

COMPARISON OF THREE METHODS TO MEASURE ACIDITY OF COAL-MINE DRAINAGE¹

Brent Means² and Tiff Hilton

Abstract. Although the Standard Methods 2310 hot peroxide acidity procedure is widely used for measuring the acidity of mine drainage, little work has been done to determine if “hot acidity” data actually describe the base requirement for neutralization of mine drainage. This study compared three methods for estimating the acidity of net-acidic waters emanating from the Manor, Millerstein, Ike, and Morris coal mines in Pennsylvania: Standard Methods 2310 hot acidity titration to pH 8.2 endpoint, cold acidity titration to treatment endpoint pH as high as 11.0, and calculated acidity. The results showed poor agreement between hot acidity and calculated acidity for three of the four waters. For two of the waters, Mg hydrolysis during the hot-acidity titration indicated greater acidity than that computed based on pH and dissolved Fe, Mn, and Al. The poor agreement for the other water resulted from incomplete hydrolysis of Mn during the hot acidity titration. The agreement between the acidity measured by the treatment acidity titration and the other two acidity methods was within 16 mg/L (as CaCO₃) for the Manor and Millerstein waters, but greater than 200 mg/L (as CaCO₃) for the Ike and Morris waters. The fair agreement between all methods for Manor and Millerstein is a result of pH, Al, Fe, and Mn being the main source of acidity in the waters. The poor agreement between the acidity methods for the Ike and Morris waters is a result of the treatment acidity titration measuring a large amount of additional “acidity” at high pH from the hydrolysis of Mg and other constituents. While the exact sources of acidity measured by a treatment titration is unknown, results from PHREEQC aqueous speciation calculations showed that the formation of cation-hydroxyl complexes in the Morris water at pH 11.0 contributed 40 mg/L of acidity. The authors hypothesize that Mg hydrolysis and the formation of base-consuming complexes are the reason why acidity measured by treatment titrations at high pH is often greater than that measured by hot acidity titrations to pH 8.2 or 8.3. The authors also hypothesize that the neutralization of carbonic acid is the reason why the acidity measured by “cold” titrations at low to mid pH is often greater than that measured by hot acidity titrations. The results of this study have practical importance because they show hot acidity titrations should not be used to universally describe the acidity of mine drainage. This is especially true when estimating the acidity produced when Mg-rich mine drainage is chemically treated to high pH. This study also showed that over treating Mg-rich mine drainage not only increases chemical costs but also increases sludge production.

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²Brent Means, Hydrogeologist, U.S. Office of Surface Mining, 415 Market Street, Harrisburg, PA 17011 (bmeans@osmre.gov, Tel. 717-782-4036); Tiff Hilton, Mining Engineer, WOPEC Inc., RR2 Box 294B, Lewisburg, WV 24901 (wopec@charter.net, Tel. 304-645-7633).
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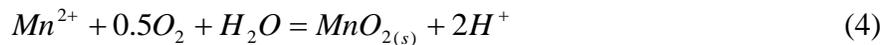
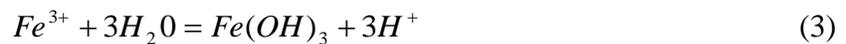
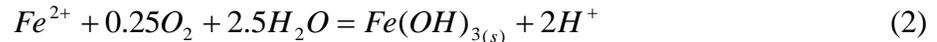
Introduction

It has long been recognized that acidity is an important measure for characterizing mine drainage (Rose and Cravotta, 1998; ADTI, 2000; Kirby, 2002). Various methods can be useful to determine the acidity of water and these methods fit into one of three categories: cold acidity, hot acidity, or calculated acidity. Both cold and hot acidity (A.P.H.A, 1998) are laboratory procedures that measure acidity by titrating water with a strong base (e.g. NaOH), while the calculated acidity method (Hedin *et al.*, 1994) determines acidity by using a pH measurement and dissolved metal concentrations. Coal-mining professionals in Appalachia have long considered a Standard Methods 2310 hot acidity titration performed to pH 8.3 (American Public Health Association, 1998) as the industry standard for measuring the acidity of mine drainage. This may have developed as a result of regulatory agencies, such as Pennsylvania Department of Environmental Protection (PADEP), requiring that acidity measurements (to 8.3) be included as part of the hydrologic data submitted in a mining permit (Pennsylvania Department of Environmental Protection, 2004). Results of hot acidity titrations are used to quantify the severity of mine drainage (Rose and Cravotta, 1998) and to calculate limestone consumption in passive treatment systems (Hedin *et al.*, 1994). Recent work by Kirby and Cravotta (2004) identifies the sources of acidity measured by a hot acidity titration. However, little work has been done to describe the acidity of mine drainage at titration endpoints higher than pH 8.3, which is consistent with active treatment methods, or to evaluate the appropriateness of ubiquitously using hot acidity results to describe the acidity of mine drainage. This paper addresses these points by comparing the results of applying cold, hot, and calculated acidity methods to four net-acidic discharges emanating from bituminous coal mines in Pennsylvania. First, a background section reviews both the geochemistry of acidity and the three acidity methods used in this study. Second, a site selection section discusses the reasoning behind choosing the four mine waters. Third, a discussion section presents the results of the applying the acidity methods to the four mine waters. Finally, practical implications of the results are discussed.

Background

Overview of Acidity in Mine Drainage

Mine drainage commonly contains elevated amounts of dissolved metals (Rose and Cravotta, 1998). In fact, U.S. Office of Surface Mining's (OSM) mine drainage inventory shows that 360 of 1470 post-primacy discharges in the Appalachian coal fields have aluminum, iron, or manganese concentration of greater than 50 mg/L (unpublished data). At favorable pH conditions, Al^{3+} , Fe^{2+} , Fe^{3+} , and Mn^{2+} metals participate in hydrolysis reactions and produce acidity:



Fe^{2+} and Mn^{2+} are redox dependent and are shown in equations (2) and (4) as precipitating as chemically oxidized solids, which are typically formed when passively treating mine drainage or after prolonged exposure of mine waters to atmospheric conditions in surface-water environments. During chemical treatment of mine drainage, Fe^{2+} and Mn^{2+} can precipitate as chemically reduced solids (Equations (5) and (6)); however, the acidity generated is identical to that expressed in Equations (3) and (4).



In addition to elevated metals, many Appalachian discharges are characterized by low pH. OSM's mine drainage inventory shows that 430 of 1470 post-primacy discharges in the

Appalachian coal fields have $\text{pH} < 3.5$ (unpublished data). Acidity from low pH (e.g. $\text{pH} < 3.0$) is substantial and can be calculated by Equation (7):

$$\text{pHacidity}(\text{mg / L of CaCO}_3) = 50,000 \times 10^{-\text{pH}} \quad (7)$$

In addition to metal acidity and pH acidity, bisulfate (HSO_4^-), carbonic acid (H_2CO_3), and hydrogen sulfide (H_2S) are known to contribute to the acidity of fresh mine drainage (Jageman *et al.*, 1988; Rose and Cravotta, 1998). Payne and Yeates (1970) also documented positive interferences from magnesium to hot acidity values.

Acidity Methods

Calculated Acidity

Equations (1) through (6) show the amount of acidity produced through hydrolysis is proportional to the concentrations of dissolved metals expressed as mole equivalents. For instance, Equation (1) shows that 3 moles of acidity are produced for every 1 mole of Al^{3+} participating in a hydrolysis reaction. This stoichiometry permits the development of an equation that uses dissolved aluminum concentration to estimate acidity generation from hydrolysis and precipitation.

$$\text{Al}^{3+} \text{ acidity} = 50 \times \left(\frac{3 \times \text{Al}^{3+}}{27} \right) \quad (8)$$

where Al^{3+} Acidity is the amount of acidity in mg/L of CaCO_3 , Al^{3+} is dissolved Aluminum concentration in mg/L, and the values of 27 and 50 are the molecular weight of aluminum and the conversion factor for expressing acidity as CaCO_3 , respectively.

Hedin *et al.*, (1994) combined Equation (7) with Equation (8) to yield an equation capable of estimating both metal (Fe, Al, and Mn) and pH acidity.

$$\text{Acidity} = 50 \times \left[\left(\frac{2 \times \text{Fe}^{2+}}{56} \right) + \left(\frac{3 \times \text{Fe}^{3+}}{56} \right) + \left(\frac{3 \times \text{Al}^{3+}}{27} \right) + \left(\frac{2 \times \text{Mn}^{2+}}{55} \right) + 1000 \times 10^{-\text{pH}} \right] \quad (9)$$

where Acidity = metal (Fe, Al, and Mn) and pH acidity as mg/L of CaCO₃ and Fe²⁺, Fe³⁺, Al³⁺, and Mn²⁺ are the analytical concentrations of dissolved metals in mg/L.

Equation (9) uses results from a field-measured pH coupled with results from a laboratory analysis for metals (dissolved) from a field-filtered sample. The accuracy of the acidity estimation for low -pH discharges is highly sensitive to the accuracy of the pH reading. For example, the pH contribution to acidity for pH 3.0 and pH 2.7 water is 50 mg/L (as CaCO₃) and 100 mg/L (as CaCO₃), respectively. This example illustrates the importance of using a calibrated pH meter to measure field pH when using Equation (9). A laboratory-measured pH should not be substituted for a field-measured pH since a lab pH could be unrepresentative if pH-altering chemical reactions, such as hydrolysis and exsolution of CO₂, occurred during sample transport (Cravotta and Kirby, 2004). It is also important that metal concentrations used in Equation (9) are from analysis of a field-filtered sample as opposed to an unfiltered or laboratory-filtered sample. It is common practice to consider chemical species contained in a field-filtered (0.45 μm) sample as dissolved, while an unfiltered sample contains both dissolved and suspended species. The use of metal concentrations from an analysis of an unfiltered sample could result in an artificially high calculated acidity, if the sample contained suspended matter (e.g. metal hydroxides and oxides) that is not actually a source of acidity (already hydrolyzed) but could not be distinguished from dissolved concentrations after sample preservation with acid. Table 1 illustrates this point.

Table 1. The effect of using metal concentrations from unfiltered samples in Equation (9)

	Results of Lab analysis for Al ³⁺ (mg/L)	Calculated Acidity from Al hydrolysis (mg/L CaCO ₃)
Sample Filtered	5	28
Sample NOT Filtered	10	56

For the purposes of comparing the results of the three acidity methods, net acidity was calculated by subtracting alkalinity from calculated acidity (Equation 9):

$$\text{Net Calculated Acidity (mg/L CaCO}_3\text{)} = \text{Calculated Acidity} - \text{Alkalinity} \quad (10)$$

Hot Acidity

The adjective “hot,” in hot acidity titration, refers to the boiling of the sample before the water is titrated with a strong base to a specified pH endpoint. Several published hot acidity procedures exist (APHA, 1998; ASTM, 1984; U.S.EPA, 1979), however, most laboratories in Pennsylvania use either Standard Methods 2310 (APHA, 1998) or EPA 305.1 (U.S. EPA, 1979) procedures (Means, unpublished data). Although the EPA (1979) procedure specifies the hot acidity titration endpoint pH of 8.2, and the APHA (1998) and ASTM (1984) procedures specify the endpoint pH of 8.3, all three methods employ consistent steps. Kirby and Cravotta (2004) offer a thorough discussion of the hot acidity titration procedure, resulting in an abbreviated discussion for this paper. The general hot acidity steps are to (1) titrate the water using a sulfuric acid to pH less than 4.5 to neutralize alkalinity; (2) add five drops of a 30% solution of hydrogen peroxide (H_2O_2) for metal oxidation; (3) boil the sample for two to five minutes to remove all carbonate species, accelerate oxidation and precipitation of metals, and then allow the sample to cool to room temperature; (4) titrate the water using a strong base to pH 8.3 to neutralize acidity; and (5) calculate hot acidity by subtracting the equivalent of acid added from the equivalent of base added and express hot acidity as mg/L of $CaCO_3$. For the purpose of this paper, there are two important points in this procedure. First, the procedure intentionally does not measure carbonate acidity (H_2CO_3). Secondly, step (5) yields a hot acidity result that characterizes water as net acidic (positive value) or net alkaline (negative value).

Treatment Acidity

The authors developed the treatment acidity procedure as a means to measure the base consumption for actual treatment of raw mine water to effluent limits. A treatment acidity titration is a variant of a “conventional” cold acidity titration. There are two general differences between a treatment titration and a cold acidity titration. First, unlike a conventional cold acidity titration, a treatment acidity titration is a group of individual titrations with each titration using a different pH endpoint. The person performing the titration determines the number of titrations and the range in pH endpoints by studying the raw water chemistry and estimating the approximate range in pH which the water will meet effluent standards (Table 2). At the end of each titration, acidity is calculated and the water is filtered and analyzed for dissolved metal concentrations. This process describes the behavior of metals as the pH of the water is increased

and provides the pH where effluent standards are met. The second difference is the point at which the titration ends. In most cases, a “conventional” cold acidity titration requires chemical be added until pH no longer drifts from the desired endpoint, whereas, a treatment titration is finished immediately after the pH endpoint is reached and pH is free to drift downwards as hydrolysis reactions continue to occur. This distinction stems from the difference in goals for each procedure. The goal of a cold acidity titration is to calculate the acidity of the water at a predetermined pH endpoint, while the goal of a treatment titration is to estimate the acidity neutralized when alkali chemical is added to the water by a full-scale treatment system. Treatment systems add sufficient treatment chemical to meet effluent standards, not a “stable” pH endpoint. As a result, the acidity measured from both methodologies will differ.

Table 2. These pH ranges do not necessarily correspond to the minimum solubility for each species, but rather correspond to the approximate ranges in pH needed to meet effluent standards for a specific metal (based on authors’ experience).

Metal	pH range needed to meet metal effluent limits
Fe ³⁺	3.5 – 4.5
Al ³⁺	4.5-6.0
Fe ²⁺	7.0 – 9.0
Mn ²⁺	9.0 – 10.5

The basic procedure for a treatment titration is as follows: (1) Pour a liter of raw water into a 2000 ml beaker set atop of a magnetic stirrer. (2) Use a Hach digital titrator and a 5N solution of laboratory grade sodium hydroxide (NaOH) to titrate the water to the target pH endpoint. Record the amount of NaOH consumed. (3) Filter approximately 125 ml of the titrated water using a hand pump and a 0.45-µm filter. Add HNO₃ until the pH of the sample is less than 2.0 to preserve the sample for laboratory metal analysis. (4) Repeat Steps 1-3 to various pH endpoints until you believe you have captured the point the water met effluent standards for metals concentration. (5) Analyze the acidified samples for metals of interest, such as iron, aluminum, manganese, magnesium, and calcium. (6) Use the laboratory analysis of metals concentration to determine the point at which the water meets effluent limits and calculate the treatment acidity.

Water Quality Collection and Analysis

Calculated Acidity

The following procedure was used to determine calculated acidities. In the field, mine drainage was passed through a 0.45- μm filter using a hand-held vacuum pump. Half of the water was preserved with reagent-grade HCl to $\text{pH} < 2.0$ for determining ferrous iron concentrations. The remainder of the water was preserved with reagent-grade HNO_3 to $\text{pH} < 2.0$. Cardan Laboratories of Northern Cambria, Pennsylvania determined metal concentrations using atomic absorption (APHA, 1998). At the time of sampling, pH was measured in the field using a Hydac pH meter calibrated in pH 4.0 and 7.0 buffer solutions. A sample was collected, placed on ice, and analyzed for alkalinity within 24 hours using a Hach alkalinity titration kit.

Hot Acidity

Unfiltered water samples were collected and placed on ice until hot acidity titrations were performed. During the manual hot acidity titrations, Cardan Laboratories performed additional steps than required by Standard Methods 2310 procedures (APHA, 1998). For example, after the hot peroxide boil a small portion of water was filtered and analyzed for metal concentrations to study the effect of the hot peroxide boil. Also, the water was titrated to pH endpoints 8.2 and 11.0 for the purpose of investigating sources of acidity at higher pH. At each pH endpoint, a portion of water was filtered and analyzed for metal concentrations to identify the sources of acidity. This paper refers to the hot acidity titration performed to pH 8.2 endpoint as “hot acidity (pH 8.2)” and the hot acidity titration performed to pH 11.0 endpoint as “hot acidity (pH 11.0).”

Treatment Acidity

Unfiltered water samples were collected and refrigerated and treatment acidity titrations were performed within 24 hours. Pennsylvania Bureau of Laboratories determined metal concentrations from the filtered water obtained at each of the different titration endpoints using inductively coupled plasma emission mass spectrometry (APHA, 1998).

Site Selection

The three acidity methods were applied to four net-acidic discharges emanating from Pennsylvania coal mines. The four discharges were selected because they possess a wide-range of water quality, which is desirable to study different sources of acidity (Tables 3 and 4). The discharges Ike, Millerstein, and Morris are from reclaimed surface mines and Manor emanates from an underground mine. Ike was selected because of its moderate metal concentrations and pH. Manor was selected because of its high ferrous iron concentration and low magnesium concentration. Millerstein was selected because of its moderate pH and low concentration of aluminum, iron, and manganese and moderate concentration of magnesium. Morris was selected because of its high concentrations of aluminum, manganese, magnesium, zinc, and sulfate, and low concentration of iron.

Table 3. Major cation and anion raw water quality data analyzed by Pennsylvania's Bureau of Laboratories [concentrations (mg/L) are from a filtered sample; pH is field measured]

Site	pH	Al	Ca	Fe ³⁺	Fe ²⁺	K	Mg	Mn	Na	SO ₄ ²⁻
Ike	4.18	5.95	150.0	<0.02	24.0	4.5	134.0	24.0	7.5	1341.2
Manor	2.98	33.0	190.0	0.03	326.0	2.8	57.0	4.7	3.81	1726.2
Millerstein	5.98	0.25	101.0	<0.02	4.12	2.8	113.0	5.2	46.0	1380.0
Morris	3.01	61.0	186.0	<0.02	0.75	3.8	460.0	57.0	18.0	4223.5

Table 4. Trace metal raw water quality data analyzed by Pennsylvania's Bureau of Laboratories [concentrations (mg/L) are from a filtered sample; pH is field measured]

Site	pH	As	Cd	Co	Cu	Ni	Se	Zn
Ike	4.18	<0.004	<0.01	0.34	0.01	0.48	<0.007	1.032
Manor	2.98	<0.004	<0.01	0.18	0.03	0.294	<0.007	1.285
Millerstein	5.98	<0.004	<0.01	<0.05	<0.01	0.11	<0.007	0.105
Morris	3.01	<0.004	<0.01	1.330	0.033	2.1	0.0074	4.122

Results

Table 5 shows the results of Cardan Laboratories analysis of the filtered raw water. These concentrations were used as input into Equation (9) to determine calculated acidity (Table 6). Tables 7 and 8 show how dissolved concentrations change at various steps during the hot acidity titration. The first column in Table 7 presents the dissolved concentrations for the raw water of Ike discharge, and the second column presents the dissolved concentrations after the hot peroxide boil. The third and fourth columns show the dissolved concentrations after the completion of the hot acidity titration to pH 8.2 and pH 11.0 endpoints. Tables 9 – 12 show the results of the treatment acidity titrations. These tables show the changes in dissolved concentrations as the raw water is incrementally titrated to numerous pH endpoints, filtered, and analyzed for dissolved metals. These tables also show the corresponding acidity for each incremental titration. The bolded rows in these tables represent the titration that resulted in (approximately) meeting effluent standards defined by Pennsylvania regulations. Table 13 provides a summary of the results for each acidity method.

Discussion of Results

Table 13 shows that the hot acidity titrations performed to the endpoint pH of 11.0 produced the highest acidity values, followed by the treatment acidity titrations. The table also shows that calculated net acidities and hot acidities (pH 8.2) are more similar than treatment acidities and hot acidities (pH 8.2). The acidity methods that produced similar results are measuring the same sources of acidity, whereas methods that produced different results are measuring different sources of acidity. In order to correctly apply each acidity method in the future, it is important to identify the sources of acidity that each method measures.

Equation (9) only accounts for acidity associated with pH, Al, Fe, and Mn components of a sample. Also, this method assumes complete hydrolysis of Al, Fe, and Mn. Table 13 shows that calculated net acidities and hot acidities (pH 8.2) for Ike are virtually identical, which suggests both methods measure the same sources of acidity.

Table 5. Raw water analyses performed by Cardan Laboratories.

	Ike Dissolved conc. of Raw water (mg/L)	Manor Dissolved conc. of raw water (mg/L)	Millerstein Dissolved conc. of raw water (mg/L)	Morris Dissolved conc. of Raw water (mg/L)
Field pH	4.22	3.02	5.98	3.01
Al	6.73	37.0	1.0	71.6
Ca	--	190.0	--	--
Fe	21.8	326.0	3.22	0.73
Mn	23.6	4.26	5.16	55.6
Mg	134.0	57.0	--	--
SO ₄ ²⁻	1341.2	1726.2	1380.0	4223.5

Table 6. Results of using Equation 9 to calculate net acidity.

Discharge Name	Calculated Acidity (mg/L CaCO₃)	Field Alkalinity (mg/L CaCO₃)	Net Acidity (mg/L CaCO₃)
Ike	122.4	2.0	120.4
Manor	845.0	0.0	845.0
Millerstein	20.7	16.0	4.7
Morris	549.4	0.0	549.4

Table 7. Hot Acidity titration for the Ike and Manor discharges [Dashes indicate not determined or not applicable].

	Ike				Manor			
	Dissolved conc. from raw water (mg/L)	Dissolved conc. after H2O2 boil (mg/L)	Dissolved conc. after Hot Acidity Titration to pH 8.2 (mg/L)	Dissolved conc. after Hot Acidity Titration to pH 11.0 (mg/L)	Dissolved conc. from raw water (mg/L)	Dissolved conc. after H ₂ O ₂ boil (mg/L)	Dissolved conc. after Hot Acidity Titration to pH 8.2 (mg/L)	Dissolved conc. after Hot Acidity Titration to pH 11.0 (mg/L)
Lab pH	4.53	3.13	8.2	11.0	2.98	2.43	8.2	11.0
Al	6.73	4.26	0.16	0.05	37.0	30.2	0.26	3.65
Ca	--	146.0	136.0	109.3	190.0	183.4	180.4	112.8
Fe	21.8	0.8	0.01	0.01	326.0	66.3	0.25	0.03
Mn	23.6	23.55	4.03	0.18	4.26	4.1	0.55	0.01
Mg	134.0	133.1	120.4	22.0	57.0	48.7	48.5	0.77
SO ₄ ²⁻	1341.2	1237.8	1165.0	1110.4	1726.2	1700.0	1587.5	1468.7
Hot Acidity*	--	--	123.0	720.0	--	--	880.0	1360.0
Lab Alkalinity*	2.0	--	--	--	0.0	--	--	--

*Expressed as mg/L of CaCO₃

Table 8. Hot Acidity titration for the Millerstein and Morris discharges [Dashes indicate not determined or not applicable].

	Millerstein				Morris			
	Dissolved conc. from raw water (mg/L)	Dissolved conc. after H2O2 boil (mg/L)	Dissolved conc. after Hot Acidity Titration to pH 8.2 (mg/L)	Dissolved conc. after Hot Acidity Titration to pH 11.0 (mg/L)	Dissolved conc. from raw water (mg/L)	Dissolved conc. after H2O2 boil (mg/L)	Dissolved conc. after Hot Acidity Titration to pH 8.2 (mg/L)	Dissolved conc. after Hot Acidity Titration to pH 11.0 (mg/L)
Lab pH	6.2	7.44	8.2	11.0	3.01	2.93	8.2	11.0
Al	1.0	0.24	0.11	0.07	71.6	54.71	1.1	0.15
Ca	--	111.2	106.0	99.1	--	195.4	189.8	109.76
Fe	3.22	0.01	0.01	0.01	0.73	0.64	0.03	0.03
Mn	5.16	3.2	3.2	0.12	55.6	43.0	21.2	0.11
Mg	--	119.8	116.7	39.5	--	477.4	424.3	9.34
SO42-	1380	1146.8	1098.3	1020.5	4223.5	3523.7	3175.0	2950.0
Hot Acidity*	--	--	16.0	1340.0	--	--	510.0	2840.0
Lab Alkalinity*	16.0	--	--	--	0.0	--	--	--

*Expressed as mg/L of CaCO₃

Table 9. Results of treatment acidity titration for Ike. Dissolved metal concentrations as a function of pH.

Titration pH endpoint	Al	As	Ca	Cd	Co	Cu	Fe ³⁺	Fe ²⁺	K	Mg	Mn	Na	Ni	Se	Zn	Treatment Net Acidity mg/L CaCO ₃	Annual Cost to treat a flow of 1 gpm**
4.18 (raw)	5.95	<0.004	150.0	<0.01	0.34	0.01	<0.02	24.0	4.5	134.00	24.0	7.5	0.48	<0.007	1.032		
5.5	1.0	<0.004	150.0	<0.01	0.314	<0.01	<0.02	19.0	4.5	138.0	24.0	25.0	0.485	<0.007	1.068	39	\$41
6.5	0.2	<0.004	150.0	<0.01	0.289	<0.01	<0.02	13.0	5.3	138.0	24.0	40.0	0.454	<0.007	0.936	70	\$74
7.0	<0.2	<0.004	144.0	<0.01	0.242	<0.01	<0.02	1.6	4.9	132.0	23.0	95.0	0.343	<0.007	0.486	207	\$218
8.0	<0.2	<0.004	141.0	<0.01	0.177	<0.01	<0.02	0.42	4.4	130.0	21.0	113.0	0.281	<0.007	0.435	232	\$244
9.0	<0.2	<0.004	141.0	<0.01	0.078	<0.01	<0.02	0.03	4.4	131.0	17.0	138.0	0.135	<0.007	0.337	305	\$320
10.0	<0.2	<0.004	133.0	<0.01	<0.05	<0.01	<0.02	0.04	4.7	124.0	5.0	190.0	<0.05	<0.007	0.334	444	\$467
11.0	<0.2	<0.004	128.0	<0.01	<0.05	<0.01	<0.02	0.03	5.6	97.0	0.1	243.0	<0.05	<0.007	0.318	589	\$616

*The bolded row represents the point at which the water approximately meets Pennsylvania effluent standards.

** Assumes the cost of a 20% NaOH solution is \$0.50/gallon

Table 10. Results of treatment acidity titration for Manor. Dissolved metal concentrations as a function of pH.

Titration pH endpoint	Al	As	Ca	Cd	Co	Cu	Fe ³⁺	Fe ²⁺	K	Mg	Mn	Na	Ni	Se	Zn	Treatment Net Acidity mg/L CaCO ₃	Annual Cost to treat a flow of 1 gpm**
2.98 (raw)	33.0	<0.004	190.0	<0.01	0.18	0.03	0.03	326.0	2.8	57.0	4.7	3.8	0.294	<0.007	1.285		
5.6	0.25	<0.004	--	<0.01	0.29	<0.01	<0.02	326.0	6.6	--	--	--	0.508	<0.007	1.824	369	\$388
7.0	<0.2	<0.004	172	<0.01	0.124	<0.01	<0.02	116.0	3.8	49	3.9	269.0	0.125	<0.007	0.486	678	\$713
9.0	<0.2	<0.004	172	<0.01	0.242	<0.01	<0.02	2.5	3.1	49	1.2	374.0	<0.05	<0.007	0.397	864	\$909
10.0	0.32	<0.004	203	<0.01	0.177	<0.01	<0.02	1.0	3.9	52	0.1	482.0	<0.05	<0.007	0.412	929	\$977
11.0	0.05	<0.004	155	<0.01	0.078	<0.01	<0.02	0.1	3.4	19	0.03	438.0	<0.05	<0.007	0.352	1024	\$1,077

*The bolded row represents the point at which the water meets Pennsylvania effluent standards.

** Assumes the cost of a 20% NaOH solution is \$0.50/gallon

Table 11. Results of treatment acidity titration for Millerstein. Dissolved metal concentrations as a function of pH.

Titration pH endpoint	Al	As	Ca	Cd	Co	Cu	Fe ³⁺	Fe ²⁺	K	Mg	Mn	Na	Ni	Se	Zn	Treatment Net Acidity mg/L CaCO ₃	Annual Cost to treat a flow of 1 gpm**
5.98 (raw)	0.25	<0.004	101.0	<0.01	<0.05	<0.01	<0.02	4.12	2.8	113.0	5.2	46.0	0.11	<0.007	0.105		
7.5	<0.2	<0.004	101.0	<0.01	<0.05	<0.01	<0.02	<0.02	3.0	113.0	4.9	55.0	0.07	<0.007	0.332	19	\$20
8.9	<0.2	<0.004	102.0	<0.01	<0.05	<0.01	<0.02	<0.02	3.6	115.0	4.9	60.0	0.06	<0.007	0.296	26	\$27
9.5	<0.2	<0.004	99.0	<0.01	<0.05	<0.01	<0.02	<0.02	3.0	110.0	3.7	63.0	<0.05	<0.007	0.255	40	\$42
10.5	<0.2	<0.004	105.0	<0.01	<0.05	<0.01	<0.02	0.05	3.3	111.0	0.019	92.0	<0.05	<0.007	0.284	96	\$101
11.0	<0.2	<0.004	102.0	<0.01	<0.05	<0.01	<0.02	0.036	3.1	107.0	0.013	101.0	<0.05	<0.007	0.272	135	\$142

*The bolded row represents the point at which the water meets Pennsylvania effluent standards.

** Assumes the cost of a 20% NaOH solution is \$0.50/gallon

Table 12. Results of treatment acidity titration for Morris. Dissolved metal concentrations as a function of pH.

Titration pH endpoint	Al	As	Ca	Cd	Co	Cu	Fe ³⁺	Fe ²⁺	K	Mg	Mn	Na	Ni	Se	Zn	Treatment Net Acidity mg/L CaCO ₃	Annual Cost to treat a flow of 1 gpm**
3.01 (raw)	61.0	<0.004	186.0	<0.01	1.330	0.033	<0.02	0.75	3.8	460.0	57.0	18.0	2.1	0.0074	4.122		
4.7	27.0	<0.004	189.0	<0.01	1.321	0.098	<0.02	0.07	4.1	460.0	56.0	113.0	2.06	0.0086	4.066	226.0	\$237
5.8	<0.2	<0.004	188.0	<0.01	1.117	<0.01	<0.02	<0.02	4.0	460.0	52.0	185.0	1.76	0.0071	2.168	401.0	\$421
7.0	<0.2	<0.004	184.0	<0.01	0.945	<0.01	<0.02	<0.02	3.8	452.0	50.0	0.2	1.57	0.0079	1.124	432.0	\$454
8.3	0.5	<0.004	191.0	<0.01	0.416	<0.01	<0.02	<0.02	3.9	457.0	41.0	229.0	0.78	0.0093	0.596	506.0	\$532
9.0	0.7	<0.004	174.0	<0.01	0.133	<0.01	<0.02	<0.02	3.8	442.0	30.0	263.0	0.21	0.0089	0.431	595.0	\$625
9.5	0.91	<0.004	174.0	<0.01	0.052	<0.01	0.034	<0.02	4.2	430.0	19.0	280.0	<0.05	0.0089	0.407	619.0	\$650
10.0	0.97	<0.004	173.0	<0.01	<0.05	<0.01	0.033	<0.02	4.1	412.0	4.6	349.0	<0.05	0.0079	0.398	749.0	\$786
11.0	<0.2	<0.004	173.0	<0.01	<0.05	<0.01	0.026	<0.02	6.0	194.0	0.1	726.0	<0.05	0.0112	0.373	1743.0	\$1,827

*The bolded row represents the point at which the water meets Pennsylvania effluent standards.

** Assumes the cost of a 20% NaOH solution is \$0.50/gallon

Table 13. Acidity determined by each of the methods.

	Calculated Net Acidity	Hot Acidity pH 8.2	Hot Acidity pH 11.0	Treatment Net Acidity
Ike	120.4	123	720	444
Manor	845.0	880	1360	864
Millerstein	4.7	16	1340	19
Morris	549.4	510	2840	749

Acidity expressed as mg/L of CaCO₃.

Identifying the sources of acidity measured by the hot acidity (pH 8.2) titrations is not as straight forward for Manor, Morris Millerstein as it was for Ike since differences between calculated net acidities and hot acidities exist. Therefore, the acidity produced during the hot acidity titrations was modeled by using difference in dissolved metal concentrations between the raw water and the end of the hot acidity titration at pH 8.2 and 11.0 as input into Equation (9). The amount of metal precipitation that occurred during the Hot Acidity titration to pH 8.2 and pH 11.0 is presented in Tables 7 and 8 for each of the four discharges. Table 14 presents the results of using data from Tables 7 and 8 as input into Equation (9) to model the acidity produced during the hot acidity titrations, first considering only the pH and concentrations of Fe, Mn, and Al, and then also considering the concentration of Mg. The results of Table 13 and Table 14 should be identical if complete hydrolysis of Al, Fe, and Mn occurred during the hot acidity titration. If the results in Table 14 are lower than the calculated acidities in Table 13, then incomplete hydrolysis of Al, Fe, or Mn occurred during the hot acidity titration.

Unlike Ike, hot acidity (pH 8.2) for the Morris water is 39.4 mg/L lower than calculated net acidity (Table 13). Likewise, the results of modeling the acidity produced from Al, Fe, and Mn during the hot acidity (pH 8.2) titration (Table 14) are lower than calculated net acidity in Table 13. Table 8 shows that 21.2 mg/L of Mn was still dissolved in the Morris water at the end of the hot acidity titration. A concentration of 21.2 mg/L of dissolved Mn equates to 38.5 mg/L of acidity. The residual Mn in solution at the end of the hot acidity titration (pH 8.2) explains why the hot acidity (pH 8.2) is lower than calculated acidity. The incomplete removal of Mn during the hot acidity titration is probably not a result of solubility constraints or insufficient addition of hydrogen peroxide. It is probably the result of the lab chemist prematurely ending the titration. This result is important because it shows hot acidity titrations (pH 8.2) do not always measure the maximum contribution of acidity from Mn.

Table 14. Results of using Equations (9) and (12) and data in Tables 7 and 8 to model acidity produced during the hot acidity titrations [Acidity expressed as mg/L of CaCO₃]

	Hot Acidity @ pH 8.2	Calculated Net Acidity @ pH 8.2 considering pH, Al, Fe, and Mn acidity	Calculated Net Acidity @ pH 8.2 considering pH, Al, Fe, Mn, and Mg acidity	Hot Acidity @ pH 11.0	Calculated Net Acidity @ pH 11.0 considering pH, Al, Fe, and Mn acidity	Calculated Net Acidity @ pH 11.0 considering pH, Al, Fe, Mn, and Mg acidity
Ike	123	113	177	720	143	609
Manor	880	846	881	1360	849	1082
Millerstein	16	4.3	17.2	1340	4.3	338
Morris	510	502	722	2840	546	2496

Unlike Ike or Morris, Table 13 shows that hot acidity (pH 8.2) results for Manor and Millerstein are higher than the corresponding calculated net acidity. Hot acidity (pH 8.2) is 35 mg/L higher than calculated net acidity for Manor and 11.3 mg/L higher for Millerstein. These results suggest that these hot acidity titrations are measuring another source of acidity not considered by Equation (9). At higher pH, magnesium and calcium can undergo hydrolysis and produce acidity, as explained below.



Empirical data from this study (Tables 7 & 8, Tables 9-12) and the authors' experience show Mg hydrolysis reactions are significant at pH > 10.0 and Ca solubility is not likely to be affected by hydrolysis reactions until pH > 11.0. The effect of the Mg hydrolysis process on Mg solubility is illustrated in Fig. 1. Fig. 1 shows, in theory, the concentration of Mg can decline over five orders of magnitude between the two hot acidity pH endpoints, from 10^{0.44} mol/L (66,980 mg/L) at pH of 8.2 to 10^{-5.0} mol/L (0.23 mg/L) at pH of 11. This solubility is consistent with that observed during some of the hot acidity titrations. Small amounts of Mg precipitation occurred during hot acidity titrations to pH 8.2 and large amounts of Mg precipitation occurred during hot acidity titration to pH 11.0 (Tables 7 & 8). Thus, Equation (13), which is consistent with Equation (8), can be used to model the acidity (mg/L of CaCO₃) resulting from Mg

hydrolysis at high pH. It should not be automatically assumed that reductions in Mg and Ca during acidity titrations resulted in acidity production. Reduction in Mg and Ca may be attributable to adsorption to precipitates or to the precipitation of calcium carbonate.

$$MgAcidity = 50 \times \left[\left(\frac{2 \times Mg^{2+}}{24} \right) \right] \quad (13)$$

While the results show that hot acidities for Manor and Millerstein are greater than calculated net acidities, the results also show Mg precipitated during the hot acidity titrations. Tables 7 and 8 show that 8.5 mg/L of Mg precipitated during the Manor Hot Acidity titration to pH 8.2 and 3.1 mg/L precipitated during the Millerstein titration. Equation (13) was used to evaluate whether the difference between the acidity measured by the hot acidity (pH 8.2) titrations and calculated acidity for Manor and Millerstein may be due to the hydrolysis of Mg. The hydrolysis of 8.5 mg/L of Mg results in 35 mg/L of acidity and hydrolysis of 3.1 mg/L of Mg results in 12.9 mg/L of acidity. As Table 14 shows, the addition of the Mg acidity to the calculated net acidity that only considers Al, Fe, and Mn hydrolysis results in acidity values that are almost identical to the hot acidities (pH 8.2) for Manor and Millerstein. The hydrolysis of Mg is the source of acidity that resulted in a higher hot acidity (pH 8.2) for Manor and Millerstein. These results suggest that for Manor and Millerstein a hot acidity titration to pH 8.2 mainly measured acidity due to pH, Al, Fe, and Mn but also measured a small amount of acidity from the hydrolysis of Mg. This is consistent with the work of Payne and Yeates (1970).

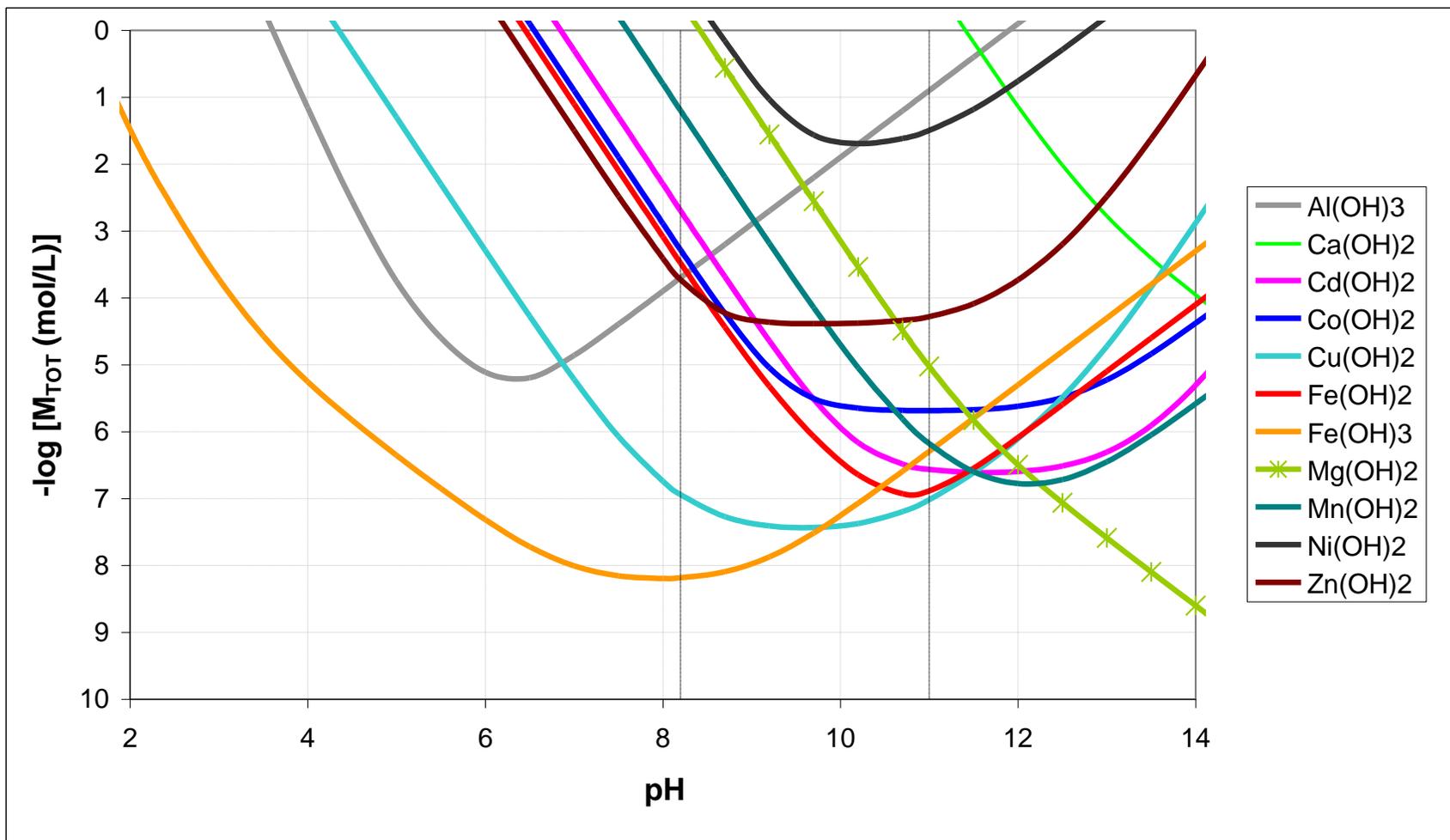


Figure 1. Comparison of metal hydroxide solubilities for constituents commonly found in acidic mine drainage (C. A. Cravotta, III, 2004, written commun.). Equilibrium constants from Ball and Nordstrom (1991) at 25 °C.

A similar process to that used above was used to try to identify the sources of acidity measured during the treatment titrations (Tables 9 – 12). It was assumed that a decline in metal concentration during the treatment titrations was a result of hydrolysis reactions. The amount of metal precipitation (via hydrolysis) that occurred between each treatment titration was calculated by subtracting the metal concentrations at the end of each treatment titration from the metal concentrations in the raw water (Tables 9 – 12). These results were then used as input into Equation (9) to calculate acidity production from pH, Al, Fe, and Mn. Tables 15 – 18 show the results of using Equation (9) to model the treatment titrations. The following discussion will focus on the bolded rows in Tables 9-12 and 15-18 since these rows represent the (approximate) point at which effluent standards are met. Tables 15-18 show that for all cases but Millerstein, the treatment titration acidity is considerably higher than the results using Equation (9). This is probably because only a small amount of Mn had to be precipitated for Millerstein to meet effluent standards, so the pH did not have to be raised as high as normally required for significant Mn removal. Tables 15-18 show that it is at high pH (e.g. pH > 9) that sources of acidity not considered by Equation (9) become significant (i.e. treatment acidities > calculated net acidities). The other waters had either high levels of Mn or Fe²⁺, which require high pH for precipitation by hydrolysis. Ike, Manor, and Morris did not meet effluent standards until the pH was raised to approximately 10.0, 9.0, and 11.0, respectively. As Tables 15, 16, and 18 show, the large difference between the calculated net acidity and the treatment titration acidity indicates that another source(s) of acidity, not considered by Equation (9) was present which resulted in much higher treatment titration acidities. Tables 9 – 12 show large reductions in Mg occurred during the Treatment Titrations at high pH. While the results of the Manor and Millerstein hot acidity titrations showed that Mg produced acidity during the hot acidity titrations, the results of Fig. 2 and Table 11 provide evidence that Mg produced acidity during the treatment titrations. Fig. 2 and Table 11 show that as the pH of the Morris water is raised from 10.0 to 11.0, treatment net acidity raises from 749 to 1743 mg/L (as CaCO₃), while the Mg concentration decreases by 218 mg/L. Therefore, Equations (9) and (13) were combined to evaluate whether Mg acidity

Table 15. Results of using Equations (9) and (12) and data in Table 9 to model acidity produced during the treatment acidity titrations for Ike [Acidity expressed as mg/L of CaCO₃]

Ike			
Titration pH	Treatment Net Acidity	Calculated Net Acidity @ considering pH, Al, Fe, and Mn acidity	Calculated Net Acidity considering pH, Al, Fe, Mn, and Mg acidity
4.18 (raw)	Raw		
5.5	39	39	39
6.5	70	54	54
7.0	207	76	85
8.0	232	82	99
9.0	305	90	102
10.0	444	111	153
11.0	589	121	275

Table 16. Results of using Equations (9) and (12) and data in Table 10 to model acidity produced during the treatment acidity titrations for Manor [Acidity expressed as mg/L of CaCO₃]

Manor			
Titration pH	Treatment Net Acidity (mg/L CaCO ₃)	Calculated Net Acidity @ considering pH, Al, Fe, and Mn acidity	Calculated Net Acidity considering pH, Al, Fe, Mn, and Mg acidity
2.98 (raw)	Raw		
5.6	369	182	182
7.0	678	611	644
9.0	864	818	851
10.0	929	822	843
11.0	1024	821	979

Table 17. Results of using Equations (9) and (12) and data in Table 11 to model acidity produced during the treatment acidity titrations for Millerstein [Acidity expressed as mg/L of CaCO₃]

Millerstein			
Titration pH	Treatment Net Acidity	Calculated Net Acidity @ considering pH, Al, Fe, and Mn acidity	Calculated Net Acidity considering pH, Al, Fe, Mn, and Mg acidity
5.98 (raw)	Raw		
7.5	19	7	7
8.9	26	7	7
9.5	40	9	22
10.5	96	16	24
11.0	135	16	41

Table 18. Results of using Equations (9) and (12) and data in Table 12 to model acidity produced during the treatment acidity titrations for Morris [Acidity expressed as mg/L of CaCO₃]

Morris				
Titration pH	Treatment Net Acidity	Calculated Net Acidity @ considering pH, Al, Fe, and Mn acidity	Calculated Net Acidity considering pH, Al, Fe, Mn, and Mg acidity	Calculated Net Acidity considering pH, Al, Fe, Mn, Mg, Mg(OH) ⁺ , Ca(OH) ⁺ , CaHSO ₄ ⁺ , and NaOH (aq) acidity
3.01 (raw)	Raw			
4.7	226.0	216	216	
5.8	401.0	373	373	
7.0	432.0	376	410	
8.3	506.0	391	2133	
9.0	595.0	410	485	
9.5	619.0	404	529	
10.0	749.0	430	630	
11.0	1743.0	442	1550	1590

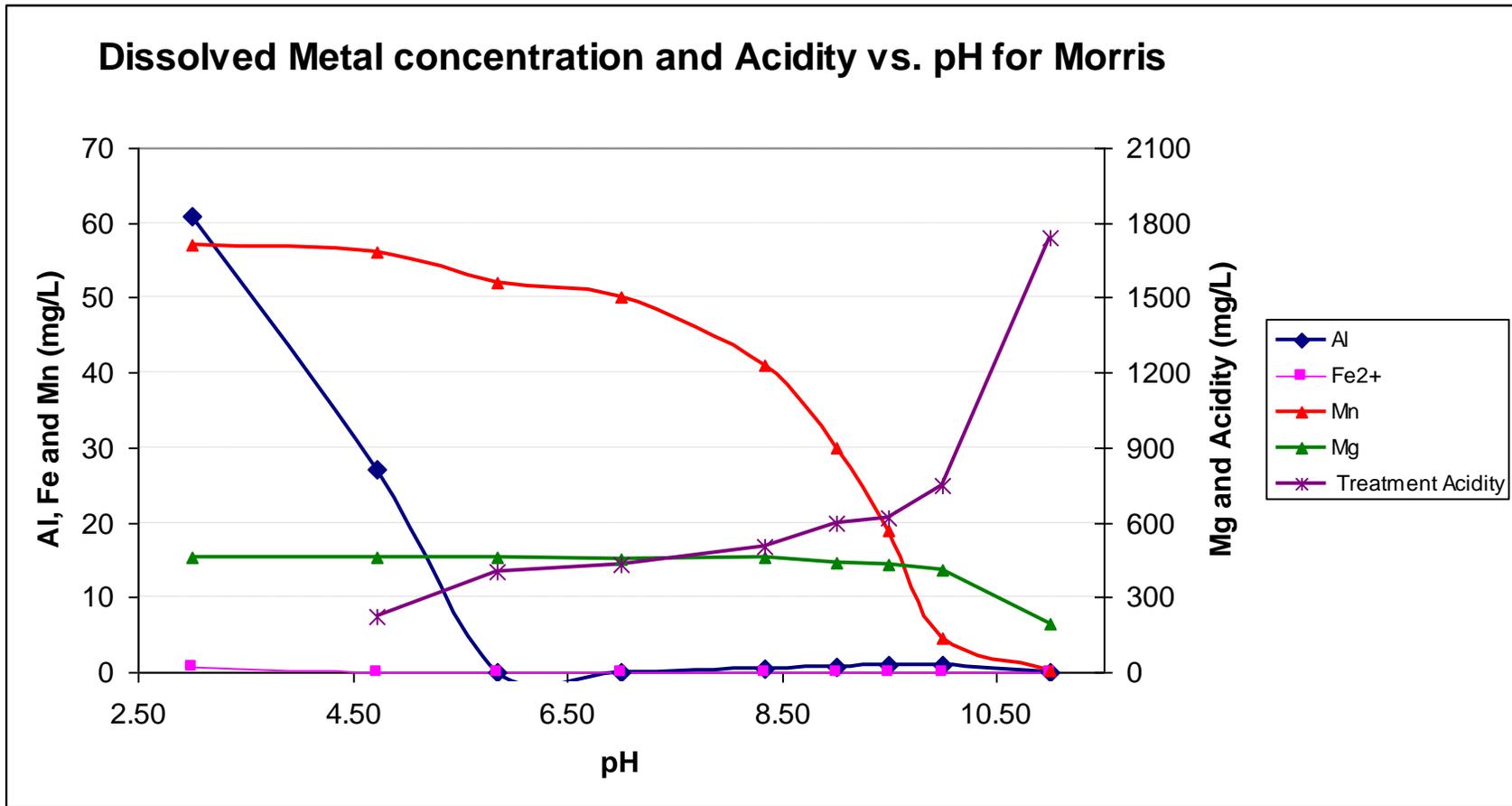


Figure 2. Results of treatment titration for the Morris water. Note the relationship between the sharp increase in acidity and the sharp decrease in Mg concentration at pH 11.0.

may explain the large difference between treatment acidities and calculated net acidities at high pH. The results in Tables 15 – 18 show the treatment titration acidities are still considerably higher than calculated acidities, even when considering Mg hydrolysis. This result suggests that additional sources of acidity, not considered by Equations (9) or (12), are being measured by the treatment titrations, especially at high pH. Other possible sources of acidity are the formation of cation-hydroxyl complexes at high pH. Waters like Morris that have large amount of Mg and Ca left in solution at high pH can consume hydroxyl to form $\text{Mg}(\text{OH})^+$, $\text{Ca}(\text{OH})^+$, and CaHSO_4^+ complexes. The base-consuming effect of these complexes may be the source of the unknown acidity. Other sources of acidity not accounted for by Equation (9) are bisulfate acidity and carbonate acidity.

While identifying the exact sources of acidity produced during all of the treatment titrations will be the focus of future work, the geochemical modeling program PHREEQC (Parkhurst and Appelo, 1999) was used to determine whether the formation of cation-hydroxyl complexes in the Morris water at pH 11.0 could account for the additional acidity measured by the treatment titrations. Table 18 shows the difference in acidity measured by the treatment titration at pH 11.0 and calculated acidity is 193 mg/L (as CaCO_3). Results of PHREEQC showed the base-consuming complexes at pH 11.0 were equivalent to 40 mg/L of acidity (as CaCO_3), which does not account for all of the unknown acidity. Further speciation calculations performed by PHREEQC show the raw water may have contained approximately 40 mg/L of bisulfate acidity. The authors hypothesize the remaining 113 mg/L of acidity may be from carbonate acidity (H_2CO_3). Lime was purposely added to the mine floor during the reclamation of the Morris site to aid in the prevention of acid mine drainage. The dissolution of the lime by acidic water would result in an increase of the partial pressure of carbon dioxide (pCO_2). While the amount of CO_2 in the Morris water was not determined by laboratory analysis, the pCO_2 would have to be approximately $10^{-1.42}$ to contribute approximately 113 mg/L of acidity (as CaCO_3).

The authors also believe that carbonate acidity is the reason why acidity measured by treatment titrations is often higher than calculated acidities at low to mid pH endpoints (Tables 15-18). Jageman *et al.* (1988) has shown that carbonic acid can be a considerable source of acidity in mine drainage. Since neither calculated acidity nor hot acidity consider carbonate acidity, treatment titrations should be used to estimate the total acidity that will need neutralized when chemically treating acid mine drainage to moderate or high pH.

Practical Considerations

This study shows that the acidity of mine drainage depends on the method used for determination and the titration endpoint. This is an important point because it proves that the commonly used Standard Methods 2310 hot acidity should not be used to universally define the acidity of mine drainage, as is commonly the case. The results of this study show that hot acidity (pH 8.2) titrations mostly measure acidity from pH, Al, Fe, and Mn, which are the regulated parameters in mine drainage. While mine drainage contains elevated levels of numerous different metals, Al, Fe, and Mn are the metals that are capable of generating considerable acidity within both the pH range of natural waters and the pH range of effluent water emanating from limestone-based passive treatment systems. Therefore, hot acidity (pH 8.2) measurements are suitable for assessing the impact to streams receiving untreated mine drainage and for predicting the non-carbonate acidity that will need neutralized when passively treating water with limestone.

This study also showed that hot acidity (pH 8.2) titrations and calculated net acidities primarily measure identical sources of acidity. Nevertheless, the authors caution against using Equation (9) as a unanimous substitution for a hot acidity titration. Low pH mine water containing high levels of sulfate is likely to contain considerable bisulfate. This source of acidity would be measured by a hot acidity titration but not considered by Equation (9). Misapplication of Equation (9) to waters containing considerable bisulfate would result in a mischaracterization of the acidity encountered in the pH range of natural waters.

Standard Methods 2310 hot acidity titration and calculated acidity (Equation (9)) are designed to measure specific sources of acidity. In fact, the Standard Methods procedure requires the addition of oxidants and boiling to ensure only the desired sources of acidity are measured. Treatment titrations indiscriminately measure acidity, including carbonate acidity, as pH is raised. As the results show, a treatment titration is the most appropriate method for measuring the acidity neutralized by chemical treatment systems treating to high pH. The results of a treatment titration are useful to operators of active treatment systems. For example, Table 11 shows the Morris water needs to be treated to (approximately) pH 10.0 to meet effluent standards. The consequence of over treating this water to pH 11.0 is severe. The acidity increases from 749 mg/L to 1743 mg/L as CaCO_3 and 219 mg/L of Mg precipitates. The effect of increased acidity and Mg precipitation is twofold. First, the annual cost to treat each gallon

per minute of flow with a 20% solution of caustic soda increases from \$786 to \$1,827 (assuming \$0.50/gal) (Table 12). Secondly, as Fig. 3 shows, the precipitation of an additional 219 mg/L of Mg results in a doubling in sludge volume. On the other hand, Table 10 shows that over treating the Manor water by two pH units will not double chemical costs, as is the case with Morris, since little Mg exists in the Manor water. Treatment titrations provide treatment plant operators with the information needed to increase treatment efficiency and reduce treatment costs.

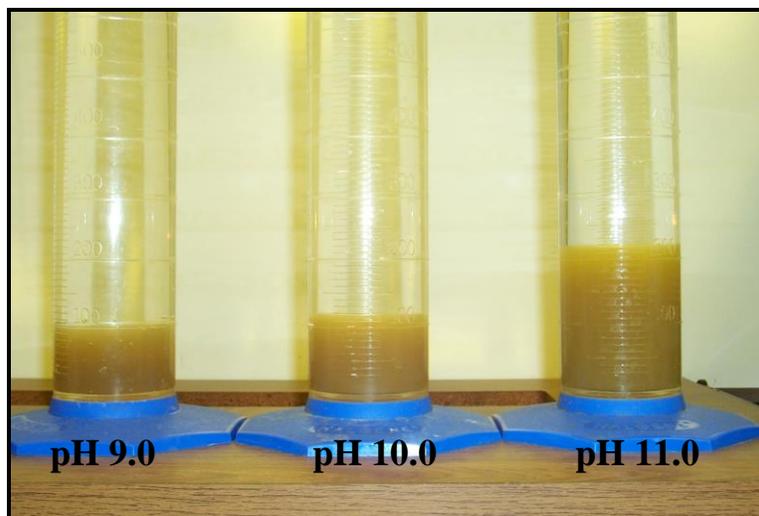


Figure 3. Sludge volumes for Morris discharge titration. Left to right, titrated to pH 9.0, titrated to pH 10.0, titrated to pH 11.0

An additional point worth mentioning is that every 1 mg/L of Mg is capable of producing 4.1 mg/L of acidity (as CaCO_3). This should be of great importance to operators treating mine water to high pH, since Mg is generally present in large amounts in mine drainage. The authors' experience is that mine drainage emanating from surface mines in Pennsylvania and West Virginia generally has greater than 80 mg/L of Mg whereas mine drainage emanating from underground mines generally has less than 80 mg/L of Mg. Over treating mine drainage may release large amounts of Mg acidity.

Conclusion

This study showed that hot acidity measurements should not be used to universally define the acidity of mine drainage. The acidity of mine drainage varies with the method used for

determination and with the titration endpoint. For the most part, this study showed Standard Methods 2310 hot acidity procedure and calculated acidity (Equation (9)) measure the same sources of acidity. These methods are suitable for estimating the noncarbonate (i.e. pH and metal) acidity encountered while using a limestone-based passive treatment system to treat mine drainage, but are not suitable for estimating the acidity encountered while chemically treating water at high pH. The results of the treatment titrations showed that large amounts of acidity are released at high pH. The data shows that the hydrolysis of Mg contributes to acidity at high pH; however, additional unknown sources of acidity exist and their identification will be the focus of future work. The authors hypothesize that the formation of cation-hydroxyl complexes may be responsible for the additional acidity. Data produced by the treatment titrations show that the behavior of Mg in mine water treated to high pH increases both chemical costs and sludge volumes.

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