Kinetic Investigation of Siderite Oxidation During Laboratory Neutralization Potential Determination

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Abstract

Accurate acid rock drainage (ARD) prediction is of major importance to any project that may expose potentially acid generating rock and mine waste to the atmosphere. One of the most important steps in any ARD evaluation is determination of neutralization potential (NP), which quantifies the material's ability to neutralize the acid produced through sulphide oxidation.

Siderite is a ferrous carbonate mineral which ultimately yields no net acidity on hydration, but can cause optimistically high values during NP determinations if it has been solubilized without oxidation of the associated Fe^{+2} ion. This paper documents a study of the Fe^{+2} and Fe total concentrations though-out the duration of standard Sobek and modified acid base accounting (ABA) NP determinations, with and without oxidation of Fe^{+2}.

Introduction

It is generally known that the presence of ferrous iron bearing minerals, especially carbonate minerals such as siderite ($Fe^{2+}CO_3^{2-}$), in mine wastes can lead to overestimation of NP values during standard Sobek and modified ABA evaluations. It is understood that the ferrous carbonate component of mine waste does not contribute to total NP due to oxidation of ferrous iron (Fe^{2+}) to ferric iron (Fe^{3+}), which releases an equivalent amount of acid through ferric iron hydrolysis (Skousen 1997). To correct for this during standard Sobek and modified ABA analyses, hydrogen peroxide is added as an oxidant to ensure the release of metal acidity from ferrous iron prior to the final NP titration. Often, the use of "siderite correction" during the modified NP determination of samples known to contain appreciable siderite may appear to have little or no apparent impact on the final NP value determined.

Use of the siderite correction is not universally considered to be warranted when completing the modified NP procedure due to the relatively low solubility of siderite at room temperature in comparison to the boiling temperatures used for the standard Sobek procedure. However, the procedure is generally of interest in ARD investigations regardless of method whenever the presence of siderite is identified.

To ascertain the efficacy of siderite correction, a kinetic investigation into the oxidation of ferrous iron was conducted on a not potentially acid generating (NPAG) waste rock high in siderite. The study was conducted over a range of dilutions using both the standard Sobek and modified NP methods, with and without hydrogen peroxide addition. Dilutions of the high siderite waste rock were prepared through mixing with an inert sand to provide insight into the impact different ranges of ferrous carbonate would have on final analysis. Solution samples were taken periodically to monitor total iron (inductively coupled plasma optical emission spectroscopy) and ferrous iron (discrete analyser - phenanthroline) concentrations to evaluate oxidation kinetics.

Materials

Testwork was conducted using a sample of waste rock collected from a Canadian iron mine known to have a high siderite concentration and a not potentially acid generating

(NPAG) ARD designation. Characterization of the samples siderite content was made by semi-quantitative x-ray diffraction (XRD) analysis using a Bruker AXS D8 Advance Diffractometer. XRD analysis determined the waste rock was predominantly quartz, with siderite making up 20.0 weight %, and pyrite making up 0.6 weight %.

Representative cuts of the pulverized waste rock were blended with pulverized Ottawa sand (85% passing 200 mesh) and sample cuts were riffled to provide representative waste rock to sand ratios of 300:300 and 180:420. In this manner samples of waste rock at 100%, 50%, 30% were prepared, plus a pure pulverized Ottawa sand sample provided to act as a control.

Methods

The standard Sobek NP determinations were made using the original US EPA acid base accounting method (Sobek 1978) by SGS at their Lakefield, ON Canada site. Only minor changes were made to the Sobek method with respect to equipment used. The modified NP determinations were completed using the Lawrence method from the Acid Rock Drainage Prediction Manual (Lawrence 1991), also at the SGS Lakefield site.

The hydrogen peroxide (H_2O_2) addition was made for the standard Sobek and the modified methods by adding 5 mL of 30% hydrogen peroxide to the suspension and boiling gently for one minute prior to the NaOH titration (Skousen 1997) to pH 7.0 for the standard Sobek, and to pH 8.3 for the modified NP.

Each of the three waste rock samples (100%, 50%, 30%) and the pulverized Ottawa sand were subjected to each method with and without siderite correction in triplicate. Samples were removed from each standard Sobek NP sample for Fe^{2+} and Fe total analysis after each step in the method. This included:

- 10 minutes after HCl acid addition,
- after the boil,
- after addition of hydrogen peroxide (siderite correction only),
- after hydrogen peroxide boil (siderite correction only), and
- after the titration to pH =7 with NaOH.

For each modified NP sample subsamples were removed for Fe^{2+} and Fe total analysis during each pH check in the method:

- Immediately after HCl acid addition (time zero),
- 0.5 hours after HCl acid addition,
- 1 hour after HCl acid addition,
- 4 hours after HCl acid addition,
- 22 hours after HCl acid addition,
- after hydrogen peroxide boil (siderite correction only), and
- after the titration to pH =8.3 with NaOH.

At each sampling point 1 mL of sample was removed and diluted into 50 mL of 2% HCl, using a 50 mL "digi-tube" and shaken well. The HCl served to preserve the Fe^{+2} concentrations. The 1 mL of sample removed was replaced with 1mL of deionized water.

The Fe total values were determined by trace level inductively coupled plasma, optical emission spectroscopy (ICP-OES) analysis. Because the Fe^{+2} and Fe total values were to be based on dissolved values, the Fe total samples were not digested prior to analysis. Hence, Fe total refers to the total Fe within the sample (Fe^{2+} and Fe^{3+}) rather than a total digestion.

The Fe^{2+} concentrations were determined using a Discrete Photometric Analyser running the Ferrous colourimetric Fe^{2+} method with phenanthroline. Prior to each use the Discrete Analyzer was calibrated with a freshly prepared calibration solution to ensure absence of Fe^{3+} due to oxidation.

The Fe^{2+} calibration solution was prepared by first diluting 5 mL of 1000 mg/L Fe stock solution into 10 mL of deionized water in a 50 mL centrifuge tube, then adding 2 ml of concentrated HCl. This results in the solution turning yellow which indicates that all the Fe present is Fe^{3+} iron. The solution was then heated to approximately 50°C by hot-block and stannous chloride was added carefully drop-wise until the solution cleared. Only sufficient stannous chloride required to discharge the yellow colour was used because excess Sn^{2+} can act as an interference for the colourimetric determination of Fe^{2+}. Once bulked to 50 mL with deionized water the solution was identified as the 100 mg/L Fe^{2+} stock solution.

The Discrete Analyzer was calibrated to run the Ferrous colourimetric Fe^{2+} method by loading the calibration standard, which was made by diluting 1 mL of the 100 mg/L stock solution into 50 mL of 2% HCl, resulting in a 2 mg/L Fe^{2+} calibrator (A-Fe2-2), and a blank solution of 2% HCl (A-Fe2-0) into one of the sample segments.

The following reagents were also required to be loaded into the Discrete Analyzer:

- FeBuffer: dissolve 12.5 g of ammonium acetate in 7 mL of deionized water, add 35 mL of glacial acetic acid and bulk to 50 mL capacity with deionized water and shake well.
- FeColour: dissolve 0.05 g of 1,10-phenanthroline into 50 mL of deionized water, add 2 drops of concentrated HCl, cap and shake well. If this solution darkens it needs to be freshly prepared.
- 2%HCl: dilute 1 mL of concentrated HCl into 50 mL of deionized water.

After the reagents and calibration solutions were loaded, the Ferrous Fe^{2+} method was selected and the calibration program initiated. Once the calibration sequence was complete, the NP samples could be immediately analyzed. To run the individual standard Sobek and modified NP samples, they were simply inserted onto one of the segments, the Ferrous method selected and the Discrete Analyzer analysis was initiated.

Because the linear range of the Discrete Analyzer Ferrous method is 0.02 mg/L to 20.0 mg/L Fe^{+2}, over-range samples had to be diluted using the 2% v/v HCl matrix in order stay in range of the method.

Results and Discussion

To reduce the data, the triplicate Fe^{2+} and Fe total results for each sample at each sampling point were averaged and then corrected by subtracting the average control value. The data for the standard Sobek NP Fe^{2+} values at each sampling point, and the average corrected NP value determined, are presented in Table 1, while the corresponding data from the Fe total analyses are given in Table 2. Similarly, the data for the modified NP are presented in Table 3 for Fe^{2+} and Table 4 for Fe total.

Data presented in Table 1 clearly illustrate that the concentration of Fe^{2+} in the standard Sobek NP solution increased dramatically after the boiling hydrochloric acid step. Although the Fe^{2+} concentration of the 50% Waste Rock sample was roughly 50% of the uncut sample, the same was not true of the 30% Waste Rock sample, which resulted in a concentration of roughly 10% of the uncut sample. After the addition of hydrogen peroxide the Fe^{2+} concentrations decreased dramatically, and there was generally some additional decrease after the hydrogen peroxide was boiled off prior to titration. After the titration for NP determination the siderite corrected samples Fe^{2+} concentrations were trending to zero after being corrected for the control. Without the siderite correction, the Fe^{2+} concentrations after titration were similar to those of the period 10 minutes after the initial hydrochloric acid addition.

Review of the Fe total data given in Table 2 indicated that essentially all of Fe in solution was in the form of Fe^{2+} up until the point where the hydrogen peroxide was first

Table 1 *Average corrected Sobek NP [Fe^{2+}] (mg/L) at time intervals with and without siderite correction.*

	10 min after acid addition	After Boil	10 min after H_2O_2 addition	After H_2O_2 boil	After titration	NP kg $CaCO_3$/tonne
Waste Rock	353	2182	---	---	424	393
50% Waste Rock	537	1012	---	---	301	178
30% Waste Rock	146	154	---	---	28.6	68.5
			With Siderite Correction			
Waste Rock	433	2139	43.2	6.79	-0.13	268
50% Waste Rock	359	1085	3.69	5.90	-0.16	176
30% Waste Rock	129	193	13.3	0.37	0.09	28.8

Table 2 *Average corrected Sobek NP [Fe] (mg/L) at time intervals with and without siderite correction.*

	10 min after acid addition	After Boil	10 min after H_2O_2 addition	After H_2O_2 boil	After titration
Waste Rock	380	2281	---	---	1055
50% Waste Rock	564	997	---	---	284
30% Waste Rock	157	159	---	---	28.4
		With Siderite Correction			
Waste Rock	476	2043	1626	1707	1.15
50% Waste Rock	397	1007	893	814	0.13
30% Waste Rock	141	197	146	151	0.85

Table 3 *Average corrected modified NP [Fe^{2+}] (mg/L) at time intervals with and without siderite correction.*

	Addition HCl Time Zero	Addition HCl 0.5 Hours	Addition HCl 1 Hours	Addition HCl 4 Hours	Addition HCl 22 Hours	After H_2O_2 Boil	After Titration	NP kg $CaCO_3$/ tonne
Waste Rock	517	564	461	635	767	---	21.4	94.9
50% Waste Rock	375	321	289	242	370	---	0.29	39.1
30% Waste Rock	358	253	195	165	145	---	0.10	10.9
				With Siderite Correction				
Waste Rock	505	493	437	601	732	7.31	0.09	70.3
50% Waste Rock	366	310	260	231	374	4.77	-0.02	50.4
30% Waste Rock	345	235	178	143	130	3.56	-0.05	20.9

introduced. Once the siderite correction was initiated the Fe total concentration was maintained, as Fe^{2+} was oxidized to Fe^{3+} and the metal acidity was released into solution. Without the hydrogen peroxide addition, the Fe total concentration was only marginally higher than the Fe^{2+}, indicating that little of the Fe^{2+} had oxidized to Fe^{3+}.

Returning to Table 1 we can see that the NP values were generally increased without the siderite correction step. The decrease in NP for the siderite corrected 50% Waste Rock was calculated to be only 2 kg of $CaCO_3$ per tonne, which is anomalous when compared with the 100% and 30% Waste Rock samples (125 kg and 39.7 kg of $CaCO_3$ per tonne, respectively).

Modified NP Fe^{2+} data, presented in Table 3, illustrates that the concentration of Fe^{2+} in the modified NP solution varied over time, but never increased dramatically in the manner observed after the standard Sobek NP boiling hydrochloric acid step. This indicated that the siderite was never brought into solution to the same extent when digested at room temperature, which was expected. However, it is notable that the Fe^{2+} concentrations in the higher siderite concentration samples increased over the 22 hours of the modified NP determination, while the 30% Waste Rock samples Fe^{2+} concentrations fell over 60% by the end of the digestion period. At the end of the modified NP digestion period the 100% Waste Rock sample's Fe^{2+} concentration was approximately double the 50% Waste Rock sample's Fe^{2+} concentration, while the 30% Waste Rock only represented about 20%. After the hydrogen peroxide addition and boiling off the hydrogen peroxide, the Fe^{2+} concentrations in the siderite corrected modified NP solutions decreased significantly. Again, after the titration for NP determination the siderite corrected sample's Fe^{2+} concentrations were trending to zero, as in the standard Sobek NP procedure, however in this case, the Fe^{2+} concentration was also relatively low without hydrogen peroxide addition.

A review of the Fe total data given in Table 4 indicated that essentially all of the iron in solution was Fe^{2+} up until the point where the hydrogen peroxide was first introduced. The Fe^{2+} concentrations were in many instances, marginally higher than the Fe total values, and as this was generally the case at higher concentration it may have been due to the higher dilutions required at high concentration to keep the Fe^{2+} measurements in range. As in the standard Sobek NP procedure, once the siderite correction was initiated, the Fe total concentration was maintained, as the Fe^{2+} was oxidized to Fe^{3+} and the metal acidity was released into solution. After titration, the drop in Fe total was apparent for all samples, regardless of whether the siderite correction had been made, and the highest value was that for the 100% Waste Rock sample without correction (21.4 mg/L). Although the siderite correction did have an impact on the modified NP Fe^{2+} concentrations, it was minimal when compared to the impact on the standard Sobek NP.

Calculated modified NP values for the Waste Rock materials are given in the final column of Table 3. Although the correction did reduce the NP of the 100% Waste Rock material, the 50% and 30% Waste Rock samples returned higher values after the correction.

Conclusions

In completing this study, it became readily apparent that the boiling step used in the standard Sobek ABA NP determination does put a great deal more Fe^{2+} into solution when compared to the room temperature modified ABA NP method. The standard Sobek ABA without the correction has a significant quantity of Fe^{2+} iron left in solution, and hence the potential metal acidity is not considered, and thus the siderite correction is quite valid. Although not unexpected, the study does illustrate that higher NP values are determined in general when using the standard Sobek ABA when compared to the modified ABA method due to the release of higher concentrations of minerals which would not have been solubilized without the boiling HCl digestion.

The study indicated that oxidation did not appear to impact the Fe^{2+} in solution over the course of the modified NP method's extended room temperature digestion period. For the 100% Waste Rock sample (20 wt% siderite) the Fe^{2+} concentrations in solution increased over the monitored 22-hour digestion period, while it decreased for the two samples with lower siderite concentrations. The Fe total concentrations mirrored these trends indicated that iron was almost entirely present in the lower oxidation state. For either method, hydrogen peroxide was necessary to oxidize soluble Fe^{2+} to Fe^{3+}.

The modified NP method puts less siderite into solution and hence has little need for correction. Results of the investigation clearly illustrate the benefit of siderite correction when completing the standard Sobek ABA method. Conversely, minimal real impact on NP determination was found through hydrogen peroxide addition when the modified ABA method was used.

Table 4 *Average corrected modified NP [Fe] (mg/L) at time intervals with and without siderite correction.*

	Addition HCl Time Zero	Addition HCl 0.5 Hours	Addition HCl 1 Hours	Addition HCl 4 Hours	Addition HCl 22 Hours	After H_2O_2 Boil	After Titration
Waste Rock	478	632	420	627	721	---	18.5
50% Waste Rock	350	230	259	180	345	---	0.60
30% Waste Rock	347	189	174	132	138	---	0.21
			With Siderite Correction				
Waste Rock	483	383	427	587	679	619	0.27
50% Waste Rock	362	302	235	235	342	360	0.06
30% Waste Rock	351	220	161	147	120	164	0.02

References

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