(OH)_2 \cdot 16H_2O + 2H^+ \quad (6)$$

$$3Fe^{3+} + 2SO_4^{2-} + K^+ + 6H_2O \rightarrow KFe^{III}_3(SO_4)_2(OH)_6 + 6H^+ \quad (7)$$

Thus, formation of Fe(III) sulfate minerals has two effects on the acidity of the mine waters. During oxidation of iron, there is an irreversible loss of acidity, which tends to keep the pH from going much lower. During solidification of the Fe(III) sulfate minerals, particularly rhomboclase, the remaining acidity is stored in a solid form. Ferric sulfate salts within Iron Mountain appear to be most abundant in hydrologic "dead ends" where oxidation and evaporation processes have maximum opportunity to proceed, whereas melanterite, the most abundant ferrous sulfate salt, occurs in areas of recent pyrite oxidation where the ferrous iron has not had time to oxidize to ferric. We suggest the unusual water compositions found at Iron Mountain are dominated by pyrite oxidation (with waters at or near to melanterite saturation) and by evaporative concentration to give pH values less than zero. Efflorescent mineral formation plays a relatively minor role in controlling the pH.

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