ESTIMATING IRON AND ALUMINUM CONTENT OF ACID MINE DISCHARGE FROM A NORTH-CENTRAL PENNSYLVANIA COAL FIELD BY USE OF ACIDITY TITRATION CURVES

By Arthur N. Ott

U.S. GEOLOGICAL SURVEY

Water-Resources Investigations Report 84-4335

U.S. DEPARTMENT OF THE INTERIOR
March 3, 1849

Harrisburg, Pennsylvania

1986

UNITED STATES DEPARTMENT OF THE INTERIOR

DONALD PAUL HODEL, Secretary

GEOLOGICAL SURVEY

Dallas L. Peck, Director

For additional information write to:

District Chief
U.S. Geological Survey
Federal Building
P.O. Box 1107
Harrisburg, Pennsylvania 17108

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FACTORS FOR CONVERTING INTERNATIONAL SYSTEM (SI) UNITS TO INCH-POUND UNITS

Multiply (SI) units	By	To obtain inch-pound units
gram (g)	0.002205	pound, avoirdupois (lb)
milligram per liter (mg/L)	0.0000622	pounds per cubic foot (lbs/cu.ft)
degree Celsius (°C)	F=9/5°C + 32	degree Fahrenheit (°F)

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ABSTRACT

Determination of acidity provides a value that denotes the quantitative capacity of the sample water to neutralize a strong base to a particular pH. However, much additional information can be obtained from this determination if a titration curve is constructed from recorded data of titrant increments and their corresponding pH values. The curve can be used to identify buffer capabilities, the acidity with respect to any pH value within the curve limit, and, in the case of acid mine drainage from north-central Pennsylvania, the identification and estimation of the concentration of dissolved ferrous iron, ferric iron, and aluminum.

Through use of titration curves, a relationship was observed for the acid mine drainage between: (1) the titratable acidity (as milligrams per liter calcium carbonate) to pH 4.0 and the concentration of dissolved ferric iron; and (2) the titratable acidity (as milligrams per liter calcium carbonate) from pH 4.0 to 5.0 and the concentration of dissolved aluminum. The presence of dissolved ferrous iron can be detected by the buffering effect exhibited in the area between pH 5.5 to 7.5. The concentration of ferrous iron is estimated by difference between the concentrations of ferric iron in an oxidized and unoxidized sample. Interferences in any of the titrations from manganese, magnesium, and aluminate, appear to be negligible within the pH range of interest.

INTRODUCTION

Rainwater and Thatcher (1960) state that a differentiation should be made "between acidity as a property of a solution and as a total concentration of acids." Generally, investigators involved in AMD (acid mine drainage) studies use the acidity in the latter context where the acidity value is a measure of a strong base required to adjust the H^+ and OH^- ions to a predetermined pH, usually 8.3.

Brown, and others (1970) state "the construction of a titration curve... permits both a more reliable understanding of the reactions taking place during the neutralization and a more judicious selection of the proper equivalence point based on the observed inflection point of the curve." In addition, Rainwater and Thatcher conclude: "To determine the concentration of a specific acid compound requires titration with a base to a practical end point at which all hydrogen ions that can be produced by the compound have been neutralized. This end point is normally taken as the inflection point, or points, on the titration curve. The inflection points differ with the acid compound, hence it is impossible to determine accurately the acid concentration of different hydrolyzable salts or mixtures by titration to a single predetermined end point."

The purpose of this report is to describe and evaluate a technique for identifying and estimating the concentration of dissolved ferrous iron, ferric iron, and aluminum in AMD and related waters found in north-central Pennsylvania by using different end points in an acidity titration curve.

METHODS OF STUDY

Water samples for laboratory analyses were collected periodically from March 1981 to March 1983, from several different mine shafts at the Anna S mine and its receiving streams in southern Tioga County, Pennsylvania. Reed (1980) provides a geologic and hydrologic description of the area. One sample was collected from the Shoff Mine in southeastern Clearfield County, Pennsylvania.* A listing of sites from which data was used in this study follows:

Site name	Station number	Latitude	Longitude
	Mine-Discharge Sites		
Mitchel No. 2 nr Antrim,PA	01548413	41°37'43"	77°18'12"
Anna S No. 1 nr Antrim, PA	01548416	41°37'26"	77°18'07"
Hunter Drift nr Antrim, PA	01548418	41°37'05"	77°18'40"
Shoff Mine at Madera, PA	01541414	40°49'30"	78°26'59"
	Stream Sites		
Bridge Run nr Antrim, PA	01548415	41°37'32"	77°17'43"
Basswood Run nr Antrim, PA	01548421	41°36'50"	77°17'38"
Wilson Creek at Morris, PA	01548423	41°35'51"	77°17'50"
Morris Run nr Blossburg, PA	01516256	41°39'47"	77°02'23"
Coal Creek at Blossburg, PA	01516260	41°40'17"	77°03'41"
Bear Creek at Blossburg, PA	01516267	41°41'00"	77°03'53"

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* Data collected by Ward (1976) of the Tioga River basin was also used for this study.

Acidity titration curves were produced under temperature controlled laboratory conditions. Metal concentrations were determined for each acidity titration performed and were correlated to the acid concentration of their respective hydrolyzable salts. The relationships obtained under controlled conditions were then tested using field titration data available from previous studies (1975-80) from the same and adjacent areas in north-central Pennsylvania.

The range in concentration in milligrams per liter for selected constituents in the AMD and related water used in this study is:

	Acidity ($CaCO_3$ equivalent)	Fe	Al	SO_4
High	2,240	690	120	2,300
Low	43	1.6	3.9	100
Mean	700	82	42	970

Field Procedures

Water samples were collected directly into 4-liter or 5-gallon polyethylene storage bottles. Temperature, specific conductance, pH and acidity determinations were made on site. Field acidities were determined on unfiltered, untreated samples at ambient temperatures inside a mobile laboratory. Samples for metal analyses were filtered through 0.45 µm membrane filters and acidified with concentrated nitric acid to pH less than 2. Anion analyses were carried out on samples which had been filtered but had no additional pretreatment. Occasional ferrous iron determinations were made on site on unfiltered samples following the colorimetric bipyridine method, I-1379-78, Skougsted, and others (1979) except that no reductant was added to reduce ferric iron in solution.

Laboratory Procedures

Samples collected in the field were reused over a period of several weeks. Samples were stored either in 2-liter polyethelene containers and refrigerated or in 5-gallon polyethelene containers packed in ice. It was expected that chemical changes would take place during this period, therefore, metal analyses were performed by the laboratory each time an acidity titration was determined.

Dissolved ferric iron, aluminum, and on occasion, dissolved ferrous iron were investigated in this study. Ferrous iron was originally believed not to be a factor in the AMD sampled since initial ferrous iron concentrations were found to be 1.5 mg/L (milligrams per liter) or less. This was in line with the general conclusions of previous investigators (Reed and Ward, oral communication, 1981) for the AMD found in the north-central Pennsylvania area.

According to Payne and Yeates (1970), there are numerous methods available for the determination of mine drainage acidity with most methods advocating use of hydrogen peroxide and hot or boiling temperatures to hasten metal hydrolysis. However, Salotto and others (1967), state that "the determination of total acidity under hot titrating conditions presents more difficulties than it solves." It appears that the hot temperature: (1) hastens the formation of the aluminate ion and causes a rapid fading of the end point; (2) causes titration of magnesium acidity as low as pH 7.5; and (3) includes complete titration of manganese acidity by pH 8.3.

Acidity titrations were performed at 25°C. Sample aliquots of 25 ml (milliliters) or 50 ml were titrated with standard 0.02N NaOH to pH 8.3 without an oxidant or additional heating. Sample beakers were partially submerged in a Haake model FK Constant Temperature Circulator[1/]. Samples were magnetically stirred by setting the sample beaker atop an immersible compressed air, turbine-driven stirrer (G.F. Smith Chemical Co.). A Beckman "Altex 71" pH meter with temperature compensation and a Beckman combination glass electrode #531013 were used in the titrations. The instrument was calibrated with pH 4.0 and pH 7.0 buffers at least once daily and occasionally checked with the pH 9.18 buffer. By calibrating with two standards the instrument automatically computed slope (corrected for temperature) and corrected offset. In order to obtain consistent results and eliminate operator judgement, the "Auto Read" function of the pH meter was used. In this mode the pH reading is locked on digital display when the pH readings change by no more than ± 0.004 pH units for 10 seconds. Titrant increments were generally on the order of 0.25 ml, and were added manually. Requested laboratory constituent analyses varied with samples. All samples were analyzed for iron, aluminum, manganese and sulfate. Calcium, magnesium, sodium, potassium, zinc, copper, silica, chloride and phosphorus were analyzed for selected samples. Samples for cation analysis were filtered through a 0.45 micron membrane filter, and acidified with nitric acid to a pH less than 2. Samples for anion analysis were filtered and in the case of phosphorus, kept chilled. Laboratory analyses were performed according to procedures described by Skougstad, and others (1979). Results of chemical analyses used for this study can be found in Appendix A.

[1/] The use of the brand name in this report is for identification purposes only and does not constitute endorsement by the U.S. Geological Survey.

TITRATION-CURVE CHARACTERISTICS

Buffer Zones

Examples of acidity titration curves representative of AMD samples from north-central Pennsylvania are presented in figure 1. Although the acidity and ionic concentrations for the AMD samples differ, all curves show the same characteristic two tier buffer zones below pH 6.0. Salotto and others (1967) showed these same characteristic buffer zones when titrating the acidity of a 0.02N sulfuric acid solution containing ferric iron and aluminum salts. Buffering below pH 4.0 occurred with ferric iron salts, and between pH 4.0 and 5.0 with aluminum salts. Similar titration curves were obtained by Payne and Yeates (1970) for titrations of ferrous iron in sulfuric acid and ferric iron in sulfuric acid after both solutions had been subjected to oxidation with 3 percent hydrogen peroxide.

The titration characteristics below pH 5.0 for AMD samples appear to be due to the neutralization of free acid

$$2NaOH + H_2SO_4 \longrightarrow Na_2SO_4 + 2H_2O \qquad (1)$$

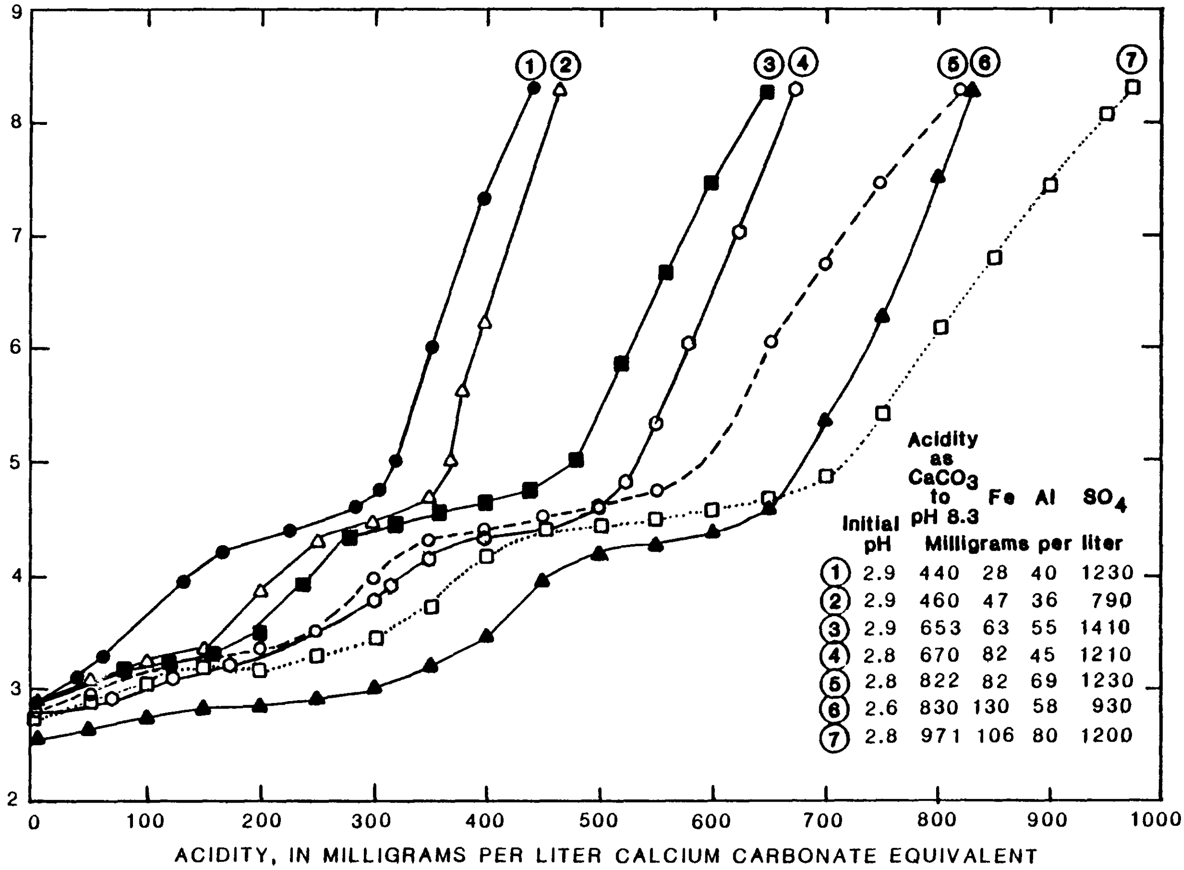
and the subsequent hydrolysis of ferric and aluminum sulfates which produce additional free acid

$$Fe_2(SO_4)_3 + 6H_2O \longrightarrow 2Fe(OH)_3 + 3H_2SO_4$$
$$Al_2(SO_4)_3 + 6H_2O \longrightarrow 2Al(OH)_3 + 3H_2SO_4$$

and create the buffer effect.

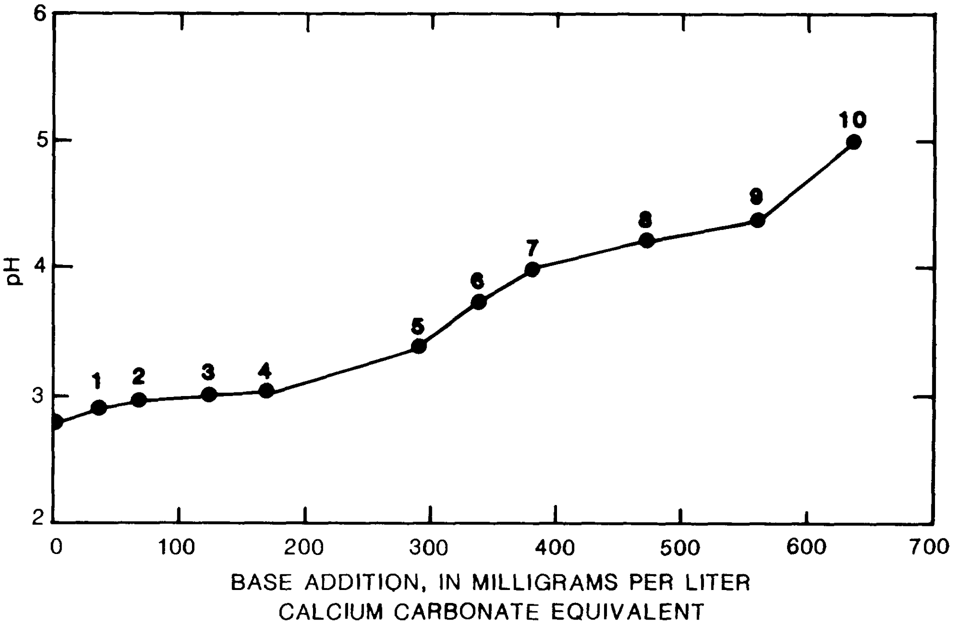
Metal Relation to Buffer Capacity

In order to see if the effects of metal hydrolysis could be separated as implied by the data of Salotto and others (1967) and Payne and Yeates (1970), samples were taken during the course of an acidity titration to determine the iron and aluminum concentration as the sample titration progressed. An initial titration was performed, curve plotted, and ten points selected along the curve where the metal determinations would be made. Amounts of titrant were added to ten subsamples equivalent to the titrant volume at the ten preselected points on the initial titration curve. Sample was stirred until its respective pH was attained and was then filtered and analyzed for iron and aluminum. The titration curve and corresponding reductions in concentrations of ferric iron and aluminum are shown in figure 2. These data show that midway into the first buffer zone, 55 percent of the iron precipitated and that 97 percent had precipitated by the time the pH had noticeably changed. The aluminum data show that at this latter point, about 25 percent of the dissolved aluminum had coprecipitated with the iron. This is supported by Kolthoff and Sandell (1937) who report that the precipitation of hydrous aluminum oxide begins at pH 3.0. The precipitation of iron appears essentially complete prior to the initiation of the second buffer zone, the area where the majority of the dissolved aluminum precipitates. The precipitation of dissolved aluminum is essentially complete by pH 5.0. Thus, although there appears to be some coprecipitation of aluminum with iron, the first buffer



Initial pH	Acidity as $CaCO_3$ to pH 8.3	Fe	Al	SO_4
	Milligrams per liter			
① 2.9	440	28	40	1230
② 2.9	460	47	36	790
③ 2.9	653	63	55	1410
④ 2.8	670	82	45	1210
⑤ 2.8	822	82	69	1230
⑥ 2.6	830	130	58	930
⑦ 2.8	971	106	80	1200

Figure 1.--Titration curves for selected acid mine discharges.



EXPLANATION

Percent Reduction

	Iron	Aluminum
(1)	6	-
(2)	12	-
(3)	55	-
(4)	73	-
(5)	97	27
(6)	99.2	-
(7)	99.5	41
(8)	-	63
(9)	-	85
(10)	-	99.4

Figure 2.--Decrease in ferric iron and aluminum content during neutralization of Mitchel 2 and discharge at 25 degrees Celsius.

zone basically represents the neutralization of the initial free acidity and the acidity produced by iron hydrolysis and the second buffer zone, the neutralization of acid produced by the hydrolysis of aluminum.

The AMD samples represented by the previously depicted titration curves contained little, if any ferrous iron. Selvig and Ratliff (1922) found that the methyl orange acidity (to pH 3.7) was a "more nearly correct" free sulfuric acid value if the ferric sulfate in the AMD sample was first reduced. This implies that ferrous iron is not a factor in the hydrolysis reactions, at least to pH 3.7. Salotto, and others (1967) showed basically identical titration curves for two sulfuric acid solutions containing equal equivalent weights of iron. One solution was made with a ferric iron salt and the other with a ferrous iron salt; the latter solution oxidized with hydrogen peroxide. These curves exhibited a buffer zone to approximately pH 4.0. In contrast, the titration of a non-oxidized sulfuric acid solution containing ferrous iron exhibited the buffer zone from approximately pH 5.5 to 7.5.

In order to determine the effect ferrous iron, in the presence of ferric iron, has on the acidity titration curve, an AMD known to have high concentrations of both ferrous and ferric iron was collected from a strip mine located in central Pennsylvania. Duplicate samples were titrated at 25°C as (1) an untreated sample and (2) an oxidized sample, treated with 5 drops 30 percent hydrogen peroxide. The resultant curves are illustrated in figure 3. The lower curve, representing the oxidized sample is two tiered and similar to the previous curves while the upper curve, representing the untreated sample contains the familiar two tiers below pH 5.0 plus a third tier from approximately pH 6.0 to 7.4. This buffer zone is similar to that found by Salotto and others (1967) in the titration of a sulfuric acid solution containing only ferrous iron.

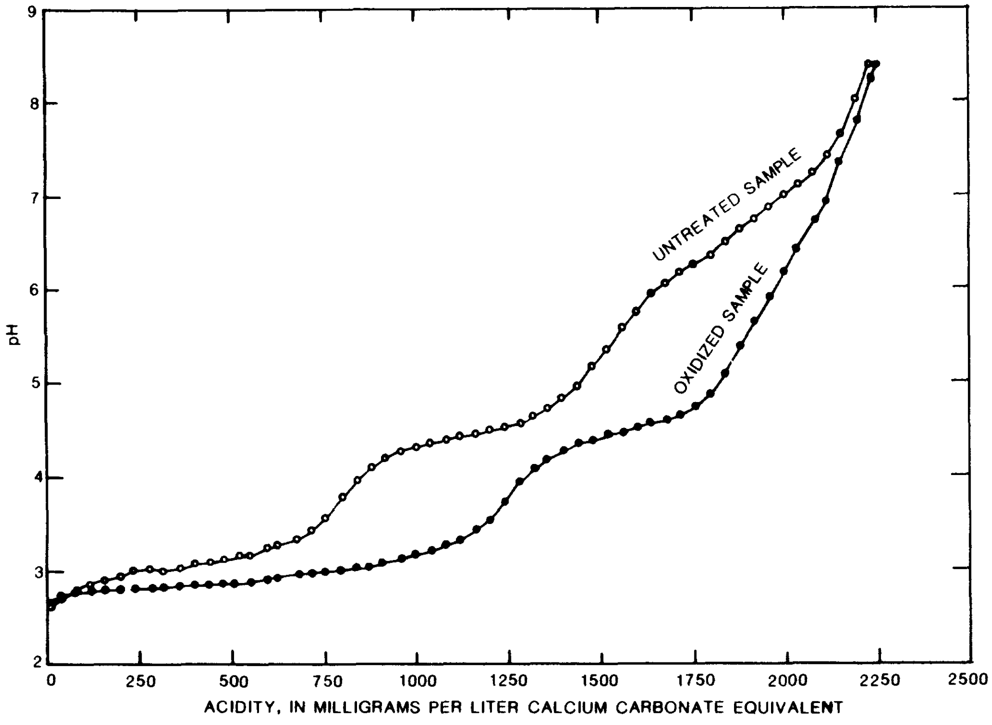


Figure 3.--Acidity titration curves for an untreated sample and an oxidized sample from Shoff Mine at 25 degrees Celsius.

ESTIMATION OF IRON AND ALUMINUM CONCENTRATION IN ACID MINE DISCHARGE

Description of Technique

Examination of figure 1 indicates a direct relation between metal concentration and buffer strength. This implies that the acid concentration may be related to the metal concentration relative to a buffer capacity. Various procedures were attempted to relate the buffer acidity (in mg/L $CaCO_3$) to metal concentration. Because of the variability encountered in accurately identifying the inflection points from titration curves representing a variety of AMD samples, arbitrary pH end points were used to separate the acidity ascribed to the hydrolysis of ferric iron and acidity due to the hydrolysis of aluminum. The method used in this report involves the relation of the ferric iron concentration to the acidity (as mg/L $CaCO_3$) required to titrate from the initial pH to pH 4.0 and the aluminum concentration to the acidity value (as mg/L $CaCO_3$) required to titrate from pH 4.0 to 5.0. A statistical analysis of the iron relation to acidity, using a nonlinear least-squares fitting procedure results in a plot (figure 4) having the general relationship:

$$y = 0.0128x^{1.5055} + 0.90 \qquad (2)$$

$$r^2 = 0.98$$

where y = ferric iron concentration, in mg/L
x = acidity, in mg/L as $CaCO_3$ equivalent.

A linear least squares fitting procedure was used to produce a plot (figure 5) with the general relationship for the aluminum relation to acidity:

$$y = 0.2139x + 1.150 \qquad (3)$$

$$r^2 = 0.97$$

where y = aluminum concentration, in mg/L
x = acidity, in mg/L as $CaCO_3$ equivalent.

The titration curves in figure 1 and corresponding data presented in table 1 are used to illustrate the estimation procedure. It can be seen that for curve No. 1 in figure 1 the acidity to pH 4.0 is 140 mg/L. The iron curve in figure 4 is entered at 140 mg/L acidity and an estimated iron value of 23 mg/L is obtained. Aluminum is estimated in a similar manner. The acidity for curve No. 1 from pH 4.0 to 5.0 is 180 mg/L. The aluminum curve in figure 5 is entered at 180 mg/L acidity and 40 mg/L is estimated.

Table 1.--Data derived from titration curve technique used in estimating iron and aluminum content of acid mine drainage [milligrams per liter]

Curve No.	Acidity as $CaCO_3$ to pH 4.0	Iron laboratory	Iron estimate	Acidity as $CaCO_3$ pH 4.0-5.0	Aluminum laboratory	Aluminum estimate
1	140	28	23	180	40	40
2	212	47	42	158	36	35
3	243	63	51	227	55	50
4	327	82	79	211	45	46
5	303	82	71	289	69	63
6	455	130	129	230	58	50
7	383	106	100	338	80	73

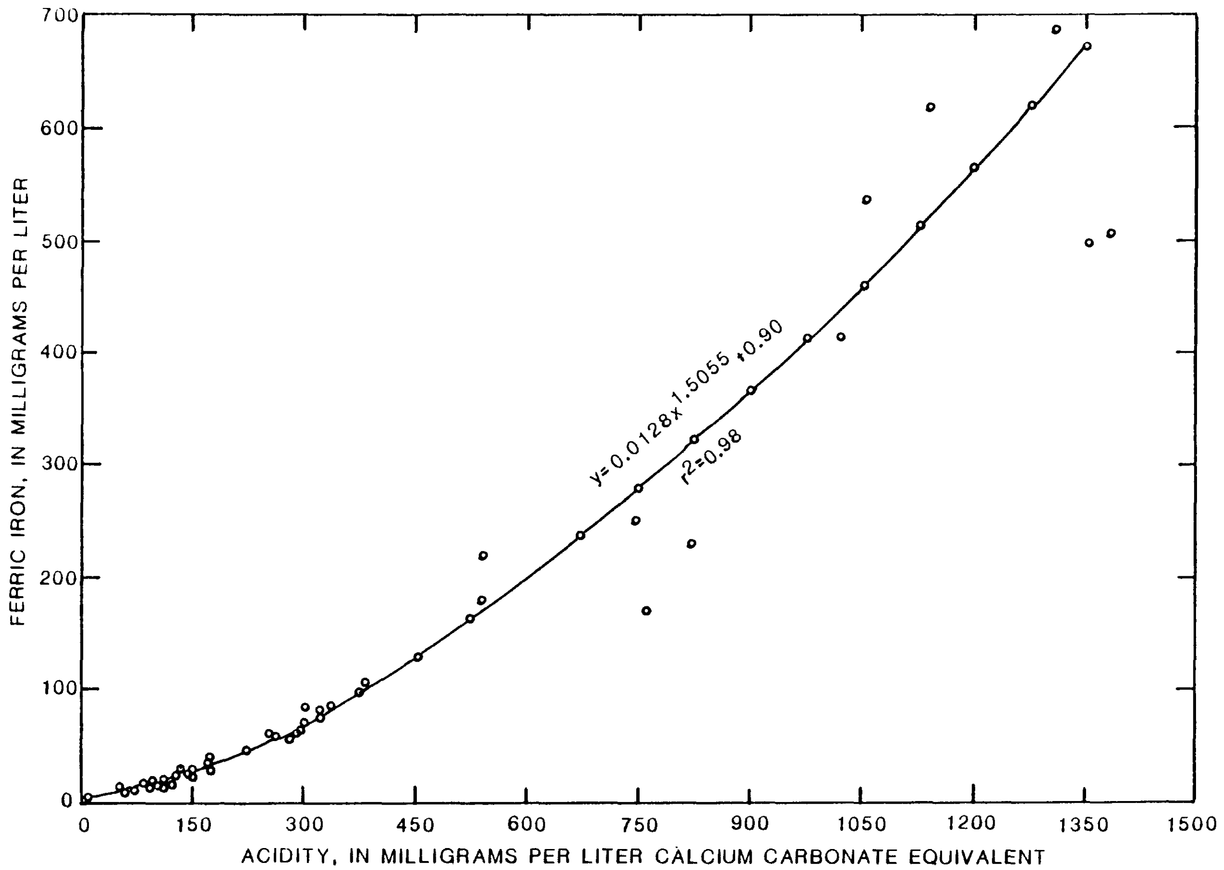


Figure 4.--Relation between ferric iron concentration and amount of calcium carbonate equivalent required to raise the initial sample pH to 4.0 at 25 degrees Celsius.

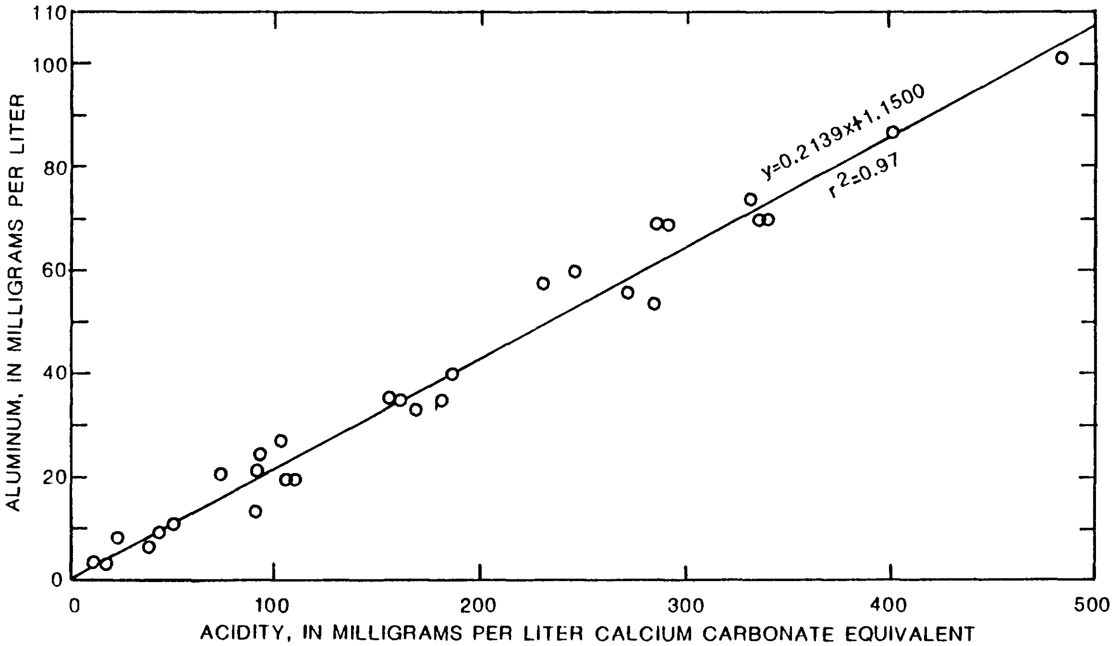


Figure 5.--Relation between aluminum concentration and amount of calcium carbonate equivalent required to raise sample pH from 4.0 to 5.0 at 25 degrees Celsius.

The regression equations can be also be used. Using the same example of 140 mg/L acidity to pH 4.0,

$$y = 0.0128 \cdot 140^{1.5055} + 0.90$$

$$y = 23 \text{ mg/L dissolved iron}$$

and 180 mg/L acidity from pH 4.0 to 5.0,

$$y = 0.2139 \cdot 180 + 1.15$$

$$y = 40 \text{ mg/L dissolved aluminum}$$

It must be emphasized that the relationship between dissolved iron and acidity to pH 4.0 is relative to ferric iron, therefore it is recommended that two titrations be performed per sample - one titration on an untreated sub sample and the other titration on a sub sample treated with H_2O_2. If the curves for the two titrations are superimposed and found to be identical, all the iron in the sample is in the ferric state and the iron estimation proceeds as previously stated. If, however, the curves diverge, the iron estimate requires a more complex calculation. The titration curves in figure 3 are used for illustration.

Iron Estimation

1. Untreated sample curve

   a. $y = 0.0128x^{1.5055} + 0.90$ = mg/L *ferric iron*

      where x = acidity to pH 4.0 as mg/L $CaCO_3$

2. Treated sample curve

   a. $y = 0.0128x^{1.5055} + 0.90$ = mg/L *oxidized iron*

      where x = acidity to pH 4.0 as mg/L $CaCO_3$

   b. oxidized iron (2a) - *ferric iron* (1a) · 1.5 = mg/L *ferrous iron*

   c. ferric iron (1a) + ferrous iron (2b) = *total dissolved iron*

The ferric iron content is estimated from the upper curve which represents the untreated sample. The untreated sub sample required 860 mg/L $CaCO_3$ to reach pH 4.0 and the iron calculation as found in 1a above estimates the ferric iron concentration to be 341 mg/L. The oxidized iron content is estimated from the lower curve which represents the oxidized H_2O_2 treated sub sample. This treated sub sample required 1,300 mg/L $CaCO_3$ to reach pH 4.0. The iron calculation as found in 2a shows the estimated oxidized iron concentration to be 625 mg/L. As shown by equation 2b, 625 mg/L oxidized iron minus 341 mg/L ferric iron · 1.5 = 426 mg/L ferrous iron. The factor 1.5 is used because the millequivalent weight of ferrous iron is 1.5 times greater (27.9 mg) than the millequivalent weight of ferric iron (18.6 mg). The calculated total dissolved iron = 341 mg ferric iron + 426 mg ferrous iron = 767 mg. Laboratory analysis determined that the sample contained 690 mg/L total dissolved iron consisting of 330 mg/L ferric iron and 360 mg/L ferrous iron. The percent difference between the estimated and the analytical values for total, ferric, and ferrous iron is +11, +3, and +18 percent, respectively.

Although the acidity to pH 4.0 is equated to the acid generated by the hydrolysis of ferric iron, the acidity to pH 4.0 also includes the free mineral acidity present before any hydrolysis of ferric iron takes place as well as the acidity produced by aluminum hydrolysis as it coprecipitates with iron. This nonferric associated acidity appears to be satisfactorily taken into account by the non-linearity of the ferric iron regression equation.

In the case of the aluminum region from pH 4.0 to 5.0, the aluminum related acidity is, in fact, only a part of the total dissolved aluminum acidity since some aluminum hydrolyzes prior to the solution reaching pH 4.0. The linear relationship of the regression equation suggests that although some aluminum hydrolysis occurs below pH 4.0, the total dissolved aluminum is directly proportional to the dissolved aluminum in solution between pH 4.0 and 5.0. It must be stressed that the above premise may only apply to AMD associated with the geological setting of north-central Pennsylvania.

Application of Technique to Field Acidity Data

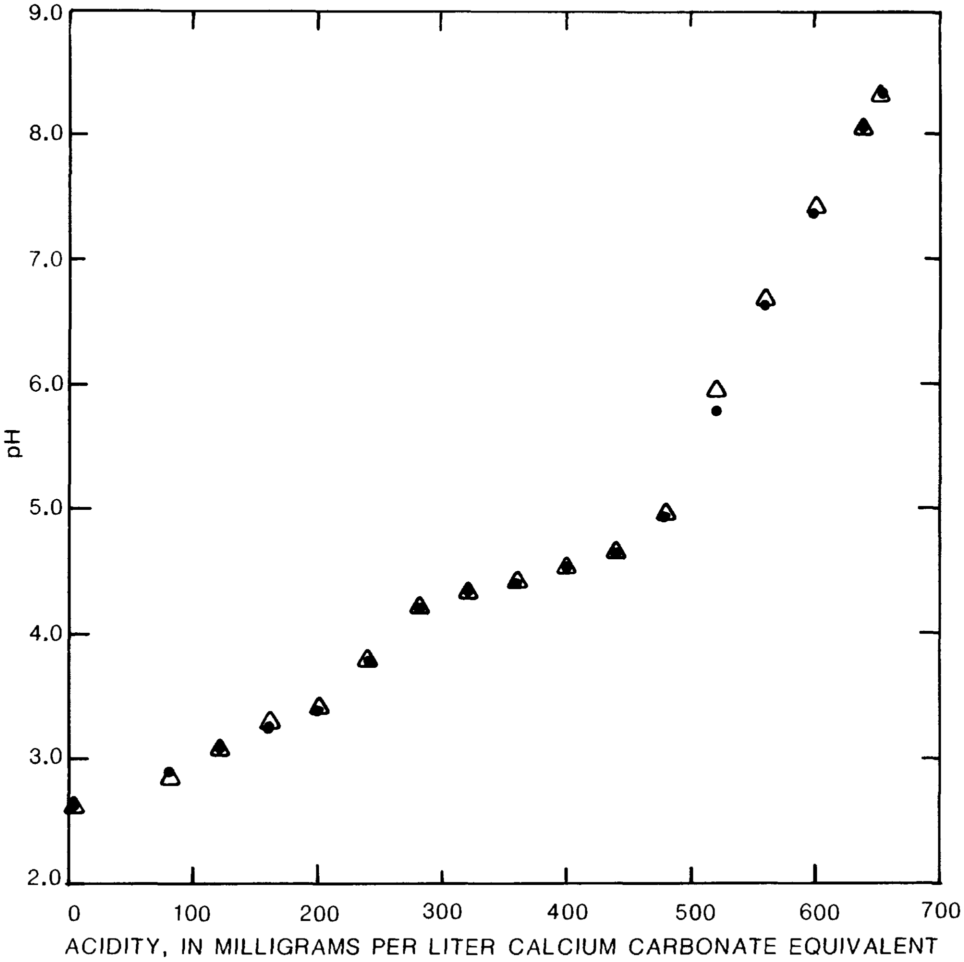
Since the metal estimation relationships were developed in the laboratory under controlled conditions, their application to field acidity data needed to be explored. Variables associated with field data such as individual titration techniques, precision and accuracy of various pH electrodes and meters, and range in ambient sample titration temperature, introduce uncertainty to the estimation technique in field reconnaissance efforts.

Titration Reproducibility

One potential field problem which can readily be addressed is the effect of a time lag on the estimation technique. Titration reproducibility should be known because there are field situations when a sample has, for a myriad of reasons, its acidity titration delayed until the following morning. The titration results for duplicate, refrigerated, oxidized samples titrated 18 hours apart are shown in figure 6. The data show good agreement after 18 hours, and therefore, implies that a short time delay prior to sample titration does not show a negative effect on the estimation technique.

Temperature Effect

A decrease of 1.0 to 1.5 pH units was observed by Salotto and others (1967) for the inflection points of iron, aluminum, and manganese titration curves derived at 90°C as opposed to the inflection points obtained for titration curves at 25°C. Temperature appears, therefore, to be an important factor when use is made of the metal estimation technique.



EXPLANATION

CaCO3 MILLIGRAMS PER LITER	pH 6/17/82	pH 6/18/82 x
0	2.68	2.61
80	2.91	2.87
120	3.11	3.08
160	3.28	3.30
200	3.42	3.40
240	3.80	3.80
280	4.22	4.21
320	4.37	4.33
360	4.46	4.42
400	4.55	4.52
440	4.67	4.65
480	4.93	4.97
520	5.79	5.94
560	6.61	6.68
600	7.35	7.40
640	8.06	8.02
654	—	8.30
656	8.35	—

	LAB	ESTIMATE
	MILLIGRAMS PER LITER	
Iron	55, 54	56
Aluminum	57, 57	49

Figure 6.--Effect of 18-hour time delay on reproducibility of the titration curve.

Curves for duplicate AMD samples titrated at 4°C and 35°C are depicted in figure 7. The samples contained 96 and 69 mg/L of iron and aluminum, respectively. The estimated iron and aluminum concentrations at 4°C are 82 and 42 mg/L, respectively and at 35°C are 98 and 61 mg/L, respectively. This indicates that, particularly in the case of aluminum, poor estimates are obtained from titrations run at low temperature.

Fortunately, field titrations are probably seldom performed at these temperatures because of the care required to adjust the electrolyte concentration of the pH electrode filling solution. The electrolyte used to fill the electrode at room temperature will "salt out" at low temperatures due to supersaturation and will be undersaturated at the elevated temperatures. Either case will produce erroneous pH readings unless the electroloyte concentration is adjusted.

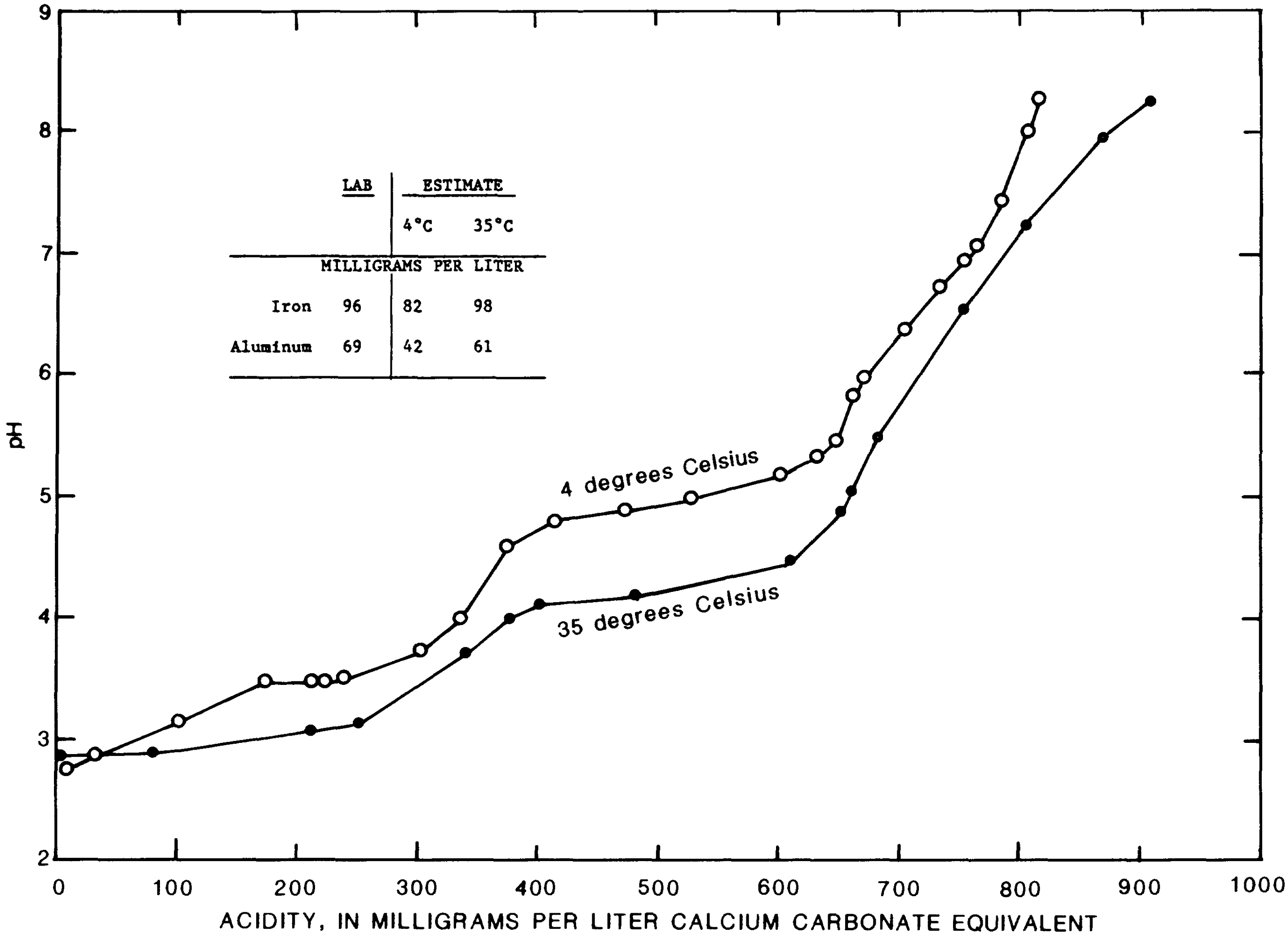


Figure 7.--Effect of temperature on titration-curve characteristics.

Evaluation of Estimation Technique

Field titration data for AMD samples from the same general area sampled for this study were obtained and compiled from two separate studies conducted between 1975 and 1980. Field data pertain to three mine discharges and 6 streams affected by AMD. Titrations were run on samples of 25 or 50 mL, normality of sodium hydroxide titrant was either 0.02N or 0.1N, and titrant increments ranged from 0.5 to 11.4 mL. In addition, titrations were performed by five field analysts using a variety of battery operated pH meters. Estimated and laboratory determined metal concentrations, pH and total acidity values from the above field studies are tabulated in tables 2-8. Examination of the data show that even with the inherent variables that accompany field titrations plus the fact that the regression equations were developed from titration data obtained at 25°C, the majority of metal estimates are within 25 percent of the laboratory values.

The difficulty in estimating iron from titrations of unoxidized samples is shown by the data in tables 2-4. At the beginning of this study, ferrous iron was determined for sampled discharges from the three mine shafts at the

Anna S mines. The ferrous iron content did not exceed 1.5 mg/L for the Mitchel and Anna S discharges but were found to be up to 15.5 mg/L for the Hunter Drift discharge. Discharge from the latter shaft was not used for the lab part of this study. However, field titration data used in the estimation of iron and aluminum were from all three discharges plus Basswood Run, a receiving stream for the Hunter Drift discharge.

Data in table 2 show that 72 percent of the iron estimates from Hunter Drift are below and only 25 percent above the laboratory values and simularly Basswood Run data (table 3) show 73 percent of the iron estimates below and only 7 percent above the laboratory values. The large number of low estimates conform to the expectation of obtaining low estimates when comparing laboratory total iron values which include both ferrous and ferric iron to estimated ferric iron values.

In comparing laboratory iron values to titration values of samples believed to contain little or no ferrous iron, the data show that, for all the estimated iron values in tables 3 and 4, 50 percent are above and 44 percent below the laboratory values. This conforms to the expectation that, when ferrous iron is not present, the estimated iron values are distributed normally.

Results of the estimation data are summarized in table 9. These data show that 75 percent of the iron estimates for 122 AMD related water samples (having iron concentrations ranging from 4-280 mg/L) were < ± 25 percent of the lab determined values while less than 1 percent were > ± 50 percent of the lab values. Estimation of aluminum showed a slight increase in accuracy over iron in that 84 percent of the aluminum estimates for 96 samples (with aluminum concentrations ranging from 1-120 mg/L) were ≤ ± 25 percent of the lab values while 3 percent were > ± 50 percent of the lab values.

The estimation technique may be used as a decision making tool in determining if a laboratory rerun is necessary. Laboratories are confronted with analytical problems from time to time as indicated by the following data for split AMD samples. Samples were analyzed by the two laboratories which provided all the constituent analyses acquired for this and the 1975-80 studies.

Concentration, in mg/L

	Sample 1		Sample 2		Sample 3		Sample 4	
	Iron	Aluminum	Iron	Aluminum	Iron	Aluminum	Iron	Aluminum
Lab 1	47	36	120	80	130	58	870	96
Lab 2	40	14	110	30	110	22	383	69
Estimate	42	37	140	88	136	58	690	104

Table 4.--Summary of pH, acidity, and estimated and laboratory determined iron and aluminum concentration values for Mitchel 2 Mine discharge, 1977-81

[Constituent concentrations, except pH, in milligrams per liter]

Date	pH	Acidity as $CaCO_3$			Iron		Aluminum	
		to pH 4.0	pH 4.0 to 5.0	to pH 8.3	laboratory	estimate	laboratory	estimate
1977								
Nov. 2	2.7	300	181	650	62	70	86	40
Nov. 30	2.7	186		410	29	34		
Dec. 29	2.9	172		390	37	31		
1978								
Feb. 9	2.7	205	129	450	44	40	31	29
Mar. 1	2.6	268		600	59	59		
May 2	2.5	255		500	50	55		
June 15	2.4	473		960	130	137		
July 13	2.5	520	300	1,090	95	158	73	65
Aug. 2	2.4	332		1,260	77	81		
Sept. 7	2.4	374		1,570	94	97		
Sept. 28	2.4	752	488	1,690	250	275	100	106
Dec. 5	2.6	541	307	1,200	180	168	82	67
Dec. 27	2.5	452		1,060	150	128		
1979								
Jan. 29	2.8	364		850	120	93		
Feb. 23	2.6	452		1,040	150	128		
Mar. 19	2.6	318	162	700	90	76	42	36
Apr. 25	2.8	290		670	72	66		
July 2	2.7	503	330	1,220	140	150	74	72
July 27	2.7	674		1,550	170	233		
Sept.18	2.5	542		1,370	220	168		
Oct. 11	2.6	620	320	1,480	150	206	70	70
Nov. 15	2.7	470		1,220	126	136		
Dec. 18	2.3	640	240	1,430	120	216	64	52
1980								
Jan. 15	2.9	355	229	890	120	89	54	50
Feb. 15	2.5	375	255	920	100	97	55	56
Apr. 23	2.8	310	232	760	73	73	46	51
May 21	2.7	400	273	995	132	107	60	60
June 17	2.7	434	299	1,130	120	121	68	65
July 16	2.5	760	404	1,740	170	279	100	88
Aug. 13	2.4	840	514	2,030	230	324	100	111
Sept. 9	2.6	700	380	1,520	180	247	110	82
Oct. 8	2.5	675	463	1,750	200	233	120	100

Table 5.--Summary of pH, acidity, and estimated and laboratory determined iron and aluminum concentration values for Anna S 1 Mine discharge, 1977-80

[Constituent concentrations, except pH, in milligrams per liter]

Date	pH	Acidity as $CaCO_3$			Iron		Aluminum	
		to pH 4.0	pH 4.0 to 5.0	to pH 8.3	laboratory	estimate	laboratory	estimate
1977								
Dec. 1	2.9	89		230	12	12		
Dec. 29	3.0	98		230	17	14		
1978								
Mar. 3	2.8	105		220	13	15		
May 4	2.8	98		200	14	14		
Aug. 2	2.9	99		230	19	14		
Sept. 7	2.8	132		310	22	21		
Sept. 29	2.8	143	91	350	25	23	25	21
Oct. 25	2.8	142		340	25	23		
Dec. 4	2.8	158	110	380	29	27	28	25
1979								
Jan. 29	2.9	176		390	39	32		
Feb. 23	2.8	112		270	16	16		
Mar. 19	2.6	150	79	300	26	25	21	18
Apr. 25	2.9	98		230	12	14		
May 31	3.0	96		240	11	13		
July 2	2.9	106	75	240	12	15	16	17
July 27	2.9	112		260	13	16		
Sept. 18	3.0	124		350	16	19		
Oct. 10	2.6	233	167	560	46	48	33	37
Nov. 15	2.8	149		400	19	25		
Dec. 18	2.3	213	92	430	28	42	20	21
1980								
Jan. 15	3.0	108	77	270	18	16	18	18
Feb. 15	2.7	118	64	270	16	18	16	15
Apr. 23	2.9	113	72	285	20	17	7	17
May 21	2.9	104	64	250	15	15	60	15
June 17	3.0	110	73	260	12	16	12	17
July 16	2.8	129	71	280	15	20	17	16
Aug. 13	2.7	132	110	330	21	21	17	25
Sept. 9	2.8	155	95	350	21	26	21	21

Table 2.—Summary of pH, acidity, and estimated and laboratory determined iron and aluminum concentration values for the Hunter Drift Mine discharge, 1977-80

[Constituent concentrations, except pH, in milligrams per liter]

Date	pH	Acidity as $CaCO_3$			Iron		Aluminum	
		to pH 4.0	pH 4.0 to 5.0	to pH 8.3	laboratory	estimate	laboratory	estimate
1977								
Nov. 3	2.8	212	88	410	46	42	23	20
Dec. 1	2.7	174		310	28	31		
Dec. 30	2.8	169		330	32	30		
1978								
Feb. 9	2.6	184	74	310	35	34	28	17
Mar. 1	2.5	235		430	49	48		
Apr. 13	2.8	136	58	240	22	22	13	14
May 4	2.7	175		320	38	31		
June 15	2.5	178		320	30	32		
July 13	2.6	260	120	480	54	56	28	27
Aug. 2	2.7	283		550	56	63		
Sept. 7	2.7	289		530	59	66		
Sept. 29	2.7	302	140	610	78	70	35	31
Oct. 25	2.6	336		690	92	82		
Dec. 4	2.6	354	186	850	100	89	42	41
Dec. 27	2.6	326		570	82	79		
1979								
Jan. 29	2.7	242		460	63	51		
Feb. 23	2.6	274		660	100	61		
Mar. 20	2.7	228	145	530	72	46	36	32
Apr. 25	2.8	236		560	75	49		
July 2	2.8	450	326	1,100	190	127	76	71
July 27	2.3	667		1,200	210	229		
Sept. 18	2.7	667		1,600	210	229		
Oct. 10	2.6	787	438	1,700	280	294	90	95
Dec. 18	2.4	500	340	1,200	170	149	70	74
1980								
Jan. 15	2.9	355	257	900	140	89	66	56
Feb. 15	2.7	445	355	1,200	210	125	82	77
Apr. 23	2.8	292	224	770	110	67	29	49
May 21	2.9	265	249	750	91	58	53	54
June 17	2.8	431	294	1,000	150	119	75	64
July 16	2.7	650	350	1,300	230	221	86	76
Sept. 9	2.8	630		1,700	280	211		
Dec. 11	2.7	485	315	1,300	170	142	79	69

Table 3.--Summary of pH, acidity, and estimated and laboratory determined iron and aluminum concentration values for Basswood Run discharge, 1977-81

[Constituent concentrations, except pH, in milligrams per liter]

Date	pH	Acidity as $CaCO_3$			Iron		Aluminum	
		to pH 4.0	pH 4.0 to 5.0	to pH 8.3	laboratory	estimate	laboratory	estimate
1977								
Nov. 3	3.0	140	50	280	25	23	16	12
1978								
Feb. 10	2.6	118	50	210	18	18	12	12
Apr. 13	3.0	78	30	140	10	10	8	8
July 14	2.4	172	96	330	21	31	21	22
Sept. 28	2.8	200	113	390	38	38	28	25
Dec. 4	2.9	105	40	215	19	15	13	10
1979								
Mar. 19	2.6	142	83	300	34	23	21	19
July 3	2.9	250	170	590	70	53	41	38
Oct. 11	2.7	490	320	1,100	150	145	60	70
Dec. 19	2.8	285	240	840	74	64	42	52
1980								
Mar. 20	2.9	190	102	360	36	35	20	23
June 18	2.9	308	257	780	95	72	53	56
Sept. 9	2.7	370	380	1,400	180	95	85	82
Dec. 11	2.8	235	190	650	52	48	44	42
1981								
Mar. 18	2.8	180	125	830	52	33	44	28

Table 6.--Summary of pH, acidity, and estimated and laboratory determined iron and aluminum concentration values for Bridge Run discharge, 1977-80

[Constituent concentrations, except pH, in milligrams per liter]

Date	pH	Acidity as $CaCO_3$			Iron		Aluminum	
		to pH 4.0	pH 4.0 to 5.0	to pH 8.3	laboratory	estimate	laboratory	estimate
1977								
Nov. 3	3.0	47	26	100	6.0	5	6.7	7
1978								
Apr. 13	3.1	46	19	94	5.8	5	5.9	5
July 13	2.9	54	33	110	5.1	6	7.0	8
Sept. 28	3.0	54	34	120	7.6	6	8.6	8
Dec. 5	3.0	46	34	120	5.7	5	6.2	8
1979								
Mar. 20	3.1	39	19	90	5.2	4	4.6	5
July 3	3.2	45	31	120	4.7	5	4.3	8
Dec. 19	3.1	38	28	120	4.3	4	5.8	7
1980								
Dec. 11	3.2	20	15	54	4.3	2	5.6	4

Table 7.--Summary of pH, acidity, and estimated and laboratory determined iron and aluminum concentration values for Wilson Creek discharge at Morris, 1977-80

[Constituent concentrations, except pH, in milligrams per liter]

Date	pH	Acidity as $CaCO_3$			Iron		Aluminum	
		to pH 4.0	pH 4.0 to 5.0	to pH 8.3	laboratory	estimate	laboratory	estimate
1977								
Nov. 3	3.9	2	12	39	0.96	<1	4	3
1978								
Feb. 9	3.7	4	14	38	1.3	<1	3	4
Apr. 14	3.7	3	9	26	1.3	<1	2.4	2
July 13	3.1	24	34	76	1.2	2	7.7	8
Sept.28	3.7	11	35	69	1.3	1	9.4	8
Dec. 5	5.1	<1	<1	17	.65	<1	1.1	<1
1979								
Mar. 20	3.7	8	16	47	2.7	<1	3.3	4
July 3	3.9	6	37	74	1.5	<1	6.7	9
Oct. 11	3.3	27	43	116	8	3	8	11
Dec. 19	4,7	-	10	80	2.9	<1	6.4	2
1980								
Jan. 5	4.0	-	12	32	1.2	<1	3.1	3
Feb. 15	3.5	10	23	88	2.6	1	9.4	5
Mar. 20	3.7	5	17	42	2.6	<1	3.1	4
Apr. 23	3.7	9	30	62	3.5	1	4.3	7
May 21	3.6	6	24	48	.26	<1	.1	6
June 18	3.4	24	44	126	4.6	2	8.9	11
July 18	3.3	30	47	122	2.7	3	10	11
Aug. 13	3.2	32	76	170	2.7	3	2.7	18
Sept. 9	3.2	50	70	220	2.8	5	18	17

Table 8.--Summary of pH, acidity, and estimated and laboratory determined iron and aluminum concentration values for discharges from Morris Run near Blossburg, Coal Creek at Blossburg, and Bear Creek at Blossburg, 1975-76

[Constituent concentrations, except pH, in milligrams per liter]

Date	pH	Acidity	Iron		Aluminum	
			laboratory	estimate	laboratory	estimate
Morris Run near Blossburg						
1975						
July 8	2.9	440	28	22	40	43
Dec. 9	3.0	370	16	8	24	23
1976						
Mar. 8	3.0	200	13	8	22	21
Sept. 7	2.7	500	28	22	44	49
Coal Creek at Blossburg						
1975						
July 8	2.8	670	82	80	45	52
Dec. 9	2.8	550	78	52	35	36
1976						
Mar. 8	2.6	410	55	41	28	29
Sept. 7	2.6	800	90	85	19	48
Bear Creek at Blossburg						
1975						
July 8	2.9	270	11	16	21	24
Dec. 9	3.0	222	13	12	16	18
1976						
Mar. 8	2.9	120	7	7	8.2	8
Sept. 7	2.6	290	12	18	23	23

Table 9.--Compilation of number of iron and aluminum estimates from tables 2-8 into categories of metal concentration and percent error

Range in mg/L	Percent Error Between Estimate and Laboratory Value					
	≤ ± 25	± 26-50	> ± 50	< ± 25	± 26-50	> ± 50
	number of iron values			number of alumimum values		
0-10	10	1	—	17	8	2
11-50	42	12	—	40	3	1
51-100	20	7	—	22	1	—
>100	20	9	1	2	—	—
Subtotal	92	29	1	81	12	3
Total	122			96		

SUMMARY AND CONCLUSIONS

The acidity determination provides a value that denotes the quantitative capacity of the sample water to neutralize a strong base to a particular pH. However, much additional information can be obtained from this determination when a titration curve is constructed from recorded data of titrant increments and their corresponding pH values. Through use of these titration curves, a technique was developed for estimating the concentration of dissolved ferrous and ferric iron and aluminum contained in AMD found in north-central Pennsylvania.

A nonlinear regression equation with a correlation coefficient of 0.98 was determined for the relation between the titratable acidity (as mg/L $CaCO_3$) to pH 4.0 and the concentration of ferric iron. This correlation was achieved despite the fact that the titratable acidity is due not only to the hydrolysis of ferric iron but also to the free mineral acidity and to the hydrolysis of some aluminum which coprecipitates with the iron.

Estimation of ferrous iron can be achieved by the use of two titrations--one for an untreated sample and the other for a duplicate sample oxidized with hydrogen peroxide. The estimated ferric iron concentration for the oxidized sample represents the combined concentration of ferrous and ferric iron. The estimated ferric iron concentration for the untreated sample represents the actual amount of ferric iron in the original sample. Subtraction of the two values yields the estimated concentration of ferrous iron.

A linear regression equation with a correlation coefficient of 0.97 was derived for the relation between the titratable acidity (as mg/L $CaCO_3$) from pH 4.0 to 5.0 and the concentration of aluminum. The relationship suggests that although some aluminum hydrolysis occurs below pH 4.0, the total dissolved aluminum is directly proportional to the dissolved aluminum in solution between pH 4.0 and 5.0.

The estimation method was tested on field titration data collected from 1975 to 1980 for AMD and related waters from north-central Pennsylvania and compared to the corresponding laboratory determined iron and aluminum values. Of 122 estimates of iron ranging in concentration from 4 to 280 mg/L, 75 percent were $< \pm 25$ percent of the laboratory determined value while less than 1 percent were $> \pm 50$ percent of the laboratory values. For 96 aluminum estimates ranging from 1 to 120 mg/L, 84 percent were $< \pm 25$ percent, whereas 3 percent were $> \pm 50$ percent of the laboratory values.

The estimation technique can be a useful tool in reconnaissance studies of AMD sites, at least in north-central Pennsylvania, and can be an aid in determining the acceptability of laboratory-generated iron and aluminum values.

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APPENDIX A

Chemical Analyses of Acid Mine Drainage (AMD) and Related Waters

[Concentrations are in milligrams per liter, unlese otherwise indicated]

Date of Collection	pH	Specific conductance (microeiemens et 25 C)	Acidity (CaCO$_3$ equivalent)	Calcium (Ca)	Magnesium (Mg)	Sodium (Na)	Potassium (K)	Iron (Fe)	Aluminum (Al)	Manganese (Mn)	Zinc (Zn) ug/L	Copper (Cu) ug/L	Silica (S.O$_2$)	Phosphorus (P)	Cholride (Cl)	Sulfate (SO4)
Mitchel 2 Mine Discharge (01548413)																
1981																
March 18	2.7	2,450	890					91	64	38				0.01		1,900
April 20	2.7	2,310	790	79				83	120	34	5,400		42			1,300
October 15	2.7	3,160	1,290					160	25	69						2,300
1982																
January 28	2.6	3,140	1,390	150	150	1.7	0.9	26	50	62	9,800		30		13	2,200
March 31	2.6	2,580	855	103	102	1.3	0.9	75	65	36	5,970	420	20	.01	1.0	1,530
April 14	2.8	2,490	822	102	91	1.4	1.1	82	69	43	6,050	400	19	.01	2.0	1,230
May 18	2.8	2,820	971	144	137	1.7	0.8	106	70	43	6,600	450	47	.04	1.0	1,200
June 7	2.8	2,200	629	91	75	1.4	1.4	66	55	32	4,180	410	35	.03	2.0	1,410
June 24	2.8	2,420	660	118	106	1.7	0.9	57	53	33	4,920	370	41	.02	2.0	870
July 16	2.8	2,580	796	142	120	1.8	2.2	74	56	34	5,240	370	17	.03	1.0	1,200
August 13	2.7	3,000	840	128	112	0.8	1.1	92	63	34	5,150	330	50	.03	3.0	1,050
Anna S Mine Discharge (01548416)																
1981																
March 18	2.8	1,800	400					40	28	10				.01		750
April 20	2.8	1,600	410	59				34	35	13	2,600		36			630
June 9	3.2	1,500						24	20	8.5						540
October 15	2.7	1,620	487					43	21	15						720
1982																
January 28	2.7	1,620	497	66	42	2.7	1.4	39	33	15	2,600		33		1.9	690
Hunter Drift Mine Discharge (01548418)																
1981																
March 18	2.7	2,090	800					110	60	22						1,600
April 20	2.7	1,865	617	41				84	72	14	2,900		35			800
June 9	2.9	2,400						130	59	22						1,200
Bridge Run (01548415)																
1981																
March 18	3.1	705	140					4.9	5.8	3.4						220
April 20	3.3	650	80	30				3.9	4.5	3.1	210		18			200
June 9	3.3	780						4.3	6.0	3.7						230
Wilson Creek at Morris (01548423)																
1981																
March 18	3.5	500	140					3.5	8	3.5					.01	180
April 20	3.7	317	43	16				2.3	3.9	2.1	300		8.5			100
June 9	3.7	430						1.6	5.0	3.4						160
Shoff Mine Discharge (01541414)																
1983																
March 11	2.6		2,242					690		8.2						

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