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From Novel Laboratory Methodologies to Field Implementation: Assessing CO_2 and O_2 Flux in Northern Europe Mine Waste

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Abstract

The demand for metals in net-zero technologies has increased mining waste. This study examines carbon sequestration in ultramafic mine waste in Northern Europe. In collaboration with research partners, innovative methods assess CO_2 sequestration and emissions. Closed-system experiments showed O_2 depletion from 21% to negligible values (mg/L) due to sulfide oxidation. CO_2 removal is evaluated by monitoring atmospheric CO_2 and carbonate formation, considering CO_2 from acid mine drainage neutralisation. Results suggest carbonation can reduce CO_2 emissions, informing scalable carbon management. Open-barrel tests simulate field conditions, supporting sequestration strategies and contributing to the EU-funded C-SINK project.

Keywords: Gas flux monitoring, Carbon sequestration, Mine waste, Carbonation, Field trials

Introduction

This study expands on prior carbon capture and sequestration (CCS) research by Mine Environmental Management (MEM) Ltd. and Geochemic Ltd., focusing on CO_2 removal through mine waste materials. The increasing demand for metals essential to net-zero technologies has intensified mining activities, leading to significant waste production. Mine waste, particularly from ultramafic deposits, has the potential to sequester atmospheric CO_2 through mineral carbonation. However, challenges remain in quantifying CO_2 removal, understanding O_2 flux changes due to sulfide oxidation, and developing scalable carbon management strategies. Building on previous studies (e.g., Savage, 2019, 2023; Shiimi, 2022; Schoen, 2022), this study further investigates CO_2 sequestration potential using laboratory-scale and mesocosm experiments. The research integrates enhanced weathering (EW) techniques with improved monitoring, reporting, and verification (MRV) frameworks. Additionally, preparations for field-scale testing aim to refine carbon dioxide removal (CDR) strategies in mining contexts, bridging the gap between controlled experiments and real-world applications.

Methods

Sample Preparation, Collection and Characterisation

Mine waste samples, obtained from waste rock storage facilities (WRSF) and tailings storage facilities (TSF) at Northern European mine sites, were characterised according to British (BS) and European (EU) standards. Characterisation focused on mineralogical (SEM-EDX, optical microscopy), elemental (ED-XRF for elemental distribution and carbon capture potential), geochemical (NAG, ANC, total carbon and sulfur, pH, EC), and geotechnical (specific gravity, particle size distribution, water content) properties. These analyses identified oxidation and carbonation potential, assessed carbon sequestration capacity, and informed experimental design. Tailings were tested in Xylem WTW OxiTop®-C/B (Oxitops and Carbitops) and open-barrel setups, while waste rock underwent similar experiments. Historical MSc and PhD data (e.g., Savage *et al.* 2019, Chmielarski 2020, Schoen 2022, Shiimi 2022, Savage 2023, Cole 2023) supported sample selection and methodology

Closed-System Experiments

Laboratory-scale closed experiments utilised established methodologies to evaluate carbon capture. Oxitops experiments, conducted over 30 days at 8–10 °C, followed the WTW Soil BOD manual (2010a, 2010b) to measure O_2 consumption and CO2 produced using a NaOH solution. Carbitops experiments, also lasting 30 days, were performed at 5% CO_2 and 8–10 °C to assess CO_2 consumption under elevated conditions. Sealed barrel experiments, spanning over 365 days, employed bespoke vessels developed by Schoen *et al.* (2023), using controlled starting gas compositions (O_2, CO_2) at 8–10 °C. Throughout these experiments, pressure and gas concentration changes were monitored to evaluate CO_2 production and consumption rates, enabling detailed carbon balance calculations.

Open-System Experiments

An open barrel mesocosm test (Fig. 1) was designed to simulate field conditions, in Northern Europe, providing a platform to evaluate sensor performance before upscaling to field trials. The experiment operated under atmospheric O_2 and CO_2 conditions at 8–10 °C, with the objective of developing and setting up an open-barrel equipment test to monitor gas flux and geochemical behavior in mine tailings under semi-controlled open system conditions. This development represents a new approach to understanding carbonation processes in mining contexts. As part of a broader EU-funded carbon sequestration project, open system experimentation is considered part of the plans for an upscaled field trial at a Northern European mine site.

Results

Characterisation of ultramafic mine waste

Waste rock samples had a moisture content of 7.5% added before experiments, as water is necessary for the carbonation process. Carbon dioxide dissolves in water to form carbonic acid, which reacts with Mg- and Ca-bearing silicates to produce secondary carbonate minerals. Particle size distribution (PSD) curves for waste rock revealed well-graded material ranging from gravel to fines, with smaller particle sizes contributing increased surface area for oxidation and

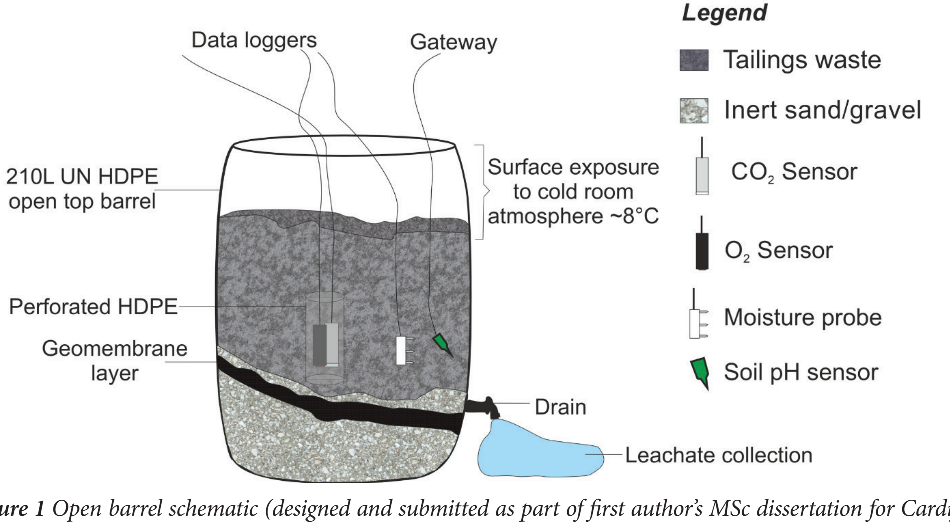

Figure 1 *Open barrel schematic (designed and submitted as part of first author's MSc dissertation for Cardiff University).*

carbonation reactions. Elemental analysis from prior studies was used to evaluate the carbon capture potential (CCP) for waste rock and tailings. Waste rock demonstrated a higher CCP (~370 kg CO_2/tonne) compared to tailings (~330 kg CO_2/tonne). Calcium concentrations remained consistent (~10%) across both materials. Magnesium content was higher in waste rock, potentially explaining its elevated CCP due to magnesium's role in carbon capture. The mineralogical compositions of waste rock and tailings were broadly similar featuring sulfides, silicates and carbonates. Target minerals such as pyrrhotite, pyrite, calcite, and dolomite were identified, alongside gangue minerals including diopside, enstatite, tremolite, serpentine, and chlorite. These minerals are critical for carbonation reactions, as sulfides generate acidity, carbonates neutralise it to produce CO_2, and magnesium silicates react with CO_2 to form carbonates.

Carbon Balance by Oxitops and Carbitops

Under low-temperature conditions (10 °C), the carbon balance of the analysed Oxitops and Carbitops mine waste samples demonstrated net CO_2 sequestration potential (Fig. 2). CO_2 production rates estimated from both the back titration and TIC methods were estimated between 0.40 and 1.24 kg CO_2/tonne/year for tailings and less than 0.10 kg CO_2/tonne/year for waste rock. In a 5% CO_2 atmosphere, CO_2 consumption rates ranged from 1.90 to 2.11 kg CO_2/tonne/year for tailings and 1.16 to 1.25 kg CO_2/tonne/year for waste rock. Net CO_2 sequestration rates were higher in waste rock, ranging from 1.09 to 1.20 kg CO_2/tonne/year, driven by limited CO_2 production from sulfide oxidation and carbonate dissolution, coupled with notable CO_2 uptake by silicate minerals. For tailings, net sequestration rates were estimated between 0.67 and 1.71 kg CO_2/tonne/year, with higher CO_2 production from sulfide oxidation offset by greater CO_2 uptake via carbonation reactions.

Passive Carbonation in Closed Barrels

Two sealed barrels (Fig. 3) stand out as they directly compare to the hypotheses for atmospheric conditions developed by Schoen *et al.* (2023). A waste rock barrel, exposed to atmospheric conditions, showed O_2 concentrations starting at ~20% (≈278 mg/L), in November 2022, which gradually decreased over time due to sulfide oxidation, reaching complete depletion by April 2024. This aligns with the hypothesis for atmospheric CO_2 conditions, which predicted that O_2 concentrations would fall as sulfides were oxidised, leading to a reduction in available O_2. CO_2 concentrations in this barrel began at ~400 ppm (≈0.56 mg/L) and steadily increased, peaking at ~1.6% (≈16,000 mg/L) in April 2024, coinciding with the complete O_2 depletion. This supports the hypothesis that CO_2 levels would initially increase due to the rapid occurrence of sulfide oxidation and primary carbonate dissolution, releasing CO_2 before passive carbonation (CO_2 uptake) becomes dominant. From mid-April 2024 onward, CO_2 concentrations began to decline, reaching ~1.3% (≈13,000 mg/L) by November 2024. A control barrel, which contained quartz chips, showed little change

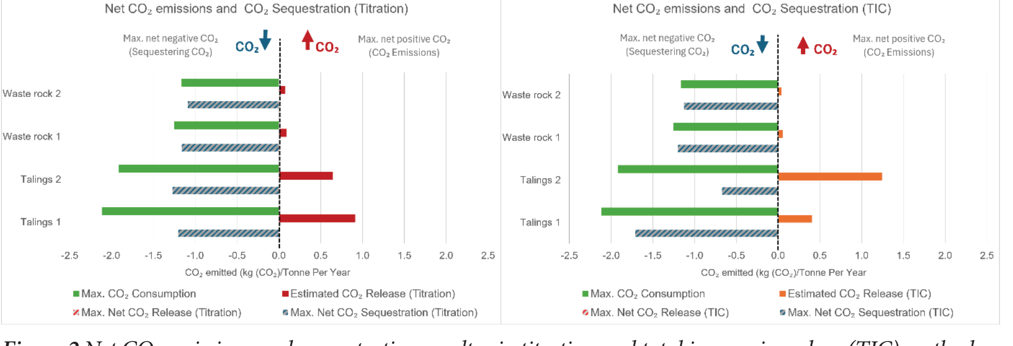

Figure 2 *Net CO_2 emissions and sequestration results via titration and total inorganic carbon (TIC) methods.*

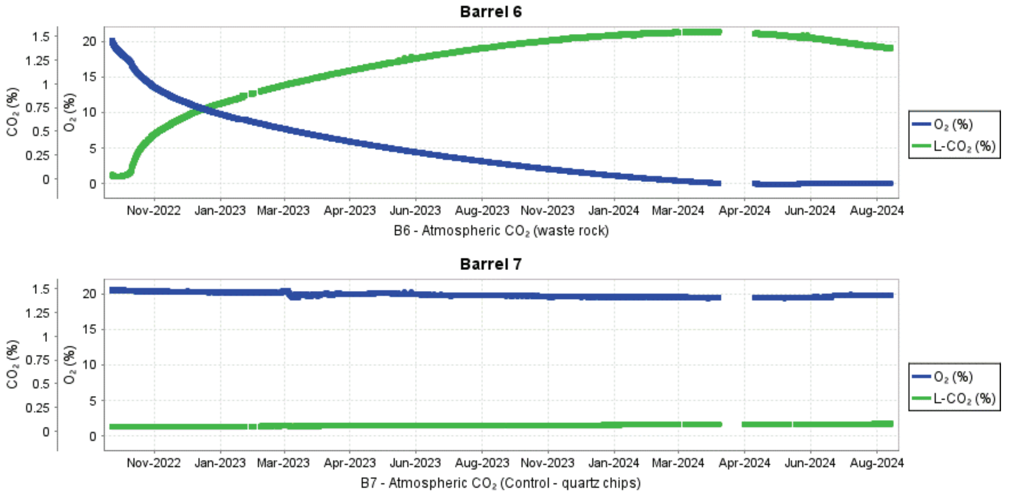

***Figure 3** Sealed barrel results after prolonged monitoring of the gas flux.*

in O_2 and CO_2 concentrations over the two-year period. A minor deflection in O_2 levels between November 2023 and May 2024 was attributed to sensor corrosion, confirming that no reaction-driven gas exchange occurred in this control barrel.

Commissioning the Open Barrel Equipment Test

The open barrel was commissioned and filled with mine tailings sourced from a Northern European mine site. The barrel is instrumented with O_2, CO_2, pH, temperature, and soil moisture sensors (Fig. 4). The barrel will be irrigated, and leachate collected for geochemical analysis. The open barrel contains 120 kg of homogenised mine tailings at 20% moisture content, with a base layer of 25 kg of DI-rinsed river aggregate gravel and 20 kg of inert sand mix. The system also includes a geomembrane to contain and prevent contamination of the materials. The open barrel mesocosm test will enable more precise measurements of the factors influencing carbonation processes, which is vital for optimising carbon sequestration strategies. Real-time monitoring results from this new approach will provide valuable insights into CO_2 removal efficiency in mining contexts, paving the way for more sustainable practices and effective carbon management across the industry.

Key Observations/Discussion

Critical characterisation of ultramafic mine waste

The characterisation of waste rock and tailings include the importance of moisture content, as water is essential for carbonation by enabling CO_2 dissolution and subsequent reactions with magnesium- and calcium-bearing silicates to form carbonates. The particle size distribution showed a range of material sizes, with smaller particles offering a larger surface area for oxidation and carbonation. Elemental and mineralogical analyses revealed similarities between the materials, with both containing mafic minerals like pyroxene and amphibole, though tailings had a higher presence of olivine. Various key minerals, including pyrrhotite, pyrite, calcite, and dolomite, were identified as important for carbonation processes. These characteristics suggest that both waste rock and tailings possess the necessary conditions for carbonation, with mineral composition playing a considerable role in their carbon sequestration potential.

Nature of the closed system experiments

The Oxitop and Carbitop tests demonstrated that both tailings and waste rock have the potential for CO_2 sequestration. Waste rock exhibited higher net CO_2 uptake due to lower CO_2 production from sulfide oxidation and

Figure 4 *Open barrel equipment setup.*

greater carbonation of silicate minerals. In contrast, tailings generated more CO_2 from sulfide oxidation but also underwent substantial carbonation, resulting in net sequestration. The saturated nature of the tailings likely restricted CO_2 diffusion, enhancing its uptake by silicate minerals. The largely saturated conditions in the tailing's facility likely limited CO_2 diffusion relative to O_2, allowing CO_2 produced during sulfide oxidation to be consumed by silicate minerals. These findings indicate that both waste rock and tailings can achieve net CO_2 sequestration under the studied conditions, with tailings exhibiting higher carbonation rates than waste rock.

The sealed barrel tests further supported these findings. The waste rock barrel followed expected trends, with O_2 depletion due to sulfide oxidation and an initial CO_2 increase from sulfide oxidation and carbonate dissolution. Over time, CO_2 concentrations declined as carbonation reactions became dominant. The control barrel, containing quartz chips, exhibited negligible gas fluctuations, confirming the absence of reaction-driven gas exchange.

The future of the open system experiments

While initial sensor readings for the open barrel equipment test are being recorded, the timeline for carbonation development remains uncertain, and the full trends will emerge as data collection continues. The future field trials will provide more information to refine carbonation process insights and carbon sequestration strategies.

Conclusion

The project has made substantial contributions to the advancement of carbon sequestration strategies by utilizing mine waste materials. By building on prior research, this study has refined methodologies for monitoring CO_2 and O_2 fluxes, a critical aspect of assessing the carbon capture potential of mine waste. These efforts not only address Measurement, Reporting, and Verification (MRV) challenges but also enhance Enhanced Weathering (EW) frameworks for Carbon Dioxide Removal (CDR). The novel open-barrel experiment, along with upcoming field trials at the mine site, marks a crucial step in validating these strategies in real-world settings. The data gathered from these trials will offer valuable insights that will shape future carbon sequestration technologies, including those supported by the EU-funded C-SINK project. This work establishes a solid foundation for improving carbon sequestration methods and advancing efforts to mitigate atmospheric CO_2 levels. Future research should focus on modelling existing CCS data (e.g. using PHREEQC) to identify emerging trends and further refine conclusions. Additionally, enhancing O_2 and CO_2 consumption rate models using techniques such as differential or integrated rate laws will considerably improve carbon sequestration models. Investigating parameters like temperature,

O_2/CO_2 content, particle size, and mineralogy will be essential in developing more accurate and robust consumption estimation models for future carbon capture strategies.

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References

Chmielarski M (2019) An assessment of the carbon sequestration potential of ultramafic nickel mine waste rock: Investigation of impacting environmental factors (Unpublished MSc dissertation). Cardiff University.

Cole J (2023) Investigating the rate of passive carbonation and assessment of the carbon balance of metalliferous mine waste (Unpublished MSc dissertation). Cardiff University.

Savage RJ, 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:1073–1086. doi: 10.36487/ACG_rep/1915_86_Savage.

Savage R (2023) Humidity cell testing of mine wastes under a CO2 supplemented atmosphere (PhD dissertation). Cardiff University.

Schoen D (2022) Investigating the rate of passive carbonation of mine wastes with focus on a metal mine in Finland (Unpublished MSc dissertation). Cardiff University.

Schoen D, Savage R, Pearce S, Shiimi R, Gersten B, Roberts M, Barnes AK (2023) A novel empirical approach to measuring pore gas compositional change in mine waste storage facilities: A case study from northern Europe. Proceedings of the International Conference on Mine Closure. https://doi.org/10.36487/acg_repo/2315_070

Shiimi R (2022) Development of a method to assess the carbon balance of typical waste storage facilities at the Boliden Kevitsa mining operation (Unpublished MSc dissertation). Cardiff University.

Shiimi R, Savage R, Pearce S, Barnes A, Roberts M, Schoen D, Sapsford D (2023) The development of a multi-parameter respirometric laboratory testing method to estimate site-specific net carbon dioxide flux from metalliferous mine waste. International Mine Water Association (IMWA) 2023 Proceedings. Retrieved from https://www.imwa.info/docs/imwa_2023/IMWA2023_Shiimi_471.pdf

WTW, a Xylem brand (2010a) BOD application report: Respiration activity of soils (basic principles, process characteristics). Germany: 1–16.

WTW, a Xylem brand (2010b) BOD application report: Respiration activity of soils (standard test preparation). Germany: 1–8.