Evaluation of Acid Rock Drainage Potential in a Retrospective Study 25 Years after Mine Closure: Acid Base Accounting Statistics are Not Sufficient

R.V. (Ron) Nicholson[1], Sean Shaw[2], Sarah Barabash[1] and John Lundagan[3]

[1]*EcoMetrix Incorporated, 6800 Campobello Road, Mississauga, Ontario Canada, rnicholson@ecometrix.ca, sbarabash@ecometrix.ca,*
[2]*Ministry of Energy and Mines, British Columbia, Canada, Sean.Shaw@gov.bc.ca,*
[3]*ArcelorMittal Dofasco, john.lundrigan@arcelormittal.com*

Abstract
Waste rock at a former iron mine with 70 million tonnes of rock distributed in 15 discrete deposits was evaluated for acid generating characteristics. Two of the 15 deposits exhibited acidic drainage while all others remained neutral 25 to 40 years after deposition. The carbonate neutralization potential (Carb-NP) exceeded the acid potential (AP) in all deposits and only 10% of the samples represented potentially acid generating (PAG) material. The acid drainage from the 2 deposits could not be readily explained by average ABA characteristics. Differences in spatial distributions of sulphide and carbonate minerals in piles can explain differences in neutral and acidic conditions.

Keywords: ICARD, IMWA, MWD 2018, acid base accounting, iron mine, closure, acid drainage, carbonate neutralization potential

Introduction
The former Sherman Mine, located in Ontario, Canada, exploited iron oxide from a banded iron formation operated from 1968 to 1990. Reclamation of the site occurred between 1990 and 1995. Five open pits (North, South, East, West and Turtle) produced about 70 Mt of mine rock stored in 15 discrete rock deposits.

The iron deposits primarily consisted of magnetic iron oxide (magnetite) and carbonate minerals with sulphide minerals, primarily pyrite (FeS_2) and marcasite (FeS_2) that occurred in carbonaceous bands adjacent the ore in the South and East pits. Most mine rock was typically deposited adjacent to the pits. Prior to 1977, some sulphide rock was used for roadbed construction and some was deposited in rock piles. Rock that was identified after 1977 as high sulphide and potentially acid generating from the South and East Pits was segregated and deposited within saturated tailings.

Two of 15 rock deposits exhibited acidic drainage. All others had neutral drainage 25 to 40 years after deposition. One area that exhibited acidic drainage represented a pile of mine rock from the early mining of the South Pit. The other area represented a road embankment (East Embankment) that was constructed from South Pit mine rock early in the operation. While the acid drainage reports to an on-site lake, the acid and metals are assimilated in the receiving environment and the water meets stringent regulatory requirements for the protection of aquatic life prior to leaving the former mine site.

This study focused on the sampling of the rock piles and contact waters from the individual piles and deposits to assess the characteristics that could be used to understand the differences between the piles that produced acidic drainage and those that produced neutral drainage. The rock was assessed for acid base accounting (ABA) characteristics and the porewaters evaluated for chemical constituents related to sulphide oxidation and neutralization reactions.

Methods
As part of an investigation of acid generation at the mine site in 2014, over 500 individual mine rock samples were collected from the 15 mine rock deposits. These samples were re-

covered. More than 200 rock samples, from 48 boreholes and 42 test pits, were submitted for ABA analysis and 58 test pit samples were subjected shake flask extraction (SFE) tests to assess porewater concentrations. The porewater concentrations were calculated from the soluble masses of constituents from the SFE divided by the measured water contents of the rock samples. The number of rock samples collected from each individual deposit was approximately proportional the rock mass in each pile relative to the total rock on site. Mineralogy was assessed quantitatively on selected sample using the QEM Scan method.

Acid Base Accounting Results for all Rock Samples

Carbonate minerals within the mine rock from the West and North pits were primarily composed of calcite and dolomite, with siderite and ankerite making up a substantial portion of the carbonates in the rock from the South, East and Turtle pits. Overall, carbonate contents ranged from 0.06% to 18% CO_3 with a geometric mean value of 2.2% CO_3 (50 kg-$CaCO_3$/tonne). The acid base accounting (ABA) characterisation included carbonate analysis on all samples and modified Sobek test (Lawrence and Wang, 1996) with siderite correction (Skousen et al., 1997).

Comparison between the modified Sobek and siderite corrected NP values showed excellent agreement (Figure 1). The calculated carbonate neutralisation potential (Carb-NP) and the Sobek-NP results gave a strong correlation coefficient (R2 = 0.98) with slightly smaller Carb-NP values than Sobek-NP values below levels of 100 kg $CaCO_3$/t (Figure 1). The Carb-NP values were considered to represent the "effective" NP and were therefore used to calculate the NP/AP ratios (NPR) in order to classify samples for the potential to generate acid or not (Price, 2009).

The mine rock contains sulphide minerals, mainly pyrite, with sulphide-sulphur contents ranging from 0.01% to 5% S and a geometric mean value of 0.24% S. About 50% of the samples contained less than 0.1%S. The sulphide-sulphur content represents approximately 88% of the total sulphur in the mine rock, and 12% of the total sulphur is present as sulphate, which is consistent with weathering for three decades or more.

The geometric mean Carb-NPR values for all mine rock was 9.5, suggesting that all rock combined should represent non-PAG material. About 10% of the 210 samples had Carb-NPR values less than 1, representing PAG rock and 83% had Carb-NPR values greater than 2, representing non-PAG rock (Figure 2).

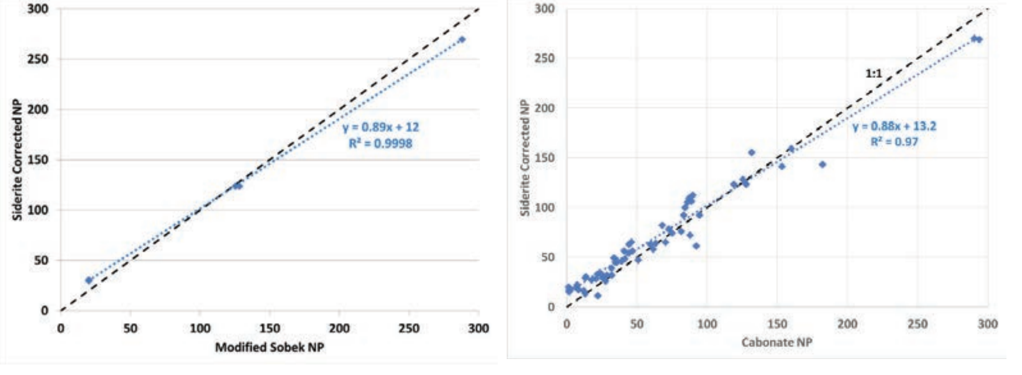

Figure 1. Siderite corrected NP compared to modified Sobek NP (left) and carbonate NP (right).

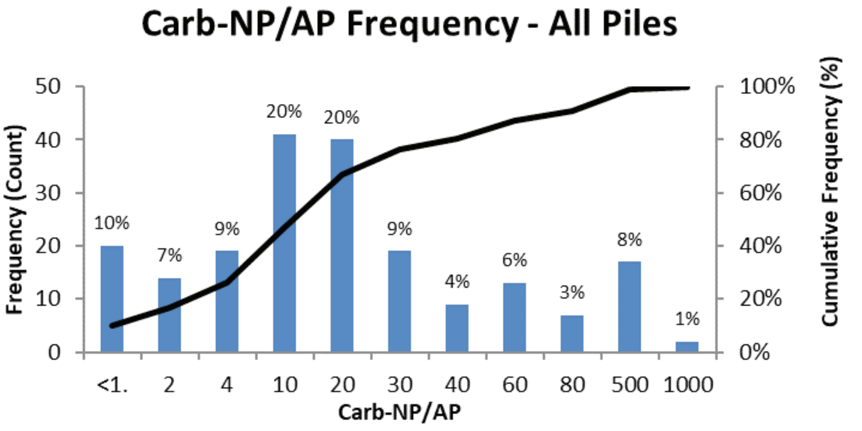

Figure 2: A frequency distribution plot of Carb-NPR for all rock samples.

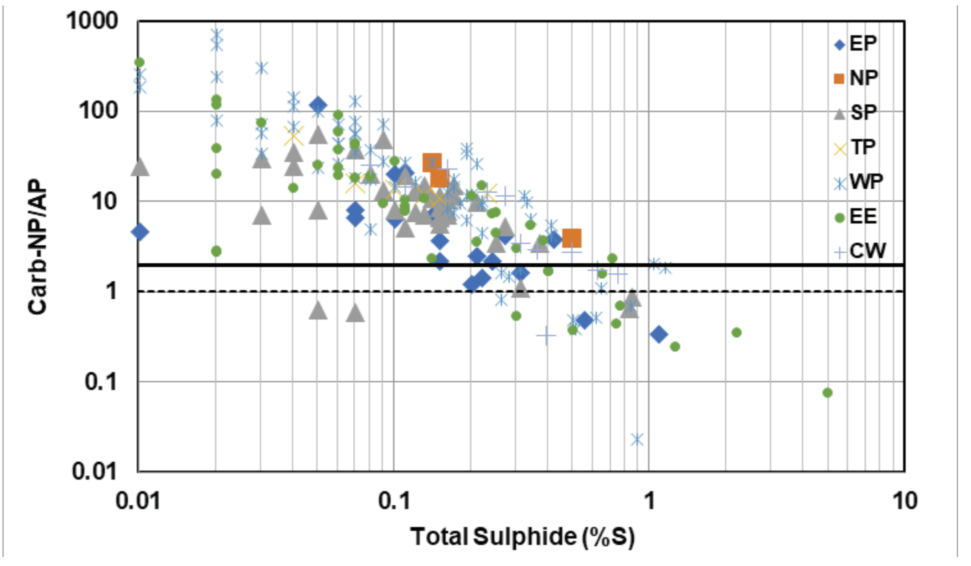

Figure 3. Carb-NP in relation to sulphide content for samples from the individual pits.

Acid Base Accounting Results from Individual Piles

The results for the various piles, including those from the East Pit (EP), North Pit (NP), South Pit (SP), Turtle Pit (TP), West Pit (WP), the East Embankment (EE) and Causeway (CW) were examined separately. The Carb-NPR and sulphide sulphur results in Figure 3 show that rock samples from all pits have similar ranges of values and all but the North Pit and Turtle pit have samples with NPR values less than 1. The thee highest sulphide contents were in samples from the East Embankment.

Assuming that the neutralization potential is effective and that it will maintain neutral pH conditions when consuming acid, a sample with a Carb-NPR of greater than two will be considered non-PAG. A sample with a Carb-NPR less than one will be classified as PAG and a sample with a Carb-NPR between one and two will be classified as uncertain. The statistics for the Carb-NPR values for rock from the individual piles and/or pits are summarized in Table 1. The results show that only 20 of the 210 samples had Carb-NPR values less than one and would be considered as PAG. The percentage of samples representing PAG material in individual piles or pits range from 0 to 15%. The two rock deposits exhibiting acidic drainage, the East Embankment and South Pit-northeast (SP-NE) are highlighted with 15% and 8% of the samples, respectively, having Carb-NPR values less than one. About 6% of the samples had Carb-NPR values between one and two and represent an uncertain classification. The remaining 81% of the samples represent non-PAG material.

The geometric mean value for Carb-NPR values of the individual rock units range from 2.1 to 14 with an overall geometric mean of 9.5, suggesting statistically that the rock piles overall should represent non-PAG material. The two rock piles exhibiting acidic drainage had geometric mean Carb-NPR values of eight, similar to the overall geometric mean of 9.5. Many of the rock units had 10th percentile Carb-NPR values less than one with an overall 10th percentile of 0.8, consistent with 10% of the overall samples having Carb-NPR values less than one.

The frequency distributions for sulphide-sulphur and Carb-NP for all rock samples were similar among all deposits. However, t-test results show that the mean Carb-NP values are significantly different ($p<0.01$) between the East embankment and all other rock samples and F-test results indicate that the variances in sulphide and Carb-NP are significantly different ($p<0.001$) for the East embankment samples compared to all others. Nonetheless, these statistically significant differences do not provide a strong indication of the potential for acid generation.

Porewater Chemistry from Individual Piles

The results of the shake flask extractions (SFE) were used to estimate the concentrations of products of sulphide oxidation and acid neutralization in the porewaters of the waste rock pile. All SFE rinse waters had neutral pH with values greater than or equal to six. A plot of calcium plus magnesium with sulphate is shown in Figure 4. In theory, the neutralization of the acid by the dissolution of carbonate minerals should result in a slope between one and two depending on whether one or two moles of calcium-magnesium carbonate solids dissolved to neutralize the two moles of acid produced with one mole of sulphate.

The calcium plus magnesium to sulphate molar ratios vary with the concentrations of sulphate in the porewaters as shown in Figure 4. At sulphate concentrations greater than about 1000 mg/L, the calcium plus magnesium to sulphate ratio is consistently equal to one and the calcium concentration is likely controlled by precipitation of gypsum ($CaSO_4 {*} 2H_2O$) and this reaction likely plays a role in the control of the calcium plus magnesium to sulphate ratios. At sulphate concentrations between 100 and 1,000 mg/L, the average calcium plus magnesium to sulphate ratio is equal to about two. A ratio of two agrees with the theoretical upper bound value for dissolution of calcium-magnesium carbonate minerals by acid in an open system. This suggests that an NP/AP ratio of two is appropriate to classify non-PAG materials in these waste rock piles. At sulphate concentra-

Table 1. Summary of Carb-NPR values from individual pits and piles. Piles with acid drainage are highlighted.

Mine Rock Stockpile	Number of Samples	Geometric Mean	10th Percentile	90th Percentile	# of Samples Carb-NPR < 1.0	% of Samples Carb-NPR < 1.0	# of Samples Carb-NPR < 2.0, >1.0	% of Samples Carb-NPR < 2.0,>1.0
Causeway	12	5	0.7	26	1	8%	2	17%
East Embankment	47	8	0.5	68	7	15%	3	6%
EP	19	2.1	0.5	7	2	11%	3	16%
NP	3	13	7	26	0	0%	0	0%
SP-NE	24	8	1.7	36	2	8%	0	0%
SP-SW	19	11	3.0	32	2	11%	0	0%
TP	15	14	4	81	0	0%	0	0%
WP	71	14	0.7	143	6	8%	5	7%
All	**210**	**9.5**	**0.8**	**75**	**20**	**10%**	**13**	**6%**

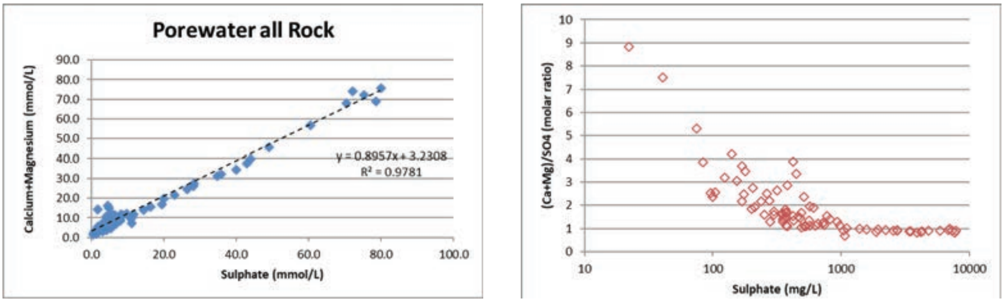

Figure 4. Calcium plus magnesium concentrations (left) and calcium plus magnesium to sulphate molar ratios (right) variations with sulphate concentrations.

Table 2. Geometric mean concentrations of calcium, magnesium and sulphate concentrations and average calcium plus magnesium to sulphate molar ratios in porewaters from individual pits and piles. Piles with acid drainage are highlighted.

Mine Rock Stockpile	Number of Samples	Ca (mg/L)	Mg (mg/L)	SO4 (mg/L)	Average (Ca+Mg)/ SO4 molar ratio
East Embankment	16	491	136	1391	1.6
EP	9	140	124	503	1.9
NP	2	176	42	446	1.3
SP-NE	9	229	76	515	2.5
SP-SW	7	251	62	554	1.6
TP	10	163	77	448	2.9
WP	29	183	70	466	1.9
All	82	220	85	557	2.0

tions of less than 100 mg/L, the calcium plus magnesium to sulphate ratios increase well above two suggesting that carbonate mineral dissolution is not controlled by acid produced by sulphide oxidation in the few samples with the lower sulphate concentrations.

The calcium, magnesium and sulphate concentrations in the porewaters in the East Embankment, that generates acid drainage, were typically two times greater than those from the other piles and pits (Table 2) and the calcium and sulphate values appear to be near gypsum solubility. The porewater concentrations in the other acid generating pile (SP-NE) do not appear to be different than those from the other non-acid generating piles.

The average calcium plus magnesium to sulphate ratios for individual piles range between 1.3 and 2.9 with an overall average of 2.0 (Table 2). There are no evident differences in the ratios between the acid generating and neutral drainage piles.

The depletion rates for sulphide and carbonate solids in the piles were estimated from concentrations in porewater samples adjusted to loading rates (Table 3). The porewater concentrations in samples collected from the top 5 m of the various rock piles were converted to a loading rates assuming a one-year residence time. Sulphide depletion rates were based on geometric mean sulphate loadings and carbonate depletion rates were based on geometric mean calcium plus magnesium loadings. Depletion times were then calculated from the geometric mean sulphide and carbonate contents, assuming 50% of the total sulphide and total carbonates were available for reaction measured values.

The sulphide depletion times for the individual rock piles ranged from 6 to 40 years from the date of sampling in 2014. The carbonate depletion times ranged from 44 two 800 years. The carbonate depletion times in the acid generating piles (EE and SP-NE) were in the low end of the range but estimated to be many decades into the future and other neutral drainage piles had similar depletion times.

Discussion

The results of this investigation have shown through many lines of evidence regarding the ABA characteristics of the waste rock materials that, on average, the rock at this former iron mine is non-PAG. This raises important questions. How does acid generation occur in a rock pile with excess carbonate neutralization potential? And, how do we avoid this risk in studies that are intended to predict future behaviour of waste rock for proposed mines?

A modelling study by Pedretti et al. (2017) addressed the generation of acidity in the rock piles as a function of different spatial distributions of acid generating and acid neutralizing minerals within the pile. The authors demonstrated that rock piles with the same overall NPR could produce either neutral or acidic drainage as a result of different distributions of sulphide and carbonate solids. In addition, the study showed that there may be high probabilities of producing acidic drainage in rock piles with average NPR values of two, a value that would typically be used to characterize rock as non-PAG. In a mixed pile containing PAG and non-PAG rock, maintaining a low probability of generating acid in the future may require an average NPR as high as 10 or greater. These results highlight the risks of using simple averages for acid base accounting to predict the acid generating potential of waste rock piles containing mixtures of PAG and non-PAG materials.

To date, strategies such as layering and encapsulating PAG materials with non-PAG materials in rock piles to mitigate acid generation have not been encouraging. Segregation of PAG from non-PAG rock for special management of the high-risk materials may be necessary to reduce the cost risks associated with potentially acidic drainage in mixed piles.

Conclusions

On average, the rock at the former Sherman mine had adequate neutralization potential to consume all potential acid produced by sulphide mineral oxidation. All piles had geometric mean Carb-NPR values that ranged from 2.1 to 14 and statistically would be classified as non-PAG piles. There were no obvious ABA characteristics that differentiated the acid generating pile from those with neutral drainage. No discernible differences were noted in the porewater chemistries between piles that were acid generating and those that had neutral drainage. The differences between the production of acid drainage in two piles and neutral pH drainages in the other 13 deposits were attributed to differing distributions of sulphide and carbonate minerals as suggested if a modelling

Table 3. *Geometric mean sulphide and carbonate contents and calculated depletion times of rock in individual piles in 2014. Piles with acid drainage are highlighted.*

Pile	Sulphide Sulphur %S	Carbonate $\%CaCO_3$	Sulphide Depletion Time (a)	Carbonate Depletion Time (a)
EE	0.13	3.3	6	61
EP-N	0.21	1.9	34	98
EP-NE	0.23	1.2	24	44
NP-N	0.22	8.7	29	464
SP-NE	0.11	2.6	12	98
SP-SW	0.14	3.6	15	141
TP-E	0.08	2.9	6	87
TP-N	0.14	5.1	6	132
TP-NE	0.09	5.6	39	503
WP-N	0.21	5.1	14	151
WP-NE	0.24	4.6	20	155
WP-S	0.09	7.7	14	404
WP-SE	0.12	2.5	14	103
WP-SW	0.05	9.7	15	806

investigation by Pedrettia et al. (2017). Mixing PAG and non-PAG rock with overall NPR values of greater than 2 does not guarantee neutral drainage. However, the risk of acid generation is likely low for the piles that have geometric mean NPR values greater than 10. Segregation of PAG rock for special management, when it represents smaller proportions of the total mine rock inventory, may represent a low rick alternative to mitigate acid generation.

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