Carbonation of Magnesium Silicate Minerals in Mine Waste: Practical Laboratory Testing Methods to Assess the Dual Opportunity for Carbon Capture and AMD Mitigation

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Abstract

Mineral carbonation has been widely recognised as an important mechanism in the sequestering of CO_2 into mining wastes and by-products. The generation of fast-reacting carbonates in the carbonation process may also have important implications for the mitigation and prevention of acid mine drainage (AMD). Laboratory-scale methods have been developed to assess carbonation potential in mine by-products from an active nickel mine site in Finland. Utilized methods allow assessment of key parameters controlling the carbonation process. It has been demonstrated that the methods can influence waste pore water chemistry and geochemistry as a result of the carbonation process.

Keywords: Carbon Sequestration, Acid Mine Drainage, Geochemistry, Carbonation, Mine Drainage

Introduction

This paper presents the findings of the effects of mineral carbonation on mine waste rock acid neutralising capacity following short-term carbonation experiments.

The primary aim of the research was to improve the understanding of the carbon capture potential (CCP) of mafic and ultra-mafic waste rock materials excavated from Boliden AB's Kevitsa Ni-Cu-PGE mine in northern Finland. The secondary aim of the study was to verify and further test a number of novel experimental procedures devised by the research group for the determination of CCP from mining waste as a whole. We have attempted to assess the influence of carbon capture on the geochemical properties of mining waste and the ability of treated mining waste to neutralize acidity generated from sulfide oxidation.

It is well understood that Mg and Ca silicate-rich materials have the potential to sequester atmospheric carbon dioxide through the dissolution of minerals such as forsterite ($Mg2SiO4$) and anorthite ($CaAlSiO_4$) together with subsequent precipitation of stable carbonate minerals or through fixing CO_2 in the dissolved phase where mineral saturation does not occur (Li *et al.*, 2018, Wilson *et al.*, 2009, Harrison, Power and Dipple, 2013 and Renforth 2019). Previous studies (i.e. Declercq *et al.*, 2020) have shown that mineralogical changes occurring in ultramafic mining waste, have potential to increase the carbonate NP and overall acid neutralising potential determined through standard test methods (e.g. EN15875:2011).

A preliminary study undertaken by this research group identified the potential of two relatively low-cost, rapid methods to

assess carbon capture potential in mine waste rock. These methods include manometric determination of CO_2 sequestration rate and carbonation columns (Savage *et al.*, 2019). This study extends the work to examine the effects of temperature, particle size distribution (PSD), moisture content and CO_2 concentration on the relative rates of carbonation.

Within this paper the effect of carbonation on acid neutralisation is discussed with a view to potential benefits to mine drainage mitigation.

Methods

Sample Preparation

All testing was undertaken at the Geochemic Ltd laboratory facility located in Wales, UK. Testing was undertaken on composites of individual discrete waste rock samples obtained through screening of 100 mm diameter sonic drill core intervals to 22 mm. The sonic drilling program was undertaken on the existing Kevitsa waste rock dumps and therefore represented material of variable age of atmospheric exposure and states of weathering. As part of the study, each discrete pre-screened (sub-22 mm) core interval sample was further screened through dry sieving into <2.36 mm ('fines') and 2.36 mm to 22 mm ('coarse') size fractions. From the discrete size fractions two composites samples, 'Fine composite' (<2.3 mm) and Sample 'Coarse composite' (2.33 mm to 22-mm), were compiled. The two size fraction composites allowed the testing of the CCP of the two size fractions relatively from the Kevitsa waste rock dump.

Basic Characterisation of Samples

A series of basic geochemical characterisation tests were undertaken on the composite samples both pre and post CO_2 treatments. The tests included the following:

- Elemental composition through Energy Dispersive X-Ray Florescence (ED-XRF) (Panalytical MiniPal-4)
- Total C and S determined through high temperature combustion (Perkin Elmer 2400)

- Determination of water-soluble components 2:1 Liquid to Solid ratio 24-hour deionised water leach, with ICP-OES analysis of leachates – EN 12457-1:2002
- Net Acid Generation (NAG) testing and NAG liquor analysis by ICP-OES – EGI (2002)
- Acid Neutralising Capacity (ANC) in accordance with EN 15875:2011
- Acid Buffering Characterisation Curve (ABCC) AMIRA 2002
- Automated modal mineralogy through SEM-EDX mapping
- Mineral phase identification through fine powder X-Ray Diffraction (XRD)

Due to limitations of the current paper, only results for core tests are given .

CO_2 Treatment Tests

In order to test the validity and variability of two CCP testing procedures devised during the previous research phase (Savage *et al.*, 2019), an experimental program was devised to look at variability of the particular testing protocols to changing experimental conditions (Table 1).

Results

Mineralogical Characterisation

SEM-EDX analysis carried out on the coarse (Sample C) and fine (Sample F) composites showed that sample mineralogy was dominated by silicate mineral groups, with magnesium silicate phases identified. Sample C was predominately composed of clinopyroxene (53.5%) and amphibole (17.0%), with lesser phases of serpentine (6.0%) and forsterite (4.4%). Sample F showed similar mineral abundances; clinopyroxene (53.1%), amphibole (15.4%), serpentine (5.9%) and olivine (4.2%).

Elemental Characterisation

Elemental analysis carried out using ED-XRF showed similar elemental contents between the 2 sample sets. The S contents were measured at 0.38% and 0.59% for sample F and sample C, respectively. The major deviations that was noted between the

Table 1 *CO₂ treatment tests and condensed test information.*

Treatment Method	Test Information	Varied Test Parameters
Carbonation rate reactor vessels	The WTW Oxitop-C® measuring heads used in this study are designed to determine aerobic respiration rates using the Warburg constant volume respirometer method in accordance with ISO 16072. It does this through measuring the pressure changes within a closed system such as a jar or bottle. Using this concept but applying CO_2 (or a mixture of **CO_2** and N_2 **rather** than oxygen as the initial gas, it is now measuring the pressure change corresponding to CO_2 consumption rate.	CO_2 Concentration – 100%, 60% (40% N_2), 30% (70% N_2) and 10% (90% N_2) Temperature – 25 ºC and 10 ºC Particle Size – coarse and fine waste rock[A] Moisture Content (wt%) – 5% and 10%
Short term (62 day) exposure CO_2 reactor columns	This experiment was designed to determine the carbonate formation potential of a variety of materials exposed to pure CO_2 marginally above atmospheric pressure All the columns were set-up and run at room temperature (20ºC) with 10% moisture content. The columns ran for two months (62 days).	CO_2 Concentration– 100%, 60% (40% N_2) and 30% (70% N_2) Particle Size – coarse and fine waste rock[A]

[A]Particle size ranges: Coarse – (2.3mm to 22mm) and Fine – (<2.3mm)
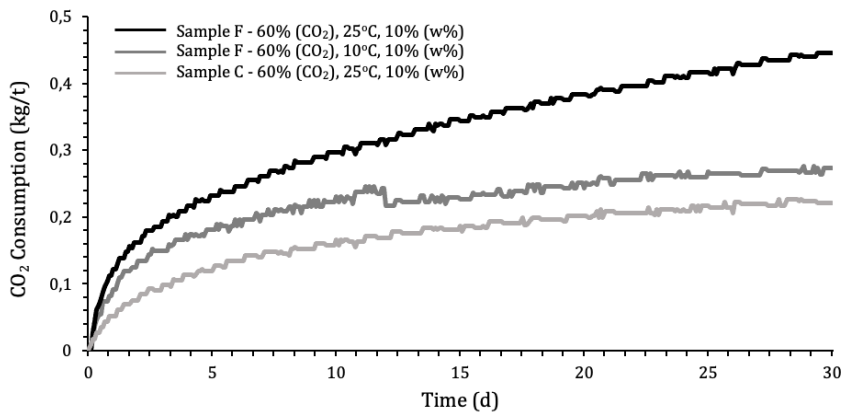

Figure 1 *Sample C (Coarse composite) and F (fine composite) carbonation rate reactor vessel outputs with varied temperature and 60% CO₂ in N₂ gas concentrations.*

sample composites were for Si and Mg. The fine sample fraction measured a Mg and Si content of 4.3% and 11.72%, while the course fraction showed higher levels of Mg and Si with readings of 12.59% and 21.66%.

Carbonation Rate Reactor Vessels

Figure 1 shows the results obtained from CO_2 consumption tests carried out on coarse composite and fine composite samples with variable temperatures (°C) with the same CO_2 concentration (60%), over a 30-day test period. CO_2 consumption was shown to be lower within vessels held at 10 °C compared to 25 °C. With the same test parameters fine samples (<2.3 mm) were shown to have faster consumption rates compared to coarse (2.3 mm to 22 mm). Results obtained from other consumption tests with varied test parameters are shown in table 2. The fastest consumption rate was measured at 6.06 kg(CO_2)/tonne/year for the fine waste rock material, exposed to 100% CO_2 at 25 °C, with a 10% moisture content (wt%).

Table 2 CO_2 *consumption vessel test parameters and measured consumption rates.*

Material	CO_2 (% by volume)	Temperature (OC)	W%	CO_2 Consumption rate[1] (kg(CO_2) /tonne/year)
Coarse Composite	100	25	10	3.8
		25	5	5.0
	60	25	10	2.69
		10	10	2.99
		25	5	3.85
		10	5	1.99
	30	10	10	1.32
		10	5	1.10
Fine Composite	100	25	10	6.06
	60	25	10	5.43
		10	10	3.32
	10	10	10	1.43

[1]Initial rate determined during first 5% of CO_2 consumption.

Implications of Carbonation on Acid Neutralisation Potential

Acid neutralising capacity (ANC) tests carried out on sample residues post CO_2 exposure showed consistent increases in neutralising potential (NP) with both particle size and CO_2 concentration. Pre-treatment ANC NP results for coarse composite and fine composite samples were 27.06 (kg $CaCO_3$ eq./t) and 26.50 (kg $CaCO_3$ eq./t), respectively. This value increased to 32.54 (kg $CaCO_3$ eq./t) within the fine composite exposed to 100% CO_2 gas mix while the coarse composite rose to 30.79 (kg $CaCO_3$ eq./t) at the same CO_2 concentration.

ANC tests on column material post treatment period showed changes in neutralising potential in all samples treated with CO_2. Figure 2 (1) shows ANC results from all coarse composite and fine composite columns. Initial baseline neutralising potential (NP) results from coarse and fine composite samples were 27.06 and 26.50 (kg $CaCO_3$ eq/t) respectively. Post treatment this increased to a maximum of 33.77 (kg $CaCO_3$ eq/t) within the coarse composite column exposed to 60% (by volume) CO_2 gas mix. The fine composite showed a greater increase in neutralizing potential (NP) post treatment

with the column exposed to 100% CO_2 giving an ANC of 39.28 (kg $CaCO_3$ eq/t). Dissolved inorganic carbon (DIC), determined with Sievers 820 TOC analyser, carried out on 24 hours 2:1 deionised water leach test leachates before and after treatment showed consistent increases with increased CO_2 concentration. It can be seen in figure 2 (2) that within the coarse composite DIC increases from 7.73 mg/L pre-treatment to 11.60 mg/L within samples exposed to 100% CO_2.

Key Observations

Adaptation of Warburg type constant volume respirometers, such as the WTW Oxitops used in this study, for the purpose of determination of CO_2 consumption is a rapid and cost-effective method for determination of initial carbonation rates of waste materials. The method has allowed determination of material response to variation in experimental conditions such as moisture content, temperature and CO_2 concentration. Due to the relative simplicity and low cost of the testing procedure, the method potentially has wider applicability to other sites and waste material types.

The CO_2 consumption vessel experiments have demonstrated that CO_2 uptake increased
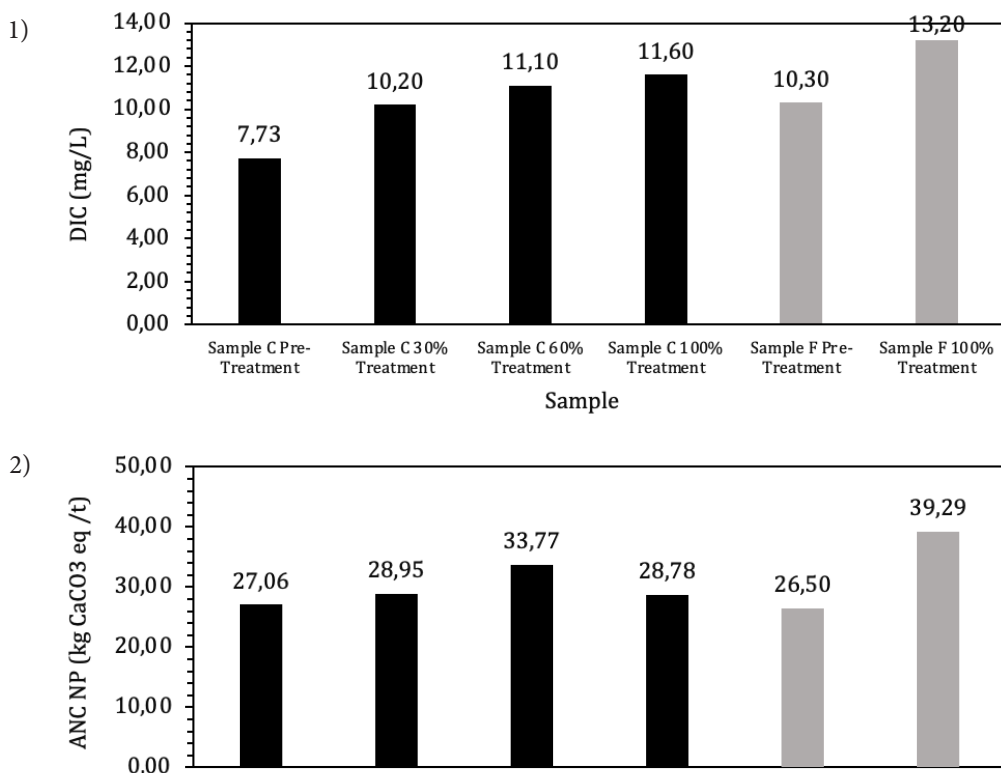
1)

2)

Figure 2 (1) Reactor column ANC results including pre and post treatment samples (% are % vol CO_2 in reaction vessel). (2) Reactor column dissolved inorganic carbon (DIC) in post-test leachate results including pre and post-treatment samples. Coarse composite sample are indicated as sample C, while fine composite samples are indicated as sample F.

in finer materials exposed to higher CO_2 concentrations. Within test runs, vessels containing the same material type with varied CO_2 concentrations those with 100% CO_2 showed consistently higher consumption rates over 30-day experiment periods. It has been demonstrated that, although the Mg and Si contents of the fine waste materials was lower than its coarse counterpart the finer waste rock fraction still showed the highest CO_2 consumption rates.

Increased consumption rates were consistently correlated with higher post experiment ANC NP. This suggests materials can yield a greater neutralising potential after only 30 days of exposure to increased CO_2, although more test work is required to confirm these findings. Temperature exerted a strong negative effect on the rate of CO_2 uptake, with the low temperature

experiments demonstrating the lowest overall CO_2 consumption rates, regardless of moisture content.

Short-term reactor column experiments showed similar trends to those observed within consumption vessel tests. Over the 62-day test period, with consistent gas throughflow and varied CO_2 concentration, column residues showed increasing ANC NP and DIC with increased CO_2 concentration. Columns containing finer waste rock material (<2.3 mm) showed the greatest increase in ANC NP. In both sets of tests, it has been demonstrated that sample F (<2.3 mm) yielded both increased consumption rates of CO_2 as well as consistently higher ANC NP and DIC post treatment. The test results indicate that the method can determine changes to pore water chemistry and geochemical properties that occur as a result of the carbonation process.

These findings support those reported in previous studies (Declercq *et al.*, 2020) in which ANC was seen to increase in long term weathering tests under ambient CO_2 conditions.

As a result of the demonstrated differences in post treatment geochemical characteristics in both materials in carbonation vessels and short-term reactor columns it can be concluded that the influence of short-term exposure to CO_2 does influence waste material drainage geochemistry. Further testing is planned to further assess the impact of moisture content on rates of carbonation as well as modelling test outputs over extended timescales to assess the implications for mine drainage systems over and beyond the life of the mine.

Current research is being undertaken by the authors is looking at long term impacts of CO_2 on kinetic weathering tests as part of a PhD program.

References

Declercq, J., Bowell, R., Brough, C., Barnes, A. and Griffiths, R. (2020). CO2 storage by mining waste; dream or reality?. *Economic Geology*, (In Press).

Harrison, A., Power, I. and Dipple, G. (2012). Accelerated Carbonation of Brucite in Mine Tailings for Carbon Sequestration. *Environmental Science & Technology*, 47(1), pp.126-134.

Li, J., Hitch, M., Power, I. and Pan, Y. (2018). Integrated Mineral Carbonation of Ultramafic Mine Deposits—A Review. *Minerals*, 8(4), p.147.

Renforth, P. (2019). The negative emission potential of alkaline materials. *Nature Communications*, 10(1).

Savage, R., Pearce, S., Mueller, S., Barnes, A., Renforth, P. and Sapsford, D. (2019). Methods for assessing acid and metalliferous drainage mitigation and carbon sequestration in mine waste: a case study from Kevitsa mine, Finland. *Proceedings of the 13th International Conference on Mine Closure*.

Wilson, S., Dipple, G., Power, I., Thom, J., Anderson, R., Raudsepp, M., Gabites, J. and Southam, G. (2009). Carbon Dioxide Fixation within Mine Wastes of Ultramafic-Hosted Ore Deposits: Examples from the Clinton Creek and Cassiar Chrysotile Deposits, Canada. *Economic Geology*, 104(1), pp.95-112.

Wilson, S., Harrison, A., Dipple, G., Power, I., Barker, S., Ulrich Mayer, K., Fallon, S., Raudsepp, M. and Southam, G. (2014). Offsetting of CO2 emissions by air capture in mine tailings at the Mount Keith Nickel Mine, Western Australia: Rates, controls and prospects for carbon neutral mining. International Journal of Greenhouse Gas Control, 25, pp.121-140.