Meliadine Gold Project: Investigation of the Buffering Capacity of Waste Rock

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ABSTRACT

The Meliadine Gold project is located near Rankin Inlet in Nunavut, Canada. The Project currently comprises six deposits along a 20 km section of the Meliadine Trend. Gold occurs in low-sulfide gold-quartz veins in a prominent fault zone, hosted in an oxide iron formation and mafic volcanic flows, a Package that is similar in all deposits. Although waste rock from each deposit has low sulfur and low acid rock drainage (ARD), the acid-buffering capacity varies between deposits. Those situated west and central to the trend possess excess calcite and dolomite-ankerite buffering capacity, while deposits located to the east are slightly more silicified and possess a greater proportion of iron-bearing carbonate minerals. Various testing methods were used to define the acid-buffering capacity of waste rock from these east-side deposits, including mineralogy, static test methods, mathematical accounting methods based on mineralogy and measured carbonate content, as well as kinetic weathering test methods. Net acid generation (NAG) and kinetic test results show the presence of active and sustained buffering capacity from carbonate minerals, which corroborate the results of modified Sobek buffer capacity tests. Conversely, mineralogy and carbonate content frequently inferred the absence of buffering carbonate minerals; this could be due to the low resolution of X-Ray Diffraction (XRD), and to the possible heterogeneity of the sample which is exacerbated at trace mineral content. The compendium of results was, therefore, used to assess the ARD potential of waste rock from these deposits. Waste rock management strategies will include mixing of rock types where the proportion of uncertain or potentially acid generating (PAG) rock is small, additional tests during operation and strategic placement of potentially acid generating waste rock, and cover where the proportion is higher. These management plans are designed to overcome uncertainty on acid generation potential where it exists and avoid acidification of PAG waste rock in the long-term.

Keywords: buffering capacity, neutralization potential, mineralogy, metal carbonates.

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INTRODUCTION

Agnico-Eagle Mines Ltd. (AEM) is currently studying the feasibility of constructing and operating a gold mine known as the Meliadine gold project located approximately 25 km north of Rankin Inlet in Nunavut, Canada. The Meliadine property comprises several gold deposits in a low sulfur mineralization system. Some of the lithologies from two of these deposits, Discovery and F Zone, have very low carbonate content but static and kinetic tests show sustained buffering. Multiple geochemical analyses and calculations were conducted to better define the long-term acid rock drainage (ARD) potential of these low sulfur and low carbonate rocks.

This article describes the analyses completed on waste rock from the Discovery and F Zone deposits and compares results of the different tests and concludes with recommendations for greater clarity on the determination of effective buffering capacity in low sulfur and low carbonate rocks.

GEOLOGY OF THE MELIADINE DEPOSITS

The gold deposits of the Meliadine property are hosted in volcanic flows and sediments of the Archean-age Rankin Inlet Greenstone Belt (Pincock Allan & Holt, 2008). Gold deposits occur along the east-west-trending splay off the regional Pyke Fault and on structures parallel to it. Gold is mostly present in quartz-vein stock works, laminated veins, and in weakly sulphidized iron formation, which is folded and sheared. The Meliadine ore deposits are low-sulfide, gold-quartz vein deposits as per the geo-environmental classifications provided in Plumlee et al. (1999).

The geology of each deposit is similar. Waste rock includes iron formation, which is both volcanichosted and sediment-hosted. It comprises greywackes, siltstones and argillites with magnetite and chert layers. Schistose and carbonate-altered mafic volcanic rocks make up most of the footwall waste rock. The hanging wall rock comprises fine-grained turbiditic meta-sediments that include greywacke, sericite-altered siltstones, graphitic argillites and gabbro dykes (AEM, 2011; AEM 2014).

PROPOSED MINE DEVELOPMENT

The six deposits to be mined includee: Wolf, Tiriganiaq, Pump, Wesmeg, F Zone and the Discovery. Waste rock from the first 4 deposits will be mixed in two large rock storage facilities. Waste rock in these mixed piles has ample excess buffer capacity; there is no concern for acidification from these stockpiles. Conversely, waste rock from F Zone and Discovery deposits will be stored in individual waste rock storage facilities adjacent to their respective open pits. Some samples of waste rock from F Zone and Discovery deposits have an uncertain acidification potential, hence the importance of defining the reactivity of the available buffering capacity of all waste rock from these deposits in order to design appropriate stockpile management plans.

ANALYTICAL METHODS

Mineralogy

Mineralogical analyses were carried out by XRD at the University of British Columbia, Earth and Ocean Sciences Department. Samples consisted of a 2 mg split of a fraction of the pulverized portion (reground to <10 μ m) of the waste rock sample. The X-Ray diffractograms were analyzed using the International Centre for Diffraction Database PDF-4 using Search-Match software by Siemens (Bruker). X-Ray powder-diffraction data were refined with Rietveld program Topas 3 (Bruker AXS). This method allows evaluating quantitatively the crystalline mineral phases with a detection limit of approximately one weight percent (1 wt%). Mineral quantities represent the relative amounts of crystalline phases normalized to 100%. Non-quantitative identification to <1% was made by UBC, however, the precision of the instrument decreases substantially below one wt% (errors margins up to 100%; M. Raudsepp, 2014, pers. comm., 27 March). Concentrations less than 1% are imprecise.

Laboratory measurement of buffering capacity

The following methods of accounting for buffering capacity were completed:

1996 *Modified NP Procedure (bulk NP)*, (MEND, 2009) – This method quantifies the total buffering capacity of a sample, including contributions from slower reacting or less reactive aluminosilicate minerals. The buffering capacity is calculated from the amount of base consumed to neutralize acid remaining from the sample acid-digested at room temperature. Bulk NP is expressed as kg CaCO₃/tonne.

Carbonate mineral NP (CaNP), (Price, 1997) – This method quantifies the buffering capacity from the carbonate content of a sample assuming that all the carbonate is present as calcite. CaNP is calculated from the carbonate (CO₃) content as follows: CaNP (kg CaCO₃/tonne) = CO₃ (wt%) *(100.09*10)/60.01. Where siderite and other divalent metal carbonates are present, the CaNP can be overestimated since these minerals release less neutralization per mole of carbonate ions than calcite or dolomite.

Mineralogical Carbonate NP (CaNP-min), (Paktunc, 1999) – This represents the buffering capacity provided by the carbonate minerals that are identified by XRD. In this study, they include calcite, ankerite and siderite. The effective carbonate NP is calculated following methods outlined in Paktunc (1999) where the amount of buffer available from each mineral is proportioned to the available carbonate ions per its idealized mineral formulae as follows: Calcite and dolomite 100%; ankerite 70%; siderite 0%. This method utilizes the weight percent (wt%) XRD results, thus it was applied only to samples subjected to mineralogical analysis. The CaNP-min value is expressed as kg CaCO₃/tonne.

Adjusted Carbonate Mineral NP (CaNP-adj) – This represents the NP from carbonate minerals (CaNP) based on the chemical content of inorganic carbon (TIC) rather than the weight percent of XRD carbonate minerals, but adjusts the buffering capacity according to the carbonate minerals present in the sample defined by XRD analysis. The adjustment is also based on the proportion of available carbonate ions from each mineral identified (Paktunc, 1999). Thus, if XRD identified that 50% of the carbonate minerals present in the sample were calcite and 50% siderite, CaNP-adj was

set at half of the CaNP value defined from TIC analysis. If a sample had no mineralogical data, it was assumed to have the average carbonated mineral content tabulated for the sample's lithology. The CaNP-adj value is expressed as kg CaCO₃/tonne.

Laboratory measurement of acid potential (AP)

There are no documented occurrences of primary sulfate minerals in the Meliadine deposit (Pincock Allan & Holt, 2008; AEM, 2011; AEM 2014). Where chemical analysis identified sulfate, it was attributed to weathering of the sample after extraction. Thus, AP was calculated from the total sulfur (S) content, based on the theory that all the sulfur in the sample occurs as available di-sulfide minerals (AP (kg CaCO₃/tonne) = $31.25 \times S$ (%)). The total sulfur content of the sample was determined by LECO furnace with a S-analyzer following ASTM E 1915. A subsample was pre-treated with cold hydrochloric acid (HCl) to remove sulfate and the resulting material was analyzed for total sulfur. The difference between the two total sulfur values was assumed to be sulfate sulfur.

Evaluation of ARD potential

The determination of the ARD potential of waste rock was evaluated by acid-base accounting (ABA) using net potential ratio (NPR) of NP to AP, whereby NPR = NP/AP. The NPR was evaluated for the various forms of NP, as follows:

- NPR = bulk NP/AP
- CaNPR = CaNP/AP
- CaNPR-min = CaNP-min/AP
- CaNPR-adj = CaNP-adj/AP

Leaching test pH and sulfate content

The distilled water shake flask extraction (SFE) (ASTM D3987-06) and the paste pH (Price, 1997) were carried out on all samples. An increase in the pH of the leaching solution (initial pH was approximately 5.5) indicated the presence of readily available buffering capacity.

The single addition net acid generation (NAG) test (AMIRA, 2002) was completed on a subset of samples from each lithology. The subset of samples selected for NAG tests was different than the subset selected for mineralogical analysis.

Kinetic weathering tests were carried out following the humidity cell test (HCT) procedure (ASTM D 5744-96) on the same subset of samples subjected to mineralogical testing. Kinetic tests were run for a period of 20 to 40 weeks. Leachates were analyzed by inductively coupled plasma - mass spectrometry. These tests were used to investigate the kinetics of mineral reaction.

RESULTS AND DISCUSSION

Mineralogy

Pyrite (FeS₂) is the most common sulfide mineral found in the waste rock away from ore zones, with lesser arsenopyrite (FeAsS), trace pyrrhotite (Fe_{1-x}S) and rare chalcopyrite (CuFeS). F Zone and Discovery waste rock have low quantity of calcite and a greater proportion of metal-bearing

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carbonate minerals such as siderite and ferroan dolomite (ankerite). The iron content of the ankerite was not defined during this study. Aluminosilicate minerals including biotite, muscovite, plagioclase feldspars and clinochlore which are documented to possess buffering capacity (Jambor et al. 2002; Jambor, Dutrizac and Raudsepp, 2007; Matson, 2009), occur in large quantities in Discovery and F Zone samples (TABLE 1).

| | | Disc | overy | | | Disco | overy | | F Zone Deposit Iron Formation | | |
|--------------------|---|------|-------|----------|------|-------|-------|------|-------------------------------------|------|------|
| Mineral | Ideal Mineral Formula | Dep | osit | | | Depo | osit | | | | |
| Group/Name | Ideal Willeral Formula | Grey | wack | e/ Silts | tone | Iron | Forma | tion | | | |
| | | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 |
| Calcite | CaCO ₃ | - | - | 0.30 | - | 0.45 | 1.0 | 1.9 | - | - | - |
| Ankerite | Ca(Fe,Mg,Mn)(CO ₃) ₂ | - | - | - | - | - | - | - | 3.7 | 3.6 | 5.8 |
| Siderite | FeCO ₃ | - | - | - | - | - | - | - | 0.59 | 2.7 | 6.5 |
| Dolomite | CaMg(CO ₃) ₂ | - | - | - | - | - | - | - | - | - | - |
| Pyrite | FeS ₂ | - | - | - | - | 0.85 | - | - | - | 0.43 | - |
| Pyrrhotite | Fe1-xS | - | - | - | - | - | 1.7 | - | 8.7 | 3.6 | 7.0 |
| Arsenopyrite | FeAsS | - | - | - | - | - | - | - | - | 0.63 | - |
| Quartz | SiO ₂ | 32 | 31 | 30 | 31 | 42 | 42 | 34 | 69 | 75 | 72 |
| Plagioclase | (Na,Ca)AlSi3O8 | 30 | 35 | 39 | 37 | 5.9 | 11 | 8.0 | - | - | - |
| Biotite | K(Mg,Fe)3(Al,Fe)Si3O10(OH,F)2 | 6.1 | 7.5 | 8.4 | 6.4 | 3.0 | 5.6 | 7.1 | - | - | - |
| Muscovite | KAl2(AlSi3)O10(OH)2 | 20 | 16 | 7.5 | 18 | - | - | - | - | - | - |
| Clinochlore | (Mg,Fe ²⁺)5Al(Si,Al)4O10(OH)8 | 11 | 9.9 | 9.2 | 7.5 | 1.2 | 5.4 | 5.4 | 4.7 | 1.4 | 2.0 |
| Magnetite | Fe ₃ O ₄ | - | - | - | - | 38 | 10 | 22 | 3.1 | 3.6 | 0.37 |
| Actinolite | Ca2(Mg,Fe)5Si8O22(OH)2 | - | - | 3.9 | - | 8.8 | 8.6 | 8.2 | - | - | - |
| Cumming- tonite | Mg7Si8O22(OH)2 | - | - | - | - | - | 14 | 12 | 10 | 9.0 | 6.6 |

Table 1 Minerals identified by XRD with Reitveld refinement

- not detected; values <1 wt% are approximate

ABA results for samples subjected to mineralogical analysis are summarized in TABLE 2 along with the average for samples from each lithology.

| Mineral | | • | Deposit Siltstor | | | on Form | ation | F Zone Deposit Iron Formation | | | | | |
|------------------------|------------|------------|---------------------|------------|----------------|-----------|----------|----------------------------------|---------------|----------|----------|----------|---------------|
| Group/Name | 1 | 2 | 3 | 4 | avg. (n=54) | 5 | 6 | 7 | avg. (n=33 |) 8 | 9 | 10 | avg. (n=7) |
| paste pH | 9.3 | 9.7 | 9.6 | 9.6 | 9.7 | 9.1 | 8.8 | 9.0 | 9.0 | 8.4 | 8.6 | 8.5 | 8.5 |
| SFE pH Net Acid | 7.9 | 8.6 | 8.2 | 8.0 | 8.4 | 7.7 | 7.7 | 7.9 | 8.0 | 8.0 | 8.0 | 7.0 | 8.0 |
| Generation (NAG) pH | 3.3 | 4.5 | 7.1 | na | 6.7 | na | na | na | 9.0 | na | na | na | na |
| Bulk NP CaNP | 7.4 1.5 | 7.3 3.1 | 12 6.5 | 8.1 1.2 | 14 6.0 | 15 2.0 | 22 12 | 44 26 | 29 19 | 31 16 | 34 34 | 53 27 | 72 56 |

Table 2 Summary of ABA results and lithological average values

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| CaNP-adj | 1.5 | 3.1 | 6.5 | 1.2 | 1.7 | 2.0 | 12 | 26 | 19 | 9.6 | 14 | 8.8 | 25 |
|--------------------|------|------|------|------|------|------|------|------|------|-----|-----|------|-----|
| CaNP-min | 0.0 | 0.0 | 3.1 | 0.0 | 0.8 | 4.6 | 10 | 20 | 12 | 26 | 26 | 41 | 31 |
| Total Sulfur (wt%) | 0.25 | 0.12 | 0.15 | 0.15 | 0.13 | 0.66 | 0.78 | 0.37 | 0.45 | 2.6 | 1.3 | 3.2 | 1.9 |
| AP | 7.7 | 3.9 | 4.5 | 4.6 | 4.1 | 21 | 24 | 12 | 14 | 81 | 42 | 100 | 59 |
| bulkNPR | 1.0 | 1.9 | 2.6 | 1.8 | 4.7 | 0.7 | 0.9 | 3.8 | 2.7 | 0.4 | 0.8 | 0.5 | 15 |
| CaNPR | 0.2 | 0.8 | 1.4 | 0.3 | 2.8 | 0.1 | 0.5 | 2.3 | 2.0 | 0.2 | 0.8 | 0.3 | 13 |
| CaNPR-adj | 0.2 | 0.8 | 1.4 | 0.3 | 0.7 | 0.1 | 0.5 | 2.3 | 2.0 | 0.1 | 0.3 | 0.09 | 5.7 |
| CaNPR-min | 0.0 | 0.0 | 0.7 | 0.0 | 0.2 | 0.2 | 0.4 | 1.7 | 0.7 | 0.3 | 0.6 | 0.4 | 0.4 |

na: not analyzed; avg: average

Evaluation of buffering capacity

Bulk NP values are consistent, and often substantially higher than CaNP indicating that a large portion of the buffering capacity accounted for in bulk NP is from non-carbonate minerals. The reactivity of this buffering capacity cannot be verified in the long-term, thus, these measurements were not retained to assess ARD potential.

Because of the documented presence of iron carbonates the use of CaNP was not retained either. CaNP is an imprecise evaluation of buffering capacity for the Meliadine project because it negates the NP-lowering effect of metal carbonate minerals and the buffering capacity of reactive silicate minerals.

Mineralogy-based CaNP (CaNP-min) tended to be the most conservative assessment of buffering capacity. However, this method was not considered appropriate for ARD assessment because of the following factors: the uncertainty of the quantitative estimate from XRD data due to the low resolution of the instrument for trace mineral content; the evidence of available buffering capacity (from paste pH, NAG pH, and kinetic testing) in samples where little to no carbonate minerals were identified by XRD; and the substantial discrepancy between carbonate content measured by chemical analysis and weight percent carbonate content from XRD results.

Adjustment of CaNP using mineralogical data (CaNP-adj) accounts for both the trace content of carbonate defined by chemical analysis and the presence of iron carbonate minerals identified in the samples. Although this method still negates buffering capacity from aluminosilicate minerals, it is considered to be appropriately conservative for NP determination.

Supporting Information

The highly alkaline paste pH values of most samples and the neutral to alkaline SFE pH values demonstrate the presence of immediately available buffering capacity in all samples, including those where no carbonate minerals were identified by XRD. This suggests that either some effective calcite or low iron dolomite was present at concentrations that are below the XRD detection limit, and/or other effective aluminosilicate minerals are available to buffer the solution pH.

Most end-pH values of the NAG tests were also above 4.5 with little acidity released, suggesting that most samples tested (which targeted low AP and low NP samples) have enough buffering capacity to avoid ARD (except for samples 1 and 2 in TABLE 2). Corresponding mineralogical data was available for three samples of Discovery greywacke/siltstone. These show that the non-potentially acid generating (NPAG) sample (sample 3) has a low, but detectable, calcite content (0.3wt %), a low sulfur content (0.15 wt%), a bulk NPR of 2.6 and a CaNPR-adj above 1. Conversely,

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samples 1 and 2 yielded acidic NAG pH values suggesting they have a potential to generate acid in the long-term. They had no detectable carbonate mineral content and lower bulk NP and CaNP-adj values than sample 3 and similar to higher sulfur contents. Samples 1 and 2 have bulk NPR values above 1 but CaNPR, CaNPR-min and CaNPR-adj values of less than 1. The relationship between CaNPR-adj, AP and mineralogy may form a trend that needs to be verified with a larger database of NAG pH values and mineralogical data.

Kinetic testing on Discovery and F Zone samples also showed active and sustained buffering capacity for the duration of testing including for samples with no XRD-detectable carbonate minerals (FIGURES 2 and 3). The very low sulfate values suggest very slow mineral reaction rates in the short to medium term. Given the dry arctic conditions at site and corresponding low leaching rate, the 40 week test duration is estimated to cover a period at site which is longer than the planned mined life (13 years).



Figure 2 Kinetic test results for Discovery greywacke/siltstone samples (blue) and iron formation samples (grey)

Figure 3 Kinetic test results for F Zone iron formation samples

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CONCLUSION

The available neutralization capacity observed for many low carbonate samples based on paste pH, kinetic testing, NAG pH (for other samples not presented here) and carbonate content was often not reflected in XRD analysis. Similarly, the presence of sulfur identified by chemical analysis did not always correspond to identifiable sulfide mineral phases in XRD, including for samples having a total sulfur content of up to 0.55 wt%. This incongruence suggests that XRD-Rietveld does not possess a sufficiently elevated resolution to identify potentially important minerals in ARD reactions in low S, low carbonate rocks. This could be due to many factors, which include: the small subsample size subjected to XRD and the heterogeneity of the sample, the imprecision in identifying minerals that occur in trace quantities, the presence of mineral solid solutions such as the dolomite-ankerite series and that mineral phases with similar diffractogram patterns are difficult to distinguish. These factors are accentuated when the targeted element or mineral is present in trace quantities.

This imprecision decreases the relevance of relying solely on mineralogy-based evaluations of NP and NPR. Notwithstanding this, mineralogical data should be used to guide evaluations of buffer capacity, in conjuction with chemical analysis of carbonate content. Indeed, imprecise mineral identification or quantification, the presence of mineral solid-solutions (such as dolomite-ankerite) and the presence of reactive aluminosilicate minerals can lead to errors in the evaluation of the potential to generate acidic drainage.

Buffer capacity evaluation methods that are based on mineralogy require a greater mineralogical database for the project studied, and more powerful and precise mineral identification techniques such as Qemscan or Scanning Electron Microscope (SEM) with energy dispersive X-Ray (EDX) or a mineral liberation analyzer (MLA). The MLA was shown to successfully identify trace quantities of minerals down to 0.01wt% ranges (Barazzuol et al, 2012). Mineralogical analysis should be done in conjunction with chemical analyses including chemical scan, carbonate content, NAG pH with NAG solution analysis to verify that all the sulfur in the sample has been oxidized.

Results from the compendium of analytical techniques used suggest that Discovery waste rock is not likely to generate ARD in the short to medium term under the arctic (very dry and cold) site conditions. However, the development of acidic conditions in the long-term is uncertain. The uncertainty stems from the lack of precision in identifying the type and availability of buffering minerals present in trace amounts. This is also the case for F Zone iron formation rock, however this lithology constitutes a minor proportion (8%) of the total quantity of waste rock to be stored in F Zone WRST, the balance of which is NPAG and has excess carbonate-mineral buffering capacity.

Waste rock management control strategies will include mixing of rock types where the proportion of uncertain or potentially acid generating rock is small, such as in the F Zone waste rock stockpile, and for Discovery PAG rock, will include strategic placement the PAG waste rock in the stockpile and placement of a thermal cover having little to no PAG rock. These methods are planned to overcome uncertainty where it exists and avoid acidification of the Discovery and F Zone PAG waste rock in the long-term.

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