

C-Sink 5 months EU actions for deployment of CDRT

Transition to net-zero economy, increased demand upon production of key resources, increasing waste and LOM GHG emissions, need for sustainable waste management/closure

Investing, approach to reduce emissions/AMD and see return on investment is EW, acceleration of natural silicate W

Calculating rate of CO2 seq. / problematic mineral assemblages

Net C-Sink / C-Source

Research by my colleagues on gas flux in mine waste presents methods to do this, im going to share



Increasing research into CDR potential of mine waste – pore gas comp important

Currently don't report emissions from WSF in scope 1 emissions, however if want reduction need to net CO2 balance

ARD major challenge for waste management, strategies to inhibit

O2 supply limiting factor, capping system deployed limit O2 ingress Pore gas/water, lack of standardised test

2papers, natural example large catchment, awareness of mining emissions



Humidity cell tests set-up

Enhanced CO2, significant increase in Ni Mg release compared to N2 control



Degassing experiment using high shear reactor show relationship pore gas and pore water quality

Degassing increased pH to where hydroxide precipitation and metal cation adsorption occurs

pH>8 metal mobility sig reduced



1 of 2 reactions affecting CO2 flux Oxidation of sulfides, pyrite, drawdown of O2 generating acidity Primary carbonates undergo dissolution releasing CO2



2nd reaction Silicates provide acid buffering capacity by consuming free protons.

Silicate weathering also releases cations (of which Mg and Ca are the most viable for sequestration).

Secondary carbonates are formed (atmospheric CO2 is taken up and 'locked' into these minerals.

CO2 consumed

Simplified schematic showing process How links to O2/CO2 change Rate affected by reactive SA



Detailed mineralogical investigation carried out on samples Nickel sulfide deposit with an ultramafic cumulate in North Europe Target and gangue mineral phases, WR and T, respective mineral abundances 3 key mineral phases

Method 1: Laboratory scale methodology development – WTW OxiTops

- Measuring O₂ consumption and CO₂ generation (Oxitops)
- Measuring CO₂ consumption (Carbitops)
- · Bespoke sealed vessels partially filled with waste
- Allowed controlling of conditions (temp, humidity, gas concentration)
- NaOH solution suspended within sealed Oxitops vessels to sequester CO₂ produced
- Net CO₂ flux estimated



Method $\frac{1}{2}$ used to measure CO2 flux – WTW Oxitops, standardised method to determine aerobic respiration rates

Use pressure sensor, determine pressure drop, closed system known volume Therefore ideal gas law to calc moles O2 / CO2



To assess the consumption of O2, 1kg sample

6 WR, 5 T, 1 TW, 1 DI control

Emulated field conditions, moisture content / T

Vessels sealed and enclosed in controlled T incubator

Diagram shows NaOH sol. Suspended, sequester CO2



CarbiTops same set-up just green and purged with 100% CO2 atm, glove box 7days



Results of Carbi show WR and T consumed CO2 T > WR Run 1 > Run 2



Results of Oxi show WR and T consumed O2 WR > T WR prone to sulfide oxidation Run 1 > Run 2

Results - NaOH back titration

- The chemical reaction between NaOH and CO₂ result in the formation of HCO₃- which is equivalent to CO₂ absorbed by the NaOH.
- The moles of HCO3⁻ are determined from the moles of HCI added because of their 1:1 mole ratio
- Moles of O₂ and CO₂ are calculated from the stoichiometric ratio of O₂:H₂CO₃ (CO₂) during:
- 1. Pyrrhotite oxidation:

 $4Fe_{(x-1)}S + \underline{9}O_2 + 10H_2O = 4Fe(OH)_3 + 8H^+ + 4SO_4^{-2}$ (MEND Report, 2019)

2. Dolomite neutralization:

 $2CaMg(CO_3)_2 + 4H_2SO_4 = 4H_2CO_3 + 2Ca^{2+} + 2Mg^{2+} + 4SO_4$

Stoichiometric Ratio = 9/4 = 0.44

NaOH back titration used to calc mass CO2 produced, at end of each run 0.44 mole CO2 / mole O2

Results - CO ₂ Production Rates					
s are calculated from	the number of moles o	f CO $_2$ absorbed by the N	laOH		
 Back titration method validate by the total inorganic carbon (TIC) method Minimal variation was observed between titration, TIC and Oxitops (stoichiometry) values 					
Run 2 - CO ² Release (kgCO2/tonne/year) (Back Titration)	Run 2 - CO ² Release (kg(CO2)/tonne/year) (TIC)	Run 1 - CO ² Release (kgCO2/tonne/year) (Oxitops)			
1.12	1.04	1.08			
0.54	0.52	0.53			
	0.54	0.54 0.52	0.54 0.52 0.53		

CO2 production rate 3 methods: NaOH back tit, TIC run 2, delta P Carbi T approx. half WR



Carbon balance WR net CO2 release, C-Source T net CO2 consumption, C-Sink

Key Observations/Discussion

- **CO**₂ **consumption rates** Idealised carbonation rates (100% CO₂ atmosphere). However, experiment can be modified to account for a range in concentrations.
- **Oxygen consumption rates** Important to determine the O₂ consumption rates (OCR) as they give an insight into sulphide oxidation which is directly related to CO₂ production.
- **CO**₂ **Production** A novel method is developed to assess CO₂ production by adding a NaOH solution to the Oxitop vessels to absorb any CO₂ produced due to pyrrhotite oxidation and dolomite neutralisation.

Back titration method validated by 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.

Idealised carbonation rate, 100% CO2 atm, can be changed, elevated CO2 in WSF

OCR sulfide oxidation, CO2 production

Novel method to assess CO2 release, NaOH, validated by TIC, off-shelf equip. small scale, controlled cond. Quick, low cost, flexible, installed on remote site (Indonesia)

Implications for mine waste management and AMD

- A novel empirical methodology to assess the carbon balance of mine wastes was developed likely to become a critical aspect for future mine waste characterisation.
- Results indicate that emissions of CO₂ are higher in the waste rock than the uptake of CO₂ where pore gas is close to atmospheric composition.
- Results also 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.
- The developed method provides a valuable tool for operational and closure mine planning, specifically for the design of waste storage facilities and assessment of opportunities and risks related to CO₂ net emissions from the short-long term storage of mine waste.

Easily replicated Atm cond. WR net CO2 release Pore gas O2 limited balance has potential to be net neutral Valuable for assessing risk of CO2 emissions form WSF AMD: additional carbonate mineral mass increase acid buffering capacity, pH>8 metal mobility reduced



Established to determine C balance, measuring CO2 / O2 key

Bespoke sealed cell

Probes to measure CO2 / O2 conc. / time

Sealed therefore any change in conc. Result of sample-air reactions

Experimental set-up - Barrels



WR and T samples from same mine Stainless steel Cold room 8degC Flushed to achieve starting gas comp. elevated CO2 8% and atm 400ppm



Showing completed assembly of probes and pictures. 3 probes: O2 %, CO2 % and ppm O rings and sealants Valves for P 4 T, 2 atm, 2 elevated CO2, T control 1 WR atm, WR control

Elevated CO2 tailings results-

decrease in CO2 in both barrels.

O2 in barrel 2 decreased steadily over 1 year and levelled off.

O2 in barrel 1 was variable suggests leak, sulfide oxidation due to O2 ingress



WR atm

Inverse relationship O2/CO2, CO2 increase in B6, lag

B7 control, constant conc

Rate: initial fast rate in first 60 days, then slower rate

Nice, science works, hypothesis correct, 52 weeks, expect to see CO2

decrease as carbonation dominant

Net CO2 reduction and time

Barrel	Net CO ₂ change (g)	Net O ₂ change (g)
number		
1	-1.93	+0.93
2	-2.11	-0.15
3	-0.017	-1.13
4	-0.012	-0.79
5	-0.012	-0.38
6	+2.012	-21.79
7	-0.012	-0.73

Discussion

- Conversion to absolute gas concentrations using Ideal Gas Law and Dalton's Law (known parameters)
- Barrel 2 with elevated initial CO₂ decrease in CO₂ demonstrates sequestration equivalent to the increase in CO₂ in Barrel 6
- Waste rock- net CO₂ release
- Sulfide oxidation dominant process for pore gas in waste rock (in positive oxygen environment)

Output probes converted to absolute values Barrel 2 decrease = Barrel 6 increase = 2g WR net C-Source, T net C-Sink

Control and B4 similar, representing physical processes - diffusion into water

Applicability

- Potential to incorporate different wastes
- Convenient to change conditions to simulate different sites/seasonality impact (different temp., water content etc.).
- Closed system- largely reflective of "covered" wastes.
- No active pH measurement currentlypotential to install



Comparable to Method 1 Potential to test different waste, change conditions Reflect capped systems Implement pH measurement



C-Sink		
If you would like to keep up the https://c-sinkproject.eu/	to date with the progress of C-Sink	

