Quantification Of Methods To Assess Carbonation In Mine Wastes - Potential Implications For Long-Term Mine Waste Drainage Quality And Acid Rock Drainage (ARD) Prediction

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ABSTRACT

It has been well established that mine waste of suitable mineralogy can act as a carbon sink through the formation of carbonate minerals upon reaction with CO_2. Studies to this point have concentrated on quantifying the suitability of mine by-products for use in large scale de-carbonation strategies. Little emphasis has been placed on the potential implications of carbonation, either passive or enhanced, upon the geochemical behaviour of mine waste materials after carbonation has taken place.

Within this study we have used standardised and modified kinetic test procedures, in the form of humidity cell tests (HCT's), to assess the potential implications of carbonation on non-carbonate bearing mine waste drainage quality and prediction. We have assessed waste rock collected from two sites with different host rock type and mineralisation: a nickel mine in Finland with ultramafic host rocks and a copper mine in Sweden with host rocks of muscovite schists and amphibole-biotite gneisses. Tests were carried out using differing gas compositions (CO_2/O_2) to assess the influence that internal pore gas space composition may have on pore water chemistry over time.

The results of the study demonstrate that changes to gas composition and temperature within HCT experiments lead to notable differences in leachate quality (Dissolved inorganic carbon, soluble metals and sulfate) over 60 weeks between control and altered cell protocols. These variations demonstrate the effect of carbonation on pore water geochemistry and thus the need for assessment in long term prediction of rock drainage quality. This may have important implications for assessing long term prediction of potential ARD and carbonation of mine wastes under both naturally occurring CO_2 sources in mine waste piles and enhanced concentrations due to intentional carbonation. Test applications such as those presented within this study may allow better long-term predication and characterisation of wastewater geochemical behaviour.

Keywords: *Carbonation, Mine Drainage, Prediction, Carbon Mineralisation, ARD*

1.0 INTRODUCTION

Within this paper preliminary results of 60-week humidity cell tests (HCT) are presented. The HCT's undertaken in this study were designed to quantify the potential implications of enhanced CO_2 concentration on mine waste weathering and subsequent long term acid rock drainage (ARD) prediction. The purpose of this study was to set the foundation for improved test methods for assessing mine drainage evolution in the presence of enhanced CO_2

concentrations. At present HCT's are used an informative tool to assess the potential onset of acidity from a waste material, although these tests are currently not site specifically tailored in their design and application (Sapsford et al. 2009). The benefit of developing such test methods creates a dual opportunity for mine planers and operators; the deployment of site-specific waste geochemical testing and an improved understanding how the application or presence of differing gas compositions within residual waste storage facilities (RWSF) may impact waste drainage characteristics.

Mineral carbonation has been identified as a potentially key method for reducing global CO_2 emissions by the IPCC (IPCC, 2005). The mining industry has a key part to play in reducing global greenhouse gas emissions with mine wastes potentially providing a key feedstock for large scale carbon capture and storage (CCS) (Renforth 2019). Previous studies have demonstrated that mineral carbonation of mining by-products is possible under low temperature conditions, with secondary carbonate precipitation demonstrated. Such studies have highlighted the potential for operational net emissions to be reduced through active and passive sequestration of tailings and waste rock materials (Mervine et al. 2018). In order for the industry to utilise the CCS potential of mining waste materials the potential impacts that such utilisation may have on the mine drainage evolution needs to be considered. Current standards for the assessment of mine waste geochemical characteristics do not take into consideration the presence of enhanced CO_2 concentrations within RWSF's.

Within this study waste rock from two active Boliden minerals AB (Boliden) mines were tested within altered HCT's. The sites that have provided materials for this study are the Kevitsa open pit Ni-Cu-PGE mine, located in northern Finland (GTK, 2020), and the Aitik open pit Cu-Au-Ag mine, located in northern Sweden (GTK, 2019). The tests were designed to provide a preliminary assessment of how altering CO_2 concentrations and varying test conditions may impact drainage characteristics. Site selection was based on assessing the potential implications on a mine waste with known CCS potential at Kevitsa (Savage et al. 2019), while widening the scope of assessment to wastes from Aitik which would not normally be viewed as having a high CCS potential, based on mineralogical characteristics.

This study forms part of a wider assessment program by Boliden to improve its environmental footprints and transition towards more sustainable mining practices.

2.0 METHODOLOGY

All experimental test work carried out within this study was undertaken at the Geochemic Ltd laboratory, located in Pontypool, UK. Elemental analysis (ICP-OES) was undertaken at Cardiff University's CLEER laboratory, located in Cardiff, UK.

2.1 Basic Sample Characterisation

Samples were characterised for elemental, geochemical and mineralogical compositions. Characterisation results have not been outlined within this study, although the major characterisation tests are outlined below:

- Mineralogical assessment: Scanning electron microscopy with energy-dispersive x-ray spectroscopy (SEM-EDX) analysis (Carried out at Petrolab, UK).
- Elemental assessment: Energy dispersive X-ray fluorescence (ED-XRF) analysis (Carried out Geochemic Ltd).
- Geochemical analysis: Acid buffering characterisation curve (ABCC), Acid neutralising capacity (ANC), total carbon and sulfur (C / S), rinse and paste pH and electrical conductivity (EC) (Carried out at Geochemic Ltd).

2.2 Sample Preparation

All sample preparation was undertaken following the ASTM D5744 standard protocols for Humidity cells (ASTM 2018). Samples used within this test work take the form of composited waste rock materials recovered from each individual Boliden AB operation. Discrete waste rock samples were recovered from 100mm diameter drill core a part of sonic drilling programs at both locations. Course sample fractions (>22mm) were crushed to <2.36mm to allow accordance with the ASTM HCT standard procedure. Large sample fractions were utilised due to both sample availability and to maximise un-weathered surface area. HCT's were loaded with 1kg of composited waste rock.

2.3 Humidity Cell Testing Procedures

Following ASTM D5744 cells were exposed to a 7-day cycle of dry/humid air flow; 3 days of dry air, 3 days of humid air flow (~95% humidity), followed by a leaching day. The aim of a humidity cell is ultimately to accelerate the rate of weathering of a waste material through the promotion of oxidation and precipitation of secondary minerals.

ASTM standard D5744 recommended test apparatus and leaching procedures were used within this study. This included the use of 1kg of waste materials in each constructed cell, an initial de-ionised water leaching volume of 1000ml (1:1 L:S), followed by weekly leaching of materials with 500ml of de-ionised water. Each week cells were leached, and leachates recovered for geochemical characterisation for key parameters such as pH, oxygen redox potential (ORP), dissolved inorganic carbon (DIC), electrical conductivity (EC) and major and trace elemental analysis. To implement test parameters that better represent site conditions enhanced CO_2 concentrations were utilised in line with EPA method 1627, designed for the kinetic assessment of coal wastes (EPA 2011). This integration of different predictive standards allows site specific conditions to be better simulated.

Nine (9) HCT cells were carried out for each sample site, with all samples run in triplicate. Gas compositions within enhanced CO_2 cells were 10% CO_2 / 90% air, while control cells were run with proportionally reduced O_2 conditions. This allowed comparison of cells without differentiation in oxidation rates potentially impacting leaching characteristics. Due to the colder climate conditions at the assessed sites a set of triplicate samples cells were assessed under reduced temperatures (10^{O}C) for both Kevitsa and Aitik. Enhanced CO_2 HCT's tested at 25^{O}C are identified as 'TC1' within this study, while enhanced CO_2 HCT's tested at 10^{O}C are identified as 'TC2'.

2.4 Weekly Leachate Analysis

Collected leachates were analysed for each HCT cell on a weekly basis. Weekly collected leachates were analysed for pH, EC, ORP, alkalinity and acidity by an automated Metrohm titration system. Elemental analysis was carried out through ICP-OES analysis of leachates using a Perkin Elmer Optima 2100 DV ICP-OES. ICP-OES analysis was carried out at Cardiff University.

3.0 RESULTS

Basic sample mineralogical characterisation summary

Mineralogical results revealed that the Aitik composite waste rock samples were comprised of primarily quartz-mica schists with rare garnet-mica schists which are all heavily foliated showing high degrees of metamorphism. Minerals present include quartz, feldspars (~27% albite and 13% anorthite), muscovite, biotite, and amphiboles. Sulfides include pyrite and pyrrhotite.

Kevitsa mineralogical characterisation demonstrated that the samples were predominantly composed of gabbroic fragments (websterite to olivine websterite in composition) containing abundant clinopyroxene which is readily altered to amphiboles and tremolite/actinolite. Sulfides include pyrrhotite, pyrite, chalcopyrite

Selective weekly leachate results

Within this study preliminary results for cumulative dissolved inorganic carbon (DIC), Ni, Mn, Mg, Ca and sulfate are presented over a 60-week period for waste rock composite samples for either the Kevitsa or Aitik mine operations. These select parameters have been selected as the research study is ongoing and therefore provide a preliminary assessment made based on initial weekly leaching results. Cells for all 3 testing conditions (TC1, TC2 and control) were carried out in triplicate. The results shown in the following figures represent the averaged triplicate value for each testing condition for both Kevitsa and Aitik waste materials.

Cumulative DIC increases greatly in cells exposed to enhanced CO_2 over the 60-week testing period, both within cells tested at 25^{O}C and 10^{O}C. It can be seen in figure 1 that samples from both Kevitsa (Figure 1a) and Aitik (Figure 1b) demonstrated greater increases cumulative DIC within cells held under testing conditions 2 (TC2), 10^{O}C, when compared to both test conditions 1 (TC1) and control values. Averaged Kevitsa triplicate cell values shown in this figure demonstrated that cumulative DIC reached 561 mg/kg for TC2 cells compared to 435 mg/kg for TC1 cells and 64 mg/kg for control cells, over the 60-week testing period.

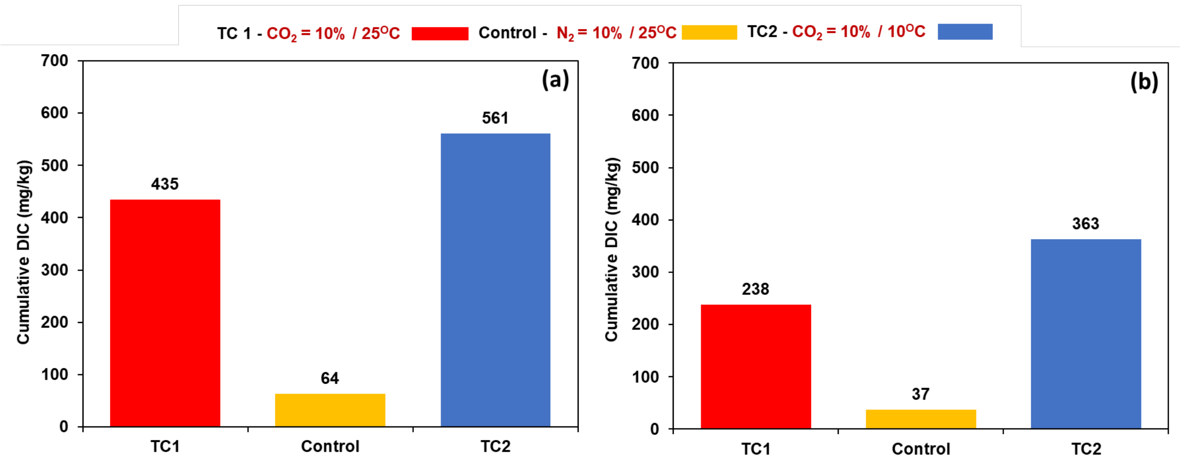

Figure 1. **Cumulative dissolved inorganic carbon (DIC) results for weekly leachates analysed between flushing cycle 0 (week 0) and 60 (week 60). Part (a) contains averaged results for the three triplicate sets of Kevitsa waste rock HCT's, while part (b) is representative of averaged Aitik triplicate cell sets.**

Cumulative Ni release increased within Kevitsa cells exposed to enhanced CO_2 concentrations, when compared to control cells (Figure 2a). This increase is most pronounced within reduced temperature cells (TC2). Within test conditions 1 (TC1) the cumulative Ni release was calculated at 1.9 mg/kg after 60 cycles, compared to 5.0 mg/kg within test conditions 2 (TC2). Both values are above the measured release in control cells, with a maximal value of 0.56 mg/kg after the same period. A similar trend is noted within Aitik for Mn (Part b), although more variation was shown within TC2 triplicate values.

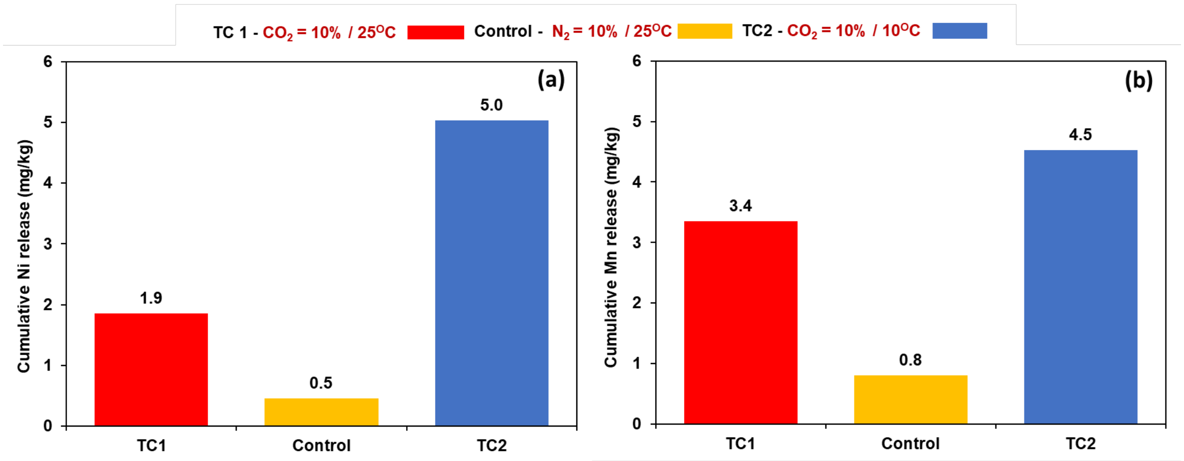

Figure 2. **Cumulative elemental results for weekly leachates analysed between flushing cycle 0 (week 0) and 60 (week 60). Part (a) contains averaged Ni results for the three triplicate sets of Kevitsa waste rock HCT's, while part (b) represents averaged cumulative Mn release from Aitik triplicate cell sets.**

Mg and Ca are important in the context of mineral carbonation due to their role in the formation of magnesium and calcium carbonates within a system with enhanced bicarbonate. In both test sets Mg and Ca release increased in CO_2 enhanced test conditions (TC1 and TC2), shown in figure 3. The greatest increase in Mg was measured in TC1 cells, with an average cumulative Mg release of 159 mg/kg, compared to 83 mg/kg measured in control cells in the same testing period. Similar results were demonstrated within part (b) of this figure with Aitik cells exposed to enhanced CO_2 showing an increase in Ca release over the testing period when compared to control cells.

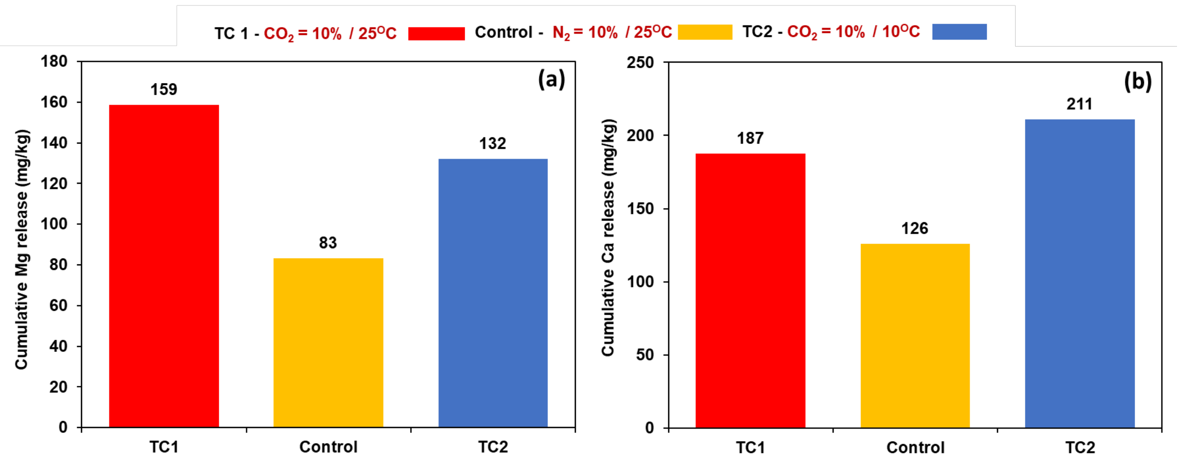

Figure 3. **Cumulative elemental results for weekly leachates analysed between flushing cycle 0 (week 0) and 60 (week 60). Part (a) contains averaged Mg results for the three triplicate sets of Kevitsa waste rock HCT's, while part (b) represents averaged cumulative Ca release from Aitik triplicate cell sets.**

As O_2 content within control cells was reduced in line with CO_2 enhanced cells the impact of differentiation sulfide oxidation due to varied O_2 content was reduced. It was noted that sulfate (SO_4) release over the 60-week test period did vary between control cells and TC1/TC2 cells for both Kevitsa and Aitik HCT experiments. The cumulative sulfate leaching results for Kevitsa cell sets are shown in figure 4. It can be seen in this figure that relative to control cells sulfate release is reduced in enhanced CO_2 cell conditions (TC1 and TC2). Although this would be expected for TC2 cells due to lower testing temperatures, TC1 cells also showed a reduction in weekly sulfate release over the preliminary test period.

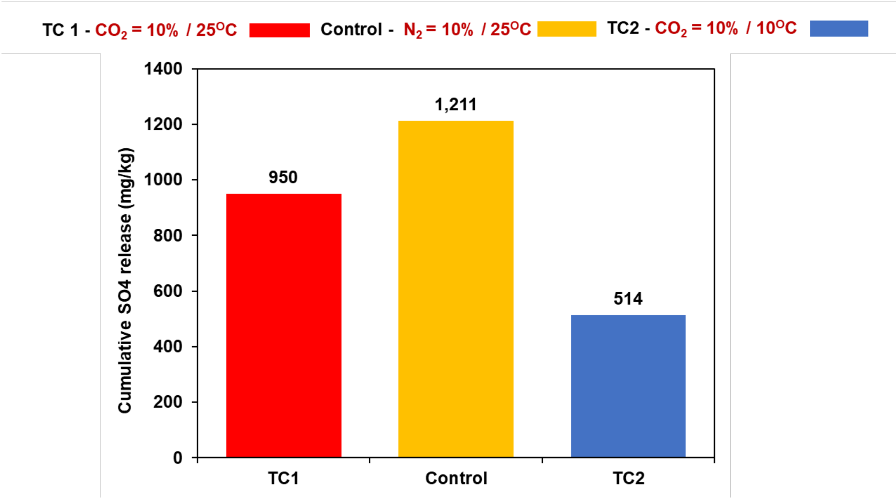

Figure 4. **Cumulative leaching results for sulfate, presented in mg/kg, for Kevitsa HCT's between flushing cycle 0 (week 0) and 60 (week 60). This figure contains averaged SO_4 results for the averaged triplicate sets of Kevitsa waste rock HCT's, under the three testing conditions.**

4.0 DISCUSSION

It has been demonstrated within the preliminary results shown in this paper that variations of HCT experimental parameters does influence cell leaching characteristics. The potential implications of this are important as they demonstrate that the introduction of enhanced CO_2 concentrations within RWSF may lead to differing drainage evolution that is not currently considered in standardised test methods, such as ASTM D5744. Alterations to cell gas composition and temperature parameters demonstrate clear changes in DIC, Ni, Mn, Mg, Ca and sulfate cumulative release within both Kevitsa and Aitik cells. The measured increase in Mg and Ca release at Kevitsa and Aitik, respectively, is particularly important in the context of carbon mineralisation. These increases are indicative of the weathering of Mg and Ca silicate minerals (such as olivine and anorthite) which is key to precipitation of stable carbonate under certain conditions.

Sulfide oxidation and increased carbonic acid formation is expected to result in the potential dissolution of existing carbonates, such as dolomite, which may lead to an increase in Mg and Ca within leachates. It is therefore acknowledged that a portion of the relative increase in these cations may be a result of this process. A reduction in sulfate release was noted in enhanced CO_2 cells, figure 4. This would be expected due to lower temperature conditions within samples under test conditions 2 (TC2), although a reduction was also noted within cells tested at control temperature (TC1). This result is interesting as it potentially suggests a preferential reduction in sulfide oxidation in CO_2 enhanced cells. This may be potentially significant for the prediction of ARD potential within such tests.

Enhanced release of Ni ad Mn within enhanced CO_2 cells at Kevitsa and Aitik is clearly demonstrated in figure 2. These results are particularly important as it may suggest that metal release in control cells is underreported, if RWRF internal gas compositions hold a CO_2 level above atmospheric conditions. For mine operators these enhanced metal releases may prove significant as they may provide a basis for enhanced metal recovery from leachates of waste materials exposed to enhanced CO_2 conditions, although the viability of this would need to be further analysed. The link between transition metals, such as Ni, mobilisation and carbon mineralisation reactions has been demonstrated in various studies (Hamilton et al. 2018). It is likely that the increased Ni released observed within this study may be due to an increased rate mineral dissolution of Mg-bearing silicates, although further mineralogical analysis is required to confirm this.

Although the results presented in this study only represent a small proportion of parameters tested as part of an ongoing research study the differentiation in leaching characteristics between control HCT cells and CO_2 enhanced cells is clear. Increased metal mobilisation is clearly observed for key trace elements at both location sites and validates the ideation that more robust testing is needed to understand the potential implications of enhanced CO_2 concentration on mine waste weathering characteristics. Increases in Mn mobilisation as well as Ca release show promise for deposits such as Aitik, where the dominant silicate mineral is anorthite. Longer term testing and further pre and post characterisation tests will identify the CCS potential of such operations waste materials and the subsequent implications for drainage quality prediction.

It is noted that these results demonstrate preliminary leaching results for selective test parameters and do not include other key parameters at this stage. Other key test parameters were assessed within the testing program, including mineralogy, elemental composition, leachate analysis (pH, ORP, EC, alkalinity), acid neutralising capacity (ANC), acid buffering capacity (ABC), total carbon and sulfur and oxidation respiration tests. The results of these tests will be published once post characterisation work has been completed.

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