# THE USE OF MEASURED AND CALCULATED ACIDITY VALUES TO IMPROVE THE QUALITY OF MINE DRAINAGE DATASETS<sup>1</sup>

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**Abstract:** The net acidity of a water sample can be measured directly by titration with a standardized base solution or calculated from the measured concentrations of the acidic and basic components. For coal mine drainage, the acidic components are primarily accounted for by free protons and dissolved ferrous iron, ferric iron, aluminum, and manganese. The base component is primarily accounted for by bicarbonate. A standard calculation is:  $Acid^{calc} = 50*(2*Fe^{2+}/56)$  $+3*Fe^{3+}/56 + 3*Al/27 + 2*Mn/55 + 1000*10^{-pH}) - Alkalinity, where acidity and$ alkalinity are measured as mg/L CaCO<sub>3</sub> and the metals are mg/L. Because these methods of estimating acidity are derived by independent laboratory procedures, their comparison can provide a valuable QA/QC for AMD datasets. The relationship between measured and calculated acidities was evaluated for fourteen datasets containing 1,484 sample analyses. All datasets consisted of samples collected from mine drainage discharges or polluted receiving streams. The datasets were variable in nature, ranging from watersheds where most of the discharges contained alkalinity to ones where all of the discharges were acidic. Good relationships were found to exist between measured and calculated acidities. The average acidity measurement was 239 mg/L CaCO<sub>3</sub> and the average acidity calculation was 226 mg/L CaCO<sub>3</sub>. Linear regressions were calculated for individual datasets and for the entire dataset. The linear regression for the entire dataset was: Acid<sup>calc</sup> =  $0.98 * \text{Acid}^{\text{meas}} - 8$ ,  $r^2 = 0.98$ . The good correlation between calculated and measured acidity is the basis for an easy and inexpensive QA/QC for AMD data. Substantial variation between measured and calculated acidities can be used to infer sampling or analytical problems and allow data corrections, when appropriate.

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### **Introduction**

Reliable water sample chemical analyses are an important component of the development of restoration plans, the design of passive treatment systems, and the assessment of restoration efforts. Ideally, analysis includes a determination of all the major constituents and the quality of the analysis is evaluated, partly, by the balance of cations and anions. This analytical detail is not feasible for most restoration activities because of its cost. The more common analytical package includes a subset of parameters; pH, acidity, alkalinity, Fe, Mn, Al, sulfate and total suspended solids. These parameters have inherent inter-relationships that are useful for an assessment of the quality of water sample analyses. This paper describes the relationship between acidity as measured by the standard titration method and as calculated from pH, alkalinity, and concentrations of Fe, Al, and Mn. The ability of the relationship to identify errant sampling or analytical results is assessed.

### **Background**

### Acidity Calculations.

The relationship between acidity and pH, alkalinity, Fe, Al, and Mn was described by Hedin et al. (1994). Mine water acidity arises primarily from metals that undergo hydrolysis reactions and, secondarily, from protons (measured as pH). Alkalinity arises primarily from bicarbonate ion. The balance of the acidic and alkaline parameters is a value that is often referred to as "net acidity." The acidic characteristics of dissolved metals are shown in the following reactions.

$\operatorname{Fe}^{2+} + \frac{1}{4}\operatorname{O}_2 + \frac{5}{2}\operatorname{H}_2\operatorname{O}  \operatorname{Fe}(\operatorname{OH})_3 + 2\operatorname{H}^+$	(A)
$Fe^{3+} + 3H_2O \rightarrow Fe(OH)_3 + 3H^+$	(B)
$Al^{3+} + 3H_2O \rightarrow Al(OH)_3 + 3H^+$	(C)
$\mathrm{Mn}^{2+} + \frac{1}{2}\mathrm{O}_2 + \mathrm{H}_2\mathrm{O}  \mathrm{MnO}_2 + 2\mathrm{H}^+$	(D)

The actual expression (release of protons) is dependent on pH and redox conditions. Standard methods consider the release of acidity under oxidizing, circumneutral conditions. These conditions are relevant because they represent the endpoint in most unpolluted receiving streams. Acidity also is derived from free  $H^+$  ions, which are measured as pH.

### Proceedings America Society of Mining and Reclamation, 2004

Some mine waters contain titratable alkalinity, which is present as bicarbonate. The importance of alkalinity is its ability to neutralize acidity that arises as the redox conditions of a sample change.

$$HCO_3^- + H^+ \rightarrow H_2O + CO_2 \tag{E}$$

Bicarbonate is only present, in measurable concentrations, when the pH is greater than 4.5. For metal-containing mine waters with pH less than 4.5, the net acidity can be estimated from the hydrolyzable metals and pH as follows:

$$Acid^{calc} = 50*(2*Fe^{2+}/56 + 3*Fe^{3+}/56 + 3*Al/27 + 2*Mn/55 + 1000*10^{-pH})$$
(F)

where acidity is measured as mg/L CaCO<sub>3</sub> and metals are measured as mg/L.

For samples with pH > 4.5, the net acidity is a result of the balance of alkaline and acidic components and is calculated as follows:

Net Acid<sup>calc</sup> =  

$$50*(2*Fe^{2+}/56 + 3*Fe^{3+}/56 + 3*Al/27 + 2*Mn/55 + 1000*10^{-pH}) - Alkalinity$$
 (G)

where the alkalinity is measured as mg/L CaCO<sub>3</sub>.

### Acidity Measurements

The acidity measurements reported in this paper were determined by titration with base following oxidation with hydrogen peroxide and boiling steps (American Public Health Association, 1999). This modification to the standard acidity titration procedure was developed in the late 1960's in order to increase the accuracy and repeatability of measurements made on samples containing hydrolyzable metal ions and dissolved carbon dioxide. The method involves the following steps:

1) the addition of known quantity of acid ( $0.02N H_2SO_4$ ) so that all alkalinity is eliminated and the pH is less than 4;

- the addition of hydrogen peroxide (30% H<sub>2</sub>O<sub>2</sub>) followed by 2-5 minutes of boiling so that all divalent metals are oxidized and dissolved carbon dioxide is exsolved;
- 3) titration of the cooled solution with base (0.1N NaOH) to pH 8.3.

For coal mine drainage samples, the addition of hydrogen peroxide assures that Fe and Mn are oxidized and form hydroxide solids during the base titration. Without the hydrogen peroxide digestion, variable amounts of  $Fe^{2+}$  and  $Mn^{2+}$  can remain in solution at the completion of the titration and result in an inaccurate measurement of acidity.

The net acidity of a sample is calculated from the difference of base additions (step 3) and acid additions (step 1). A positive result indicates that the sample has a net acidity. A negative result (more acid added in step 1 than base added in step 3) indicates that the sample has a net alkalinity.

The reporting of negative acidity values for samples with net alkalinity varies between laboratories and the standard method used. For most of the 1980s and 1990s, standard methods were unclear about the handling of negative acidity results. The  $17^{th} - 19^{th}$  Editions of APHA's Standard Methods of the Examination of Water and Wastewater instruct the reporting as follows:

"...Report pH of the end point used as follows: "the acidity to  $pH \_ = \_ mg$ CaCO<sub>3</sub>/L." If a negative value is obtained, determine the alkalinity according to Section 2320."

Section 2320 describes the conventional alkalinity determination which does not contain a hydrogen peroxide provision for waters with hydrolysable divalent metals. The method is unclear about the reporting of a negative result. Most laboratories reported samples with a negative result as having "0 acidity", or "less than 0 acidity" or as "negative." No laboratories, in the author's experience, reported the negative acidity value unless a special request was made. In these cases, the negative result was considered a non-standard method and usually reported as a FYI (for your interest) result.

The 20<sup>th</sup> Edition of Standard Methods revised the reporting instructions.

"...Report pH of the end point used as follows: "the acidity to  $pH \_ = \_ mg$ CaCO<sub>3</sub>/L." If a negative value is obtained, report the value as negative. The absolute value of this negative value should be equivalent to the net alkalinity." Laboratories have begun to recognize the change and report negative acidity values. Laboratories not yet reporting negative acidity values should be made aware of the change to the standard method.

### **Methods**

This study used the datasets from 14 monitoring programs where the goal was to quantify AMD pollution and effects on receiving streams. Samples were collected from discharges and receiving streams by watershed association volunteers, Pennsylvania Department of Environmental Protection (PADEP) personnel, and Hedin Environmental (HE) personnel. Mine water samples were collected as close to the discharge point as was reasonably possible. In all cases, two samples were collected. A raw sample was collected for measurement in the laboratory of pH, alkalinity, acidity, sulfate, and total suspended solids. An acid-preserved sample (5-10 drops of 50% nitric acid so that the pH is less than 2) was collected for measurement in the laboratory of Fe, Mn, and Al. Samples were not filtered prior to acidification. Field measurements of alkalinity, pH, and temperature (not reported in this paper) were made for five of the monitoring programs. Whenever possible, the acidity calculations were made using field pH and field alkalinity. When field data were absent or considered unreliable, laboratory measurements of pH and alkalinity were utilized.

Acidity calculations were made using equation (G). Iron speciation was only done by one laboratory for two datasets. For all other samples, the ferrous/ferric couple was assumed to be pH dependent. At pH less than 3, all iron was assumed ferric; at pH values equal and greater than 3, all iron was assumed ferrous. This split was based on the author's experience and a limited presentation of ferric iron estimates made in Hedin et al. (1994). The potential error introduced by this assumption will be discussed below and by Cravatta and Kirby (in this volume).

Five different laboratories were used to collect the fourteen datasets. Most of the laboratories were not aware of the reporting change in the 20<sup>th</sup> Edition of Standard Methods and reported negative values as zero. This is not an accurate report of the measured acidity. For laboratories using this protocol, all samples with reported acidities of zero were excluded from the datasets

and subsequent analyses. For laboratories that reported negative acidities, all data were considered in the analyses.

#### **Results**

Table 1 shows the average chemistry for each of the fourteen datasets considered. The samples ranged widely in their characteristics. The Chartiers, HowMor, and Mill sets were generally characterized by waters containing alkalinity, elevated concentrations of Fe and low concentrations of Al.. The Jon set was characterized by low pH acidic water with high concentrations of Al and low concentrations of Fe. The Cadogan, Bear, and Botanical sets were characterized by waters with very low pH and high concentrations of Fe and Al.

Table 1 shows average measured acidity (AM) and calculated acidity (AC) values. When all the datasets were combined, the average calculated acidity was 226 mg/L, only 5% less than the average measured acidity, 239 mg/L. (Relative differences calculated from the difference of the measures divided by AM.). The individual datasets ranged from an under calculation of 32% for the Chartiers dataset to an over calculation of 17% for the HowMor dataset. Variation between the laboratories was apparent. Average relative differences are presented below:

- Laboratory B, two datasets, +16%
- Laboratory S, one dataset, +3%
- Laboratory G, four datasets, -6%
- Laboratory H, two datasets, -10%
- Laboratory P, five datasets, -14%

At two sites, two laboratories split the analytical responsibilities. At the Jon site (low pH, high Al, and low Fe) calculated acidities were approximately equal to measured acidities for both laboratories. At the Anna site (low pH, high Al, Fe, and Mn), the calculated acidities for both laboratories were less than measured acidities.

Fig. 1 shows the relationships between measured and calculated acidity for the each dataset. Table 2 shows the linear regressions calculated for each individual dataset and for the entire dataset. All of the datasets exhibited strong relationships between AM and AC.

A perfect relationship between the acidity estimates would yield a linear regression with 1.0 slope and zero intercept. Most of the calculated slopes were between 0.90 and 1.10. Most of the

intercepts were between -10 and +20. The linear regression for the entire dataset had a slope of 0.98, an intercept of -8, and an r-square of 0.98.

### **Discussion**

In order to utilize the relationship between measured and calculated acidity in a quality control context, it is useful to appreciate the sources of error in the relationship. If the controllable errors can be largely eliminated, then the relationship can be used to reliably identify samples with suspect analytical results and to alert laboratories to systemic analytical problems.

# Errors Influencing Acidity Measurements

The hot peroxide method is a robust procedure as long as the titration is done carefully. Solids form as the titration proceeds and can interfere with reliable pH measurements. The sample should be stirred during the titration and decisions about titrant additions should be made only after stable pH readings are obtained. The primary error associated with acidity measurements is in the reporting of net alkaline samples. Most laboratories still report net alkaline samples as having zero acidity and the inclination is to assume that the alkalinity represents the net alkalinity. For samples that contain Fe or Mn, this assumption results in an errantly high net alkalinity because a portion of this alkalinity is consumed during the oxidation and hydrolysis of Fe<sup>2+</sup> and Mn<sup>2+</sup>. If the laboratory reports negative acidity as zero, then all acidities with zero values should be informed that the reporting protocols for samples with negative acidity have been changed in the  $20^{\text{th}}$  Edition of Standard Methods (APHA 1999). As long as the laboratory notes have been retained, it is possible to correct acidity values for samples where the negative results were not properly reported.

### Errors Associated with the Acidity Calculations

The acidity calculation as shown in equation G includes several parameters whose measurement can potentially affect the accuracy of the acidity calculation.

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Figure 1. Relationships between measured acidity and calculated acidity values for the 14 datasets.



Figure 1. (continued)







Figure 1. (continued)

	Lab	N <sup>a</sup>	рН	Alk <sup>b</sup>	Fe	Mn	AI	Sulfate	neg?	AM	AC	Dif %
Dole	Lab S	86	4.3	7	48	6	8	575	no	178	183	+3%
Farm	Lab G	295	4.5	6	28	10	14	612	yes	163	154	-6%
Cadog	Lab G	34	3.3	1	178	12	36	1,761	no	886	763	-14%
Chartiers	Lab P	43	5.3	46	57	1	2	598	no	97	66	-32%
Elk	Lab P	146	3.7	3	5	2	10	298	no	89	66	-26%
Botanical	Lab P	46	3.3	1	23	2	38	545	no	320	309	-3%
Bear	Lab G	345	4.5	7	95	7	20	631	yes	378	378	0%
Henry	Lab G	13	4.3	5	31	7	8	373	no	120	118	-2%
HowMor	Lab B	43	5.6	88	175	39	0	1,177	no	271	318	+17%
Mill	Lab B	41	4.1	24	79	41	5	927	no	215	248	+15%
Jon - P	Lab P	272	4.1	5	1	4	28	183	no	166	166	0
Jon - H	Lab H	37	4.4	3	1	5	29	286	no	174	177	+2%
Anna - P	Lab P	11	3.0	0	21	12	22	380	no	286	251	-12%
Anna - H	Lab H	72	3.0	0	19	11	20	538	no	305	238	-22%
All data		1,484	4.1	14	54	11	17	635		239	226	-5%

Table 1. Average chemical characteristics of the mine drainage datasets.

"N" is the number of samples; "Alk" is alkalinity; "neg?" indicates whether the dataset contains negative measured acidities; "AM" is measured acidity; "AC" is calculated acidity; "Dif %" calculated (AC-AM)/AM; acidity and alkalinity are mg/L CaCO<sub>3</sub>; Fe, Al, Mn, and sulfate are mg/L.

	Lab	рΗ	Fe	Al	neg?	AM	AC	Linear regression	r <sup>2</sup>
Dole	Lab S	4.3	48	8	no	178	183	AC = 1.13 AM - 17	0.98
Farm	Lab G	4.5	28	14	yes	163	154	AC = 0.92 AM + 3	0.96
Cadog	Lab G	3.3	178	36	no	886	763	AC = 0.82 AM <b>+</b> 38	0.98
Chartiers	Lab P	5.3	57	2	no	97	66	AC = 0.92 AM - 24	0.69
Elk	Lab P	3.7	5	10	no	89	66	AC = 0.79 AM - 4	0.97
Botanical	Lab P	3.3	23	38	no	320	309	AC = 1.01 AM - 17	0.98
Bear	Lab G	4.5	95	20	yes	378	378	AC = 1.00 AM - 5	0.99
Henry	Lab G	4.3	31	8	no	120	118	AC = 0.96 AM + 3	0.98
HowMor	Lab B	5.6	175	0	no	271	318	AC = 1.11 AM +17	0.96
Mill	Lab B	4.1	79	5	no	215	248	AC = 1.08 AM + 5	0.98
Jon - P	Lab P	4.1	1	28	no	166	166	AC = 1.04 AM - 7	0.99
Jon - H	Lab H	4.4	1	29	no	174	177	AC = 1.01 AM + 1	0.97
Anna - P	Lab P	3.0	21	22	no	286	251	AC = 1.13 AM - 62	0.93
Anna - H	Lab H	3.0	19	20	no	305	238	AC = 0.78 AM - 6	0.87
All data						239	226	AC = 0.98 AM - 8	0.98

Table 2. Linear regressions for the datasets where  $Acid^{calc} = a * Acid^{meas} + b, r^2$ .

"AM" is measured acidity; "AC" is calculated acidity; acidity and alkalinity are mg/L CaCO<sub>3</sub>; Fe, Al, Mn, and sulfate are mg/L.

### Absence of field measurements of alkalinity and pH.

Samples that contain both bicarbonate alkalinity and  $Fe^{2+}$  are unstable. If oxygen is introduced to the sample during sample collection or storage, iron oxidation and hydrolysis will occur in the sample bottle that is used by the laboratory for pH and alkalinity measurements. Iron hydrolysis reactions consume alkalinity and can change the pH. If the sample is net acidic, then the potential exists for the pH to decrease from a field value of 6 to a laboratory value between 3 and 4. If the sample is net alkaline, then large changes in pH are unlikely, but substantial decreases in alkalinity are possible. These problems make the measurement of field pH and alkalinity desirable.

In the absence of reliable field data, laboratory data must be used. The most substantial errors that result from the use of laboratory data occur for alkaline waters with high Fe concentrations. If an alkaline minewater sample contains 100 mg/L Fe, it is possible for the alkalinity to decrease by 180 mg/L between its collection and its treatment by the laboratory. Because samples such as these commonly have measured acidities ranging from -200 mg/L to  $\pm 200$  mg/L, an error of 100-200 mg/L in the alkalinity determination is obviously a quite substantial source of error in the acidity calculation.

Fig. 2 shows alkalinity measurements made for a discharge from an anoxic limestone drain. Field measurements were made within 30 minutes of sample collection. Laboratory measurements were made after transport to a central laboratory. Laboratory measurements were not made for at least 24 hours and could have been delayed for as long as14 days and still conformed with sample storage recommendations (APHA, 1992). The actual storage time for each sample was not known. The field measurements indicate that, after an early decline in alkalinity, the system consistently produced an effluent with 190-210 mg/L alkalinity. The laboratory data suggest a more variable effluent, with alkalinity concentrations ranging between 150 - 210 mg/L. This variability is largely due to errors introduced by variable sample storage. The lower values represent losses in alkalinity that occurred between sample collection and alkalinity measurement at the laboratory. Acidity calculations made using the laboratory alkalinity measurements suggest that the discharge is net acidic on occasions when the laboratory only measured 150-160 mg/L alkalinity. The error in this assessment is evident from the field alkalinity measurements and also from additional sampling of the passive system. (The final effluent was never acidic.)



Figure 2. Differences between field and laboratory measurements of alkalinity for an anoxic limestone drain discharge.

Substantial pH changes can occur between sample collection and treatment in the laboratory when the water contains alkalinity, ferrous iron, and is net acidic. A delay of several days (a weekend) can result in a laboratory pH measurement that is 2-3 units lower than what was measured in the field. These changes, while notable, do not affect the acidity calculation substantially. At a pH of 3.5, the  $H^+$  only contributes 16 mg/L to the acidity calculation. This increase in  $H^+$  acidity is usually substantially smaller than the loss of alkalinity that occurred while the pH was decreasing.

The extent of the changes in pH and alkalinity is dependent on the amount of aeration that occurs in sample collection and storage, the storage conditions, and the length of storage. These are difficult parameters to standardize. The preferred option is to make alkalinity and pH measurements in the field either at the sampling location or within 30 minutes of sample collection. If field measurements are not possible, then the raw samples should be collected without aeration, filled to the top of the bottle so there is no headspace for air, kept on ice, delivered to the laboratory as quickly as possible, and measurements of pH and alkalinity should be made immediately upon receipt at the laboratory.

### Presence of suspended solids in the acidified sample.

Solids that are collected into the acidified bottle are generally dissolved by the acid and subsequently measured by the metal analysis. Clay and silt particles will elevate aluminum concentrations. Iron oxide solids will elevate Fe concentrations. Solids do not undergo acid-producing hydrolysis reactions. Samples with substantial suspended solids will yield erroneously high acidity calculations.

The collection of a clean sample for the acid-preserved sample should be a sampling priority. Often the collection of suspended solids can be traced to disturbance of the sampling area by the collector. When a clean sample cannot be collected, the solids can be removed through filtration. If filtration is not possible, then the samples should be flagged as containing solids and should be considered poor candidates for acidity calculations.

Few mine drainage seeps contain suspended solids. In our sampling of hundreds of AMD discharges, we have only encountered several mine discharges that contain suspended solids at their source. The most common occurrence of samples with suspended solids in our studies are samples collected from within systems treating Fe-rich water and samples collected from receiving streams during storm events. In passive treatment systems it is common for ponds or wetlands to have water that contains visible iron oxide suspended solids. Comparisons in the 1990's by the US Bureau of Mines of filtered and unfiltered water samples from passive treatment systems indicated that the upper limit for particulate Fe was about 15 mg/L Fe (unpublished data collected by R. Hedin and R. Nairn, 1992-94). This amount of Fe, mistakenly considered as dissolved, would errantly overestimate acidity by 27 mg/L.

Suspended solids introduced by storm events into treatment systems and streams are usually re-suspended iron oxides and clays that, when dissolved, result in elevated concentrations of Fe and Al. It is not easy to adjust data to correct for this problem. Samples that are unavoidably contaminated with suspended sediments should be flagged as inappropriate for acidity calculations.

### Ferrous/ferric iron assumptions.

The acidity calculation differentiates between ferrous iron ( $Fe^{2+}$ ) and ferric iron ( $Fe^{3+}$ ). Methods exist for the determination of  $Fe^{2+}$ . No reliable low-cost method exists for  $Fe^{3+}$ , so ferric iron is determined from the difference of total dissolved iron and dissolved ferrous iron. Ferrous iron is rarely determined for mine drainage samples because it requires additional sampling (a separate sample preserved with hydrochloric acid), an added expense, and it is difficult to obtain accurate measurements. For most of the datasets analyzed here, iron speciation was estimated by pH. Ferric iron has a very low solubility at pH values greater than 4, so any dissolved iron present in the pH 4-8 range can be confidently assumed as ferrous. At pH less than three, ferric iron is highly soluble and it is commonly present in oxidized samples in the trivalent form as Fe<sup>3+</sup> and several complexed forms.

The assumption that all samples with pH less than 3 are oxidized is subject to criticism. However, a compilation of all the samples with low pH indicated that the assumption results in a very good correlation between measured and calculated acidities. Fig. 3 shows the relationship for samples with laboratory pH less than 3 and where all the iron was assumed ferric. The average sample in this subset had pH 2.69 and contained 546 mg/L Fe, 86 mg/L Al, 15 mg/L Mn, and 3,029 mg/L sulfate. The average measured acidity was 2,171 mg/L, while the average calculated acidity was 2,130 mg/L.



Figure 3. Measured and calculated acidity values for 48 samples with pH less than 3. All samples analyzed by Laboratory G.

For datasets containing many samples with pH less than 3, it is recommended that occasional measurements of  $Fe^{2+}$  be made so that an empirical estimate of the  $Fe^{2+}/Fe^{3+}$  relationship can be made. However, it is the author's experience that laboratories without experience in ferrous iron

measurements often provide inaccurate results. The laboratory should be required to assure its ferrous iron accuracy with rigorous QA/QC tests.

### Using the relationship to identify sampling and analytical problems.

If the sampling and analytical errors discussed above are minimized, then the resulting dataset should provide a good relationship between measured and calculated acidity values. The dataset summaries presented in Table 1 and Fig. 1 show that the relationship is robust and that it exists across datasets of varying water quality and different laboratories. On average, calculated acidities were 94% of the measured acidities. The relationship can be used to identify problems with individual samples. Because the sampling of mine drainage involves the collection of two samples at each location, paired samples can be occasionally mismatched. If the mismatched samples vary in chemical composition, the error should be apparent from the disagreement of measured and calculated acidity values. It is then possible to contact the laboratory and try to sort out the problems or decide that the sample pair is invalid and exclude it from the dataset.

The relationship can be used to evaluate the confidence level of a dataset. An example of this use of the relationship is shown in Fig. 4 and Table 3. The data are for a discharge considered for passive treatment. Between 1995 and 2002, seven samples were collected and analyzed by Laboratory A. Between mid-2002 and mid-2003, twelve samples were analyzed by Laboratory B. The average data for these two sampling efforts are shown in Table 3. Aluminum is an important aspect in the design of passive treatment systems because its presence complicates most passive treatment techniques. The older dataset indicated the presence of very high concentrations of Al. The recent dataset indicated low Al concentrations. Fig. 4 shows a plot of measured and calculated acidities for both datasets. The results produced by Laboratory A showed a linear relationship between the two acidity estimates and the estimated values were only 7% less than the measured values. The results from Laboratory B showed no relationship between measured and calculated acidities. The measured acidities were almost five times higher than the calculated acidities. Clearly, an acidic aspect of the water samples was missing from Laboratory B's analysis. The client was alerted to the analytical problems and is investigating the problem with additional sampling.



Figure 4. Measured and calculated acidity values for samples collected from the same discharge and analyzed by two laboratories.

Table 3. Average chemical characteristics and acidity calculations for a mine discharge as determined by two laboratories.

Lab	Period	pН	Fe	Al	Mn	Sulfate	AM	AC
А	1995-2002	2.8	13	40	3	614	357	332
В	2002-2003	2.9	14	2	4	499	516	109

"AM" is measured acidity; "AC" is calculated acidity; acidity values are mg/L CaCO<sub>3</sub>; Fe, Al, Mn, and sulfate are mg/L.

### **Summary**

A method for evaluating the quality of mine drainage has been described that compares measured and calculated acidity values. In order to assure that the comparisons are as accurate as possible, efforts should be made to collect samples without suspended solids, the pH and alkalinity should be measured in the field or immediately after delivery to the laboratory, and the laboratory should report negative acidity values when appropriate. When these conditions are followed, it is possible to identify suspect data and suspect laboratory analyses by comparing measured and calculated acidities. The method is essentially a balance of acidic and alkaline components of the mine water samples. This approach provides reliable QA/QC at a fraction of the cost of conventional QA/QC done by balancing cations and anions.

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