The Development of A Multi Parameter Respirometric Laboratory Testing Method to Estimate Site-Specific Net Carbon Dioxide Flux from Metalliferous Mine Waste

Rosalia Shiimi[1], Rhys Savage[1,3], Steven Pearce[1], Andrew Barnes[2], Mark Roberts[2],
Daniel Schoen[1,2], Devin Sapsford[3]

[1]*Mine Environment Management Ltd, Wales, UK rhys.savage@memconsultants.co.uk, rshiimi@memconsultants.co.uk, spearce@memconsultants.co.uk ,*

[2]*Geochemic Ltd, Wales, UK, mroberts@geochemic.co.uk, abarnes@geochemic.co.uk, dschoen@geochemic.co.uk*

[3]*Cardiff University, Wales, UK, sapsforddj@cardiff.ac.uk*

Abstract

The mining industry has a large part to play in the global transition to low carbon technologies, however this will involve continued production of large volumes of tailings and waste rock materials. Recent research has focused on assessing suitable silicate bearing mining wastes as potential feedstocks for large-scale carbon dioxide removal technologies (CDRT). However, reactive sulfide and carbonate minerals within certain mine wastes have also been identified as having the potential to emit CO2, while also influencing discharge water quality. At present no standardised testing methods or monitoring, reporting and verification (MRV) systems exist for the quantitative assessment of sequestering carbon dioxide using mine waste materials or consideration of net CO_2 flux within mine waste storage facilities.

Keywords: Carbon dioxide removal technologies, net CO_2 flux, respirometric measurement system, titration analysis, total inorganic carbon analysis

Introduction

This paper presents the findings from the development of a novel approach to estimate CO_2 flux balance of mining waste materials through the use of standard laboratory equipment as part of a multi parameter respirometric measurement system (RMS). The primary aim of the research is to develop a methodology for estimating the carbon balance (i.e., the balance between CO_2 emissions and CO_2 sequestration) within mining waste facilities during operations and post closure. The novel approach to validating site-specific estimates for generated CO_2 emissions was realised through the utilisation of gas pressure monitoring technology along with a NaOH absorbent media, total carbon analysis and hydrochloric acid (HCl) titrations to provide a multi analysis solution. It is important to note that testing conditions allowed simulation of site parameters meaning the results are site specific.

Methods

Sample Preparation

All testing was undertaken at the Geochemic Ltd laboratory facility located in Wales, UK. Cardiff University and Petrolab UK were also utilised for selective characterisation methods. Testing was undertaken on composites of individual discrete waste rock samples. The composite waste rock used within the study was reduced to <6.3mm size fraction. To emulate field conditions, a 7.5% water content is added to the dry composite waste rock samples.

To assess CO_2 generation and CO_2 consumption in mine wastes, the WTW OxiTop-C and OxiTop-C/B pressure measuring heads, designed to determine aerobic respiration rates according to EN ISO 16072:2011 are used within this study. To differentiate between the different gas vessels used, the O2 consumption vessels will be referred to as "Oxitops" and

CO_2 consumption vessels will be called "Carbitops." The OxiTops utilise Warburg constant (Bryant 1964) volume respirometry method where the O_2 and CO_2 consumption rates are determined through monometric determination of the pressure drop within a sealed container of fixed volume (Barnes *et al.* 2022). Within this study, the method was altered from a standard method by Platen and Wirtz (1999) and the ideal gas law is applied to calculate the moles of O_2 or CO_2 within the sealed vessels containing waste samples.

Oxitop Experiment

A novel method is developed to access CO_2 production by utilising the adjusted Oxitop method and adding a NaOH solution to the vessels to absorb any CO_2 produced during sulfide oxidation and subsequent carbonate dissolution. This absorbent media can be back titrated in order to estimate the total CO_2 emitted by a material over a set time period. This can be cross checked through total inorganic carbon (TIC) analysis. Both analyses were carried out in this study to allow validation of the novel NaOH solution method.

Carbitop Experiment

Previous studies by Savage *et al.* (2019) identified two main stages of carbon dioxide exchanges within the pressure vessels due to the observed sharp initial decrease in pressure. These two stages are assumed to be (1) Initial surface absorption and pore water dissolution and (2) Mineral weathering and subsequent carbonation reactions. Considering these assumptions within this study, waste materials were allowed to equilibrate in a CO2 enriched environment for seven days. This allowed the samples to go through the initial stage of surface absorption and pore water dissolution, reducing the impact on the initial experimental readings. Once sealed and placed in a 25°C incubator after the 7 days equilibration period, it is assumed that the measured change in pressure is predominantly due to mineral carbonation. Upon completion the moles CO2 in the vessel at each time instance were calculated using the ideal gas law.

Results

NaOH Back Titration

The chemical reaction between NaOH and CO_2 resulted in the formation of HCO_3^- which is equivalent to CO_2 absorbed by the NaOH. The moles of HCO_3^- are determined from the moles of HCl added (from pH 8.3 to 2.5) because of the 1:1 mole ratio between the two (i.e., the moles of HCl added from 8.3 to 2.5 is equivalent to the moles of HCO_3^-

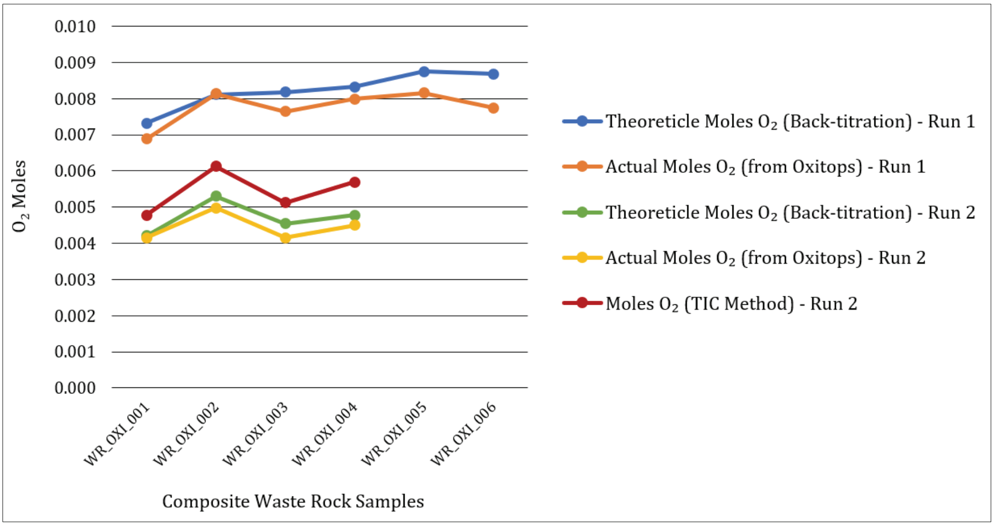

***Figure 1** O_2 moles estimated from back-titration, Oxitops and TIC method during experimental Run 1 and Run 2.*

***Table 1** Summary of average calculated CO_2 emissions generated by mining waste samples.*

Waste Material	Run 1 (Titration) kg (CO_2)/tonne/year	Run 2 (Titration) kg (CO_2)/tonne/year	Run 2 (TIC Method) kg (CO_2)/tonne/year
Waste Rock	1.95	1.12	1.04

in the solution). Given the stoichiometric relationship between pyrrhotite oxidation and dolomite neutralisation, a key finding from the back titration results show that the stoichiometric moles of O_2 calculated from the titration method compare very well with the O_2 moles estimated from the Oxitops (Figure 1). To validate the calculated CO_2 emission estimated by the titration method, the NaOH solution was analysed for carbon using the total inorganic carbon (TIC) method.

CO2 Production Rates

Back titrations were carried out on NaOH sample solutions from the waste rock Oxitops after both Run 1 and Run 2 of the experimental protocol. TIC analysis validations were carried out after run 2 and therefore were only comparable to Run 2 NaOH back titrations. Table 1 shows the calculated CO_2 emissions for the waste rock sample in Run 1 and Run 2. It can be seen that minimal variation was observed between NaOH back titration values and values measured through direct TIC analysis.

CO_2 Consumption

Carbon dioxide consumption rates of waste materials were estimated by converting changes in vessel pressure to direct consumption rates using the ideal gas law. Figure 2 shows the results obtained in Run 1 and Run 2 for waste rock material. Waste materials held an average CO_2 consumption

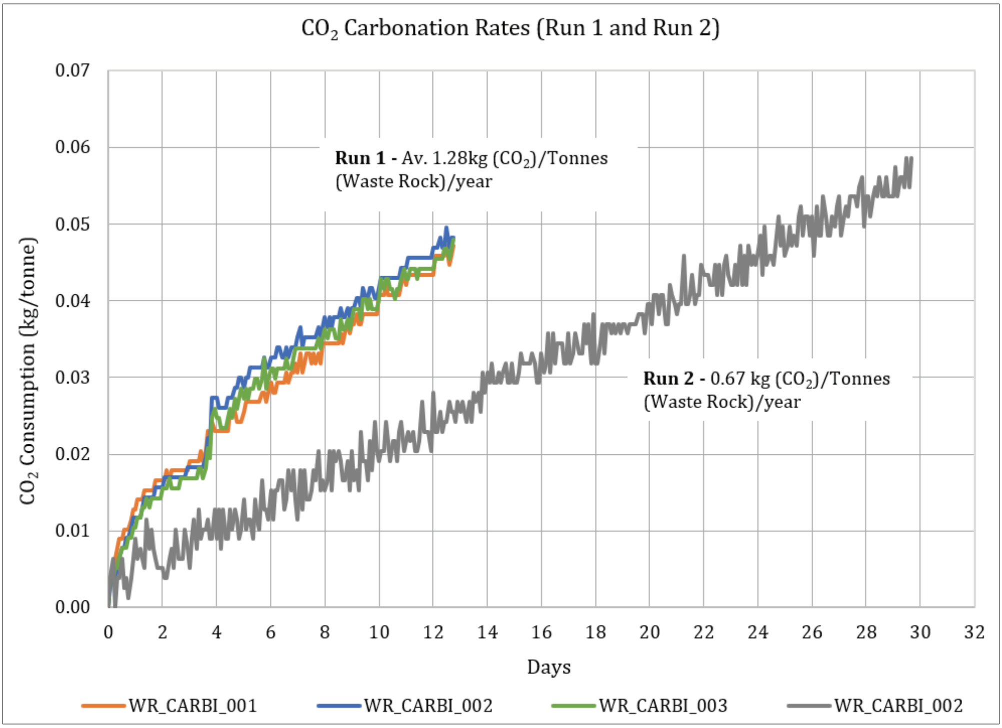

***Figure 2** Carbonation rate results measured in waste rock material.*

Table 2 Calculated net CO_2 released and sequestered (Carbon balance).

Waste Material	Estimated CO_2 Released (Back Titration	Estimated CO2 Released (TIC method)	Average Estimated CO_2 Production (Oxitops)	Estimated CO_2 Consumption (Carbitops)	Net CO_2 Emitted/ Sequested
	kg (CO_2)/tonne/year				
Waste Rock (Run 1)	1.94	-	1.94	1.28	0.66
Waste Rock (Run 2)	1.12	1.04	1.08	0.67	0.41

rate of 1.28 kg (CO_2)/tonne per year during Run 1, compared to 0.67 kg (CO_2)/tonne per year for waste rock materials during Run 2.

The Carbon Balance

Utilising the Oxitops and Carbitops results, a preliminary estimated balance between CO_2 sequestered and CO_2 emitted by mine waste materials can be estimated. Table 2 shows results of the CO_2 production rates from mine wastes, estimated from the Oxitops using the titration and TIC methods; and the CO_2 consumption rates estimated from the Carbitops. The difference between emitted and sequestered CO_2 will result in a net CO_2 release or net CO_2 consumption. The results of this test work are shown graphically in Figure 3. Based on the preliminary results of this study, the waste rock materials were identified to be potentially net carbon dioxide emitting in the presence of an oxygen rich atmosphere, although further testing is required to validate these preliminary findings.

Key Observations/Discussion

Oxygen Consumption

The pressure evolution of all the waste samples from both test runs indicate that a pressure decrease is common in all the Oxitop experiments. It was important to determine the oxygen consumption rates (OCR) as they give an insight into sulphide oxidation which is directly related to CO_2 production. According to Barnes *et al.* (2022), the weathering signature of mine waste facilities is

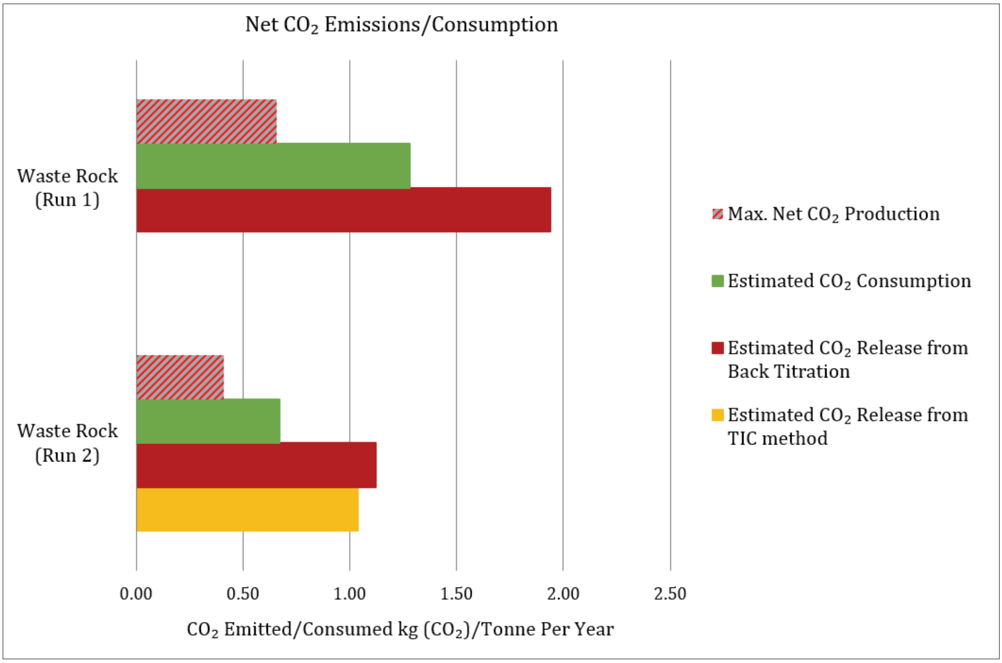

Figure 3 Net carbon emissions/consumption estimated for waste rock materials.

closely linked to the availability, depletion, and transport of oxygen. Key to these processes is the rate at which oxygen is consumed through oxidation of sulfide minerals within mining wastes. Additionally, there are many other aspects of the OCR that are inherent to the waste material, such as sulphide mineral content, type and reactivity, degree of sulphide mineral liberation, particle size distribution and exposed reactive surface area.

CO_2 Production

The pressure reduction within the Oxitops was due to pyrrhotite consuming oxygen. That coupled with the dissolution of dolomite with sulphuric acid results in the production of carbon dioxide (Torres, West and Li, 2014; Ross *et al.*, 2018). For this reason, a NaOH solution was added to the Oxitop vessels with the aim to absorb any CO_2 produced due to pyrrhotite oxidation and dolomite neutralisation. NaOH is such a rapid absorber of CO_2 that it far surpasses the rate at which the silicate minerals can absorb CO_2. Effectively, any CO_2 produced by the waste is immediately absorbed by NaOH, therefore completely separating out any CO_2 produced through sulphide oxidation and carbonate dissolution. The validation of the back titrations by analysing for carbon using the total inorganic carbon (TIC) method is novel and shows great promise for furthering the ability to estimate CO_2 emissions via lab-scale experimentation.

A very close correlation is observed between theoretical O_2 moles (calculated from the stoichiometric relationship between pyrrhotite oxidation and dolomite neutralisation) and the O_2 moles measured from Oxitops (estimated moles using the ideal gas law). The interpretation that the number of moles estimated from the Oxitops is approximately equal to the number of moles calculated from the stoichiometric ratio of O_2 and H_2CO_3 (CO_2) during pyrrhotite oxidation and dolomite neutralisation is an important outcome from this study which signifies that CO_2 production rates within a system can be estimated from Oxitops by using the estimated number of O_2 moles due to the change in pressure using the ideal gas law.

CO_2 Consumption

The estimated CO_2 consumption is based on a 100% CO_2 atmosphere, therefore, the calculated CO_2 consumption rates within this study represent idealised carbonation rates in such an atmosphere. More testing at various pCO_2 conditions are required to develop a better understating of the potential carbonation kinetic rates under varied conditions.

Carbon Balance

The CO_2 production rates estimated were between 1.04 and 1.94kg (CO_2) per tonne of waste rock per year. It should be noted that these are maximum estimated rates as they were measured at room temperature and at atmospheric oxygen concentrations. Carbitop experiments revealed idealised carbonation rates between 0.67 and 1.28kg (CO_2) per tonne per year of waste rock. These are maximum estimated carbonation rates, measured in a pure CO_2 atmosphere. The Oxitop and Carbitop experiments allowed the estimation of the net carbon emissions or net carbon sequestration by calculating the difference between maximum CO_2production and maximum CO_2 consumption rates.

In terms of the carbon balance, the data indicates that under atmospheric gas conditions waste rock material may produce more CO_2 due to sulphide oxidation and carbonate dissolution than it can consume with an estimated net CO_2 emission rate between 0.41 and 0.66 and kg (CO_2) per tonne per year. However, the results also indicate that in a gas atmosphere where O_2 availability is reduced (for example in a waste storage facility that has been encapsulated post closure), the waste rock will produce less CO_2, as sulfide oxidation is reduced. Under this gas atmosphere condition, the rate of carbon sequestration will not be impacted by lower O_2 concentrations and will be proportional to pore gas CO_2 concentrations (which are typically elevated where O_2 availability is low). As such in this situation the results indicate that the balance of the system may reverse and become net carbon negative (as CO_2 consumption is higher than production).

Conclusions

To date, no universal, robust, practical and cost/time effective benchtop laboratory method has been developed to determine empirically the potential CO_2 release and uptake (and thus balance) within typical sulfide metalliferous mine wastes (waste rock and tailings). Utilising the back titration method along with the RMS method, this study was able to quantify CO_2 emissions and uptake from samples of waste rock from a metalliferous mine, further the results were able to be validated by the TIC method. From the Oxitop and Carbitop results, this study was able to develop a novel empirical methodology to assess the carbon balance of mine wastes which is likely to become a critical aspect for future mine waste characterisation.

Using the developed carbon balance methodology, the results of the study indicates that emissions of CO_2 are likely higher in the waste rock tested than the uptake of CO_2 in a situation where pore gas is close to atmospheric composition. However, the results indicate that where pore gas conditions become oxygen limited (for example in mine waste that is stored within a facility that has engineered oxygen limiting design such as low permeability cover system), the balance has the potential to become a net neutral. As such the results of the testing produced from the method outlined allows relative and quantitative assessment of the potential carbon balance for mine waste under given scenarios. Therefore, the method provides a very valuable tool for operational and closure mine planning, specifically for the design of waste storage facilities and assessment of opportunities and risks related to CO_2 net emissions from the short-long term storage of mine waste. Future research will look to further assess the net CO_2 flux within tailings, by utilising this study’s carbon balance methodology to test tailings material.

Acknowledgements

We would like that acknowledge Cardiff University for the use of their laboratory facilities during this study as part of an MSc course placement. We would also like to thank the external mining operator that funded this experimental work as part of the first authors MSc placement. This operator has chosen to remain anonymous at the time of publication.

References

Barnes, A., Pearce, S., Savage, R., Roberts, M., Brookshaw, D., Rama, M., Kauppila, T., Mueller, S., Hertrijana, J., and Bowell, R. (2022). Application Of the Warburg Constant Volume Respirometer Method For Determination Of Oxygen Consumption Rates Of Mining Waste. International Conference on Acid Rock Drainage 2022, Australia.

Bryant, J.O. (1964). SOME ASPECTS OP GAS TRANSFER IN THE WARBURG RESPIROMETER. MSc Thesis, Rice University.

EN ISO 16072:2002 (2011). Soil quality. Laboratory methods for determination of microbial soil respiration.

Platen, H. and Wirtz, A. (1999). Application report Oxygen consumption and carbon dioxide generation. Matrix: Soils and solids Application report Respiration activity of soils (standard test preparation). Available at: http://www.fh-giessen.de/WEB_TG/uht.htm.

Ross, M.R.V., Nippgen, F., Hassett, B.A., McGlynn, B.L. and Bernhardt, E.S. (2018). Pyrite Oxidation Drives Exceptionally High Weathering Rates and Geologic CO2 Release in Mountaintop-Mined Landscapes. Global Biogeochemical Cycles 32(8), pp. 1182–1194. doi: 10.1029/2017GB005798.

Savage, R.J., 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. In: Proceedings of the International Conference on Mine Closure. Australian Centre for Geomechanics, pp. 1073–1086. doi: 10.36487/ACG_rep/1915_86_Savage.

Torres, M.A., West, A.J. and Li, G. (2014). Sulphide oxidation and carbonate dissolution as a source of CO2 over geological timescales. Nature 507(7492), pp. 346–349. doi: 10.1038/nature13030.