APPLICATION OF ACID BASE ACCOUNTING METHODS TO BARITE PROJECTS IN NEVADA

A. Prestia [1], R.J. Bowell [2], R. Warrender[2], C. Brough[2], K. Fallowfield[3]

[1] SRK Consulting (US) Inc., Suite 300, 5250 Neil Road, Reno, Nevada, 89502, USA

[2] SRK Consulting (UK) Ltd., Churchill House, 17 Churchill Way, Cardiff CF10 2HH, UK

[3] Halliburton Energy Services Inc., 912 Dunphy Ranch Rd., Battle Mountain, NV 89820, USA

Introduction

A geochemical characterization study has been conducted to assess the Acid Rock Drainage and Metal Leaching (ARDML) potential of waste rock, ore and jig by-products from Halliburton's Rossi Mine in Elko County, Nevada. Halliburton and their predecessor NL Baroid has mined barite from the Rossi Mine using open pit methods since 1947. The geochemical characterization program has been completed in support of ongoing permitting efforts and provides a basis for risk assessment and the evaluation of options for construction, operation and closure of the mine facilities.

The Rossi Mine is located near the northern end of a barite belt that runs north-south through Nevada. The barite deposits at the Rossi Mine are sedimentary in origin and occur in the Ordovician Vinini Formation that consists of brown to grey, massive to thinly bedded chert that has undergone extensive oxidation with few sulfide minerals remaining. Below the base of the planned pits the Vinini Formation is unoxidized and consists of dark grey to black carbonaceous chert with visible pyrite. The oxidation boundary defines the extent of the current mine plan and the sulfide bearing unoxidized Vinini Formation will not be mined during operations.

The primary purpose of the Rossi geochemical characterization program was to provide an understanding of the geochemical characteristics of geological materials specific to the Rossi Mine using commonly applied static and kinetic testing methods designed to address mineralogy and the potential to generate acid or leach metals. In order to accomplish the objectives of the study, samples representative of waste rock, ore and jig by-products were collected from the Rossi Mine for geochemical testing.

The geochemical test program completed for the Rossi Mine produced interesting results that illustrates the complexity of interpreting Acid Base Accounting (ABA) data for material containing barite. This highlights the importance of considering the site-specific mineralogical characteristics of the deposit in the selection of the most appropriate geochemical test methods to use in the prediction of potential acid generation.

Methodology

For this investigation, a total of 62 samples were collected that represent waste rock, ore and jig by-products from the Rossi Mine. Samples were collected from exploration drill core as well as from the surfaces of existing waste rock dumps and ore stockpiles. In addition, samples of final ore product, coarse tailings and fine tailings were collected from the operating jig plant at the mine.

The static and kinetic geochemical predictive tests used in this study were standard test methods commonly used to predict acid generating or neutralizing potential of mine waste as well as evaluate the potential for metal leaching risk. These tests include the Nevada modified Sobek ABA method, Net Acid Generation (NAG) test and the standard Humidity Cell Test (HCT). In addition, mineralogical analysis was completed using optical microscopy, scanning electron microscopy (SEM) and X-Ray diffraction (XRD).

Acid Base Accounting indicates the theoretical potential for a given material to produce net acid conditions. The technique can be considered as characterizing the 'total potential reservoir of acidity or alkalinity in a given material'. Acid Base Accounting testing was carried out using the Nevada modified Sobek method (NDEP, 2013). This method determines the sulfide sulfur and sulfate sulfur content by measuring the amount of nitric acid-extractable sulfur and the amount of hot water-extractable and hydrochloric acid-extractable sulfur. Neutralizing potential (NP) was determined by using the modified Sobek protocol that includes a digestion to expel any CO_2 followed by a back titration with NaOH to a pH of 8.3 s.u.

Static NAG testing was carried out in accordance with the method described by Miller et al. (1997) to provide a second measure of ARD potential. This method involves intensive oxidation of the sample using hydrogen peroxide, which accelerates the dissolution of sulfide minerals and has the net result that acid production and neutralization can be measured directly. The leachate is then titrated with sodium hydroxide in two stages (pH 4.5 and to pH 7) to determine the NAG value. The static NAG test differs from the ABA test in that it provides a direct empirical measurement of acid production and neutralization produced by the intense oxidation of the sample using hydrogen peroxide. As such, the NAG test can provide a better estimate of field acid generation than the more widely-used ABA method, which defines acid potential based on sulfide content. Samples with NAG pH values greater than pH 4 are predicted to be non-acid forming and NAG results greater than one kg H_2SO_4/ton indicate the sample will generate some acidity in excess of available alkalinity.

Twelve samples were selected from the static database for mineralogical analysis and were submitted for a standard suite of mineralogy tests including optical microscopy, XRD and SEM analysis. Eleven samples were also submitted for kinetic testing to address the uncertainties of the ABA predictions and confirm the results from NAG testing and mineralogical analysis. Laboratory kinetic testing selected for this project consists of the standard humidity cell test procedure designed to simulate water-rock interactions in order to predict the rate of sulfide mineral oxidation and therefore acid generation and metals mobility (ASTM D-5744-96).

Results

The ABA results indicate the presence of significant sulfide minerals (2-5 wt%) for the barite ore. However, these results are not consistent with observations made during the sample collection activities that indicate visible sulfide minerals are only observed in the unoxidized chert and no sulfides were observed for the other material types, including the oxidized chert, barite ore and jig by-products. Furthermore, no associated acid-generation was apparent from the NAG test for these samples. This discrepancy in ABA and field observations and NAG results has been attributed to the presence of barite in the samples.

Barite is a non-acid generating sulfate mineral that undergoes incomplete dissolution and extraction in the ABA tests and can result in an incorrect interpretation of the ABA data. According to Jennings (1995), most of the barite in an ABA test will report as non-extractable sulfur; however a small percentage will be removed by the nitric acid extraction. Because the nitric acid extractable sulfur fraction is considered acid generating, the presence of barite in a sample will result in an overestimate of sulfide sulfur and acid generation (i.e., false positive). Therefore, the presence of barite limits the application of Sobek-style ABA tests to the Rossi waste rock, ore and jig by-products. This was confirmed by the mineralogical analysis and kinetic testing program.

From the mineralogy study, the Rossi waste rock, ore and jig by-products predominantly consist of barite, quartz and associated kaolinite and illite. Other sulfate minerals observed include jarosite and alunite which were occasionally present as trace minerals. Pyrite was also identified in seven of the samples at trace (<1%) and ultra-trace (<0.1%) amounts. However, where present, the pyrite was very fine-grained (1-20 μm) and typically encapsulated within quartz. The sulfide sulfur concentrations predicted from the ABA test are significantly greater than the pyrite content observed in thin section for the same samples. This is the case for all samples except the two waste rock samples consisting of chert. For these samples, the mineralogy results are generally consistent with the ABA results and field observations. These results indicate that the ABA test overestimates pyrite content and results in an incorrect prediction of acid generation for material containing appreciable barite (i.e., ore and jig by-products). When barite concentrations are low (i.e., <3%), the ABA results provide a reasonable estimate of pyrite content and acid generation.

In order to address the uncertainties of the ABA, 11 samples were selected from the static test database for humidity cell testing. The humidity cells were operated for between 48 and 73 weeks. During the course of the test only one cell of unoxidized chert developed acidic conditions; the remaining 10 cells generated circum-neutral to mildly alkaline leachates with low associated metal release. In Figure 1, the Net Neutralization Potential (NNP) is plotted against the final HCT pH and shows those samples with an uncertain potential for acid generation from the ABA predictions did not produce acidic conditions in the HCT. Furthermore, the samples that were predicted to be acid generating from the ABA results with NNP values less than -20 kg $CaCO_3$ eq/t and NPR values less than 1 (i.e., barite ore and jig by-products) did not generate acid after 73 weeks of HCT testing. These results indicate the ABA results do not provide a correct classification of the potential for ARDML and over-predict acid generation potential.

The correlation between the HCT results and the acid generation prediction from the NAG results shows a better correlation and indicates the NAG test is better tool for predicting the acid generating potential of waste rock and ore material at the Rossi Mine. Samples that were predicted to be non-acid forming from the NAG test and those samples that showed a lower capacity for acid generation in the NAG test (i.e., NAG values greater than 1 but less than10 eq. kg H_2SO_4/ton) were non-acid generating in the HCT (Table 1).

Table 1. Comparison of Static Test Results to HCT Results

Cell	Material Type	ABA			NAG			HCT	
		NNP (kg $CaCO_3$ eq/t)	NPR	AP Defined by ABA	NAG pH (s.u.)	NAG (kg H_2SO_4 eq/t)	AP Defined by NAG	Final HCT pH (s.u.)	HCT Results
1	Barite	-100	0.01	PAG	5.6	0	Non-PAG	6.72	Non-Acid
10	Barite	-100	0.01	PAG	5.4	0	Non-PAG	6.52	Non-Acid
2	Jig waste	-70	0.02	PAG	5.2	0	Non-PAG	6.64	Non-Acid
3	Jig tails	-70	0.05	PAG	6.6	0	Non-PAG	6.65	Non-Acid
5	Chert	-6	0.05	Uncertain	5.5	0	Non-PAG	6.67	Non-Acid
6	Chert	0.5	1.7	Uncertain	5.9	0	Non-PAG	6.65	Non-Acid
4	Chert	-9	0.26	Uncertain	5.7	0	Non-PAG	6.56	Non-Acid
7	Chert	6.8	8.6	Uncertain	5.1	0	Non-PAG	6.59	Non-Acid
11	Chert with pyrite	6.8	2.2	Uncertain	3.6	4.5	Low-PAG	6.13	Non-Acid
8	Chert with pyrite	-20	0.08	PAG	2.5	33	PAG	2.89	Acid
9	Intrusive	1	3.3	Uncertain	8.3	0	Non-PAG	7.04	Non-Acid

ABA Criteria	PAG	NNP<-20 or NPR<1
	Uncertain	NP between -20 and +20 or NPR between 1 and 3
	Non-PAG	NNP>20 or NPR >3
NAG Criteria	PAG	NAG >10
	Low-PAG	NAG between 1 and 10
	Non-PAG	NAG <1
HCT Criteria	Acid	pH <5 s.u.
	Non-acid	pH >5 s.u.

Notes:
Net Neutralization Potential (NNP) = Neutralization Potential (NP) – Acidification Potential (AP)
Neutralization Potential Ratio (NPR) = Neutralization Potential (NP)/Acidification Potential (AP)

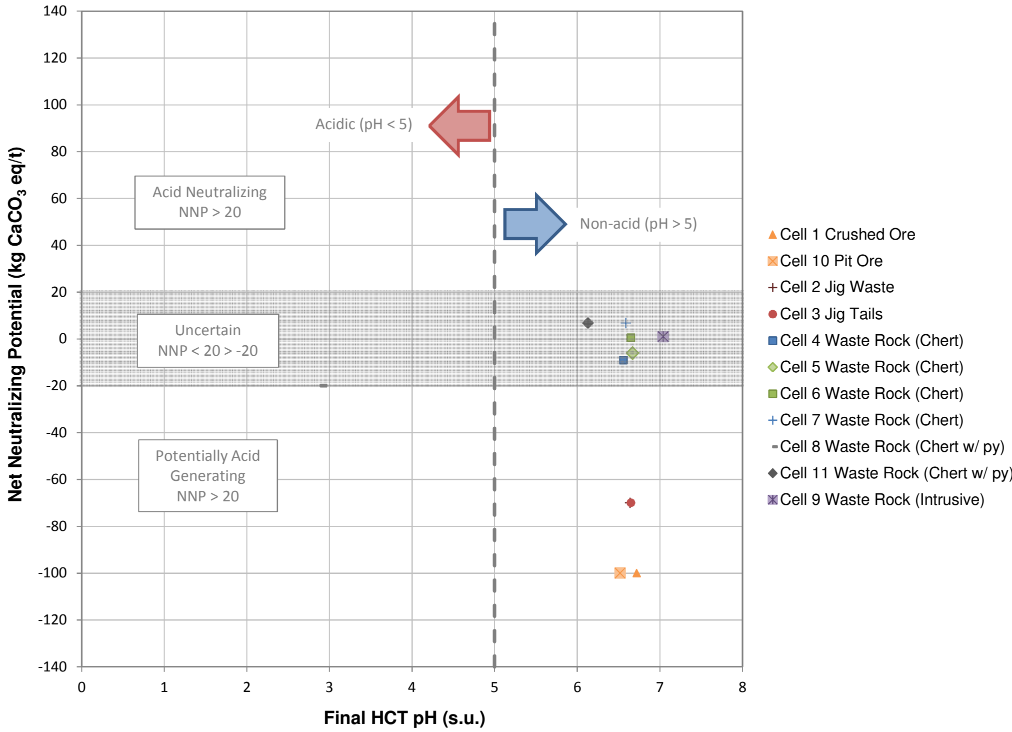

Figure 1. Net Neutralization Potential versus Final HCT pH

Summary and Conclusions

In summary, the results from the Rossi geochemical characterization program indicate acid generation is not predicted for any of the Rossi waste rock, ore or jig by-products that will be mined as part of the current mine plan. The only material type to show a potential for acid generation is the unoxidized chert that contains visible pyrite. However, this material type occurs below the base of the pits will not be mined as part of the current mine plan.

This study demonstrates the presence of barite greatly limits the application of using traditional Sobek style ABA methods. Barite will undergo incomplete dissolution and extraction in the ABA tests and will result in an over-prediction of acid generation for the Rossi materials that contain barite (i.e., ore and jig by-products). A good correlation is observed between the HCT and NAG results indicating the NAG test is a reliable indicator of acid generation for the Rossi Mine and potentially also other barite deposits throughout Nevada.

This study demonstrates the importance of considering the site-specific mineralogical characteristics of the deposit in the selection of the most appropriate geochemical test methods to use in the prediction of potential acid generation. Using the results of the ABA testing alone would have resulted in a significant over prediction of acid generation for the Rossi Mine.

References

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