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Aqueous matrix and limiting factors in steel slag carbonation under elevated CO₂ at ambient conditions

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Abstract

Alkaline industrial by-products have significant potential for permanent CO₂ sequestration, but their reaction kinetics and controlling factors are often overlooked. This study examined the direct aqueous carbonation of basic oxygen furnace (BOF) slag in a slurry setup with continuous mechanical mixing and CO₂-enriched air bubbling in ultrapure water and natural seawater, at 25% pCO₂ under ambient temperature and 1 atm for 24 h. CO₂ sequestration into carbonate minerals was higher in the ultrapure water (105±5 kg CO₂ t⁻¹ slag; 90% CO₂ capture efficiency) than in seawater (78±4 kg CO₂ t⁻¹ slag; 70% CO₂ capture efficiency). Most of the rapid mineralisation potential of Ca-(hydr)oxides was realised within 4-12 h, after which the reaction rate slowed and the system approached equilibrium. The common linear extrapolation for estimating the full mineralisation potential can be misleading, as it

neglects the multi-step dissolution process, starting with Ca-(hydr)oxide and followed by kinetically controlled reactions.

Keywords: accelerated mineralisation, alkaline waste valorisation, pH-driven precipitation, slag mineralogy, calcium carbonate polymorph

1. Introduction

The accelerating rise in atmospheric carbon dioxide (CO₂) levels due to anthropogenic activities has prompted global efforts to develop hedging strategies for carbon dioxide removal (CDR) as a mitigation measure¹. Mineral carbonation has become a promising long-term approach for CO₂ sequestration by converting the CO₂ into stable solid phases^{2,3}. The core of mineral carbonation is the formation of insoluble carbonate minerals from CO₂ with alkali and/or alkaline-earth metal-bearing minerals, such as calcium (Ca²⁺) and magnesium (Mg²⁺). Mineral carbonation can proceed through three methods: (i) direct gas-solid carbonation, where CO₂ gas directly reacts with minerals, (ii) direct aqueous carbonation, a single-step multiphase process in which CO₂ gas, water, and minerals react simultaneously, and (iii) indirect aqueous carbonation, a two-phase process in which cations are first extracted from minerals using acids or other solvents, and the resulting metal-rich solution reacts with CO₂ or carbonate-bearing solutions to form carbonate minerals.

Industrial byproducts containing oxide and hydroxide phases are prime candidates for such carbonation reactions^{4,5}. The carbonation of these materials through direct aqueous carbonation typically begins with a hydration process, where oxides react with water to form hydroxides:

44 **Equation 1** $\text{XO}_{(s)} + \text{H}_2\text{O} \rightarrow \text{X(OH)}_{2(aq)}$

45 where “X” denotes the divalent cations such as Ca^{2+} and Mg^{2+} . The hydroxides,
46 whether formed in situ from oxides (**Equation 1**) or initially present in the material
47 (such as portlandite), then react with dissolved inorganic carbon and precipitate as
48 stable carbonate minerals (**Equation 2**), although the presence of bicarbonate may
49 cause partial retention in the aqueous phase (**Equation 3**).

50 **Equation 2** $\text{X(OH)}_{2(aq)} + \text{CO}_3^{2-}_{(aq)} \rightarrow \text{X(CO)}_3(aq) + \text{H}_2\text{O} \rightarrow \text{X(CO)}_{3(s)}$

51 **Equation 3** $\text{X(OH)}_{2(aq)} + \text{HCO}_3^{-}_{(aq)} \rightarrow \text{X(HCO}_3)_2(aq) + \text{H}_2\text{O}$

52 Mineral carbonation using these materials will harness the natural thermodynamic
53 stability of carbonates, providing long-term and reliable storage^{6,7}. Despite the growing
54 interest, several fundamental aspects of mineral carbonation using alkaline synthetic
55 materials remain poorly considered. Previous studies have examined the performance
56 of CO_2 sequestration by these materials, such as CO_2 uptake per mass of the material
57 and the degree of carbonation achieved, which are further affected by physical
58 parameters such as the solid-to-liquid (S/L) ratio, temperature, pressure, and stirring
59 intensity^{6,8-13}. However, the reaction mechanism, rate-limiting steps, and mechanistic
60 interactions among the parameters have not been thoroughly studied¹⁴, particularly
61 concerning the mechanistic behaviour of carbonation under ambient pressure and
62 temperature.

63 One abundant synthetic-alkaline feedstock derived from industrial byproducts is steel
64 slag¹⁵, which offers significant potential for CDR via direct aqueous carbonation. Rate-

controlling factors and the impact of aqueous chemistry on steel slag carbonation remain underexplored, particularly under ambient pressure and temperature, limiting the predictive understanding of its reaction kinetics. Therefore, this study aims to examine the carbonation mechanism of steel slag, focusing on phase evolution and reaction kinetics at ambient temperature and elevated CO₂ exposure at 1 atm, through mechanical mixing, CO₂-enriched air bubbling, and a low S/L in a slurry setup to accelerate the reaction rate. Additionally, the alteration in mineral composition was evaluated.

Understanding the reaction kinetics and transformation pathways of steel slag during carbonation is essential for improving its efficiency and suitability for CO₂ sequestration. In particular, the degradation of reactive phases and their conversion into stable carbonate products determine both the performance and long-term stability of the material as a solid-phase CO₂ sink¹⁶. By combining mechanistic insights with performance metrics, e.g. CO₂ sequestration efficiency and uptake, this study deepens our understanding of slag carbonation and promotes the valorisation of alkaline industrial byproducts, such as steel slag, in engineered mineral carbonation systems for scalable CDR.

2. Methods

2.1. Experimental Design and Setup

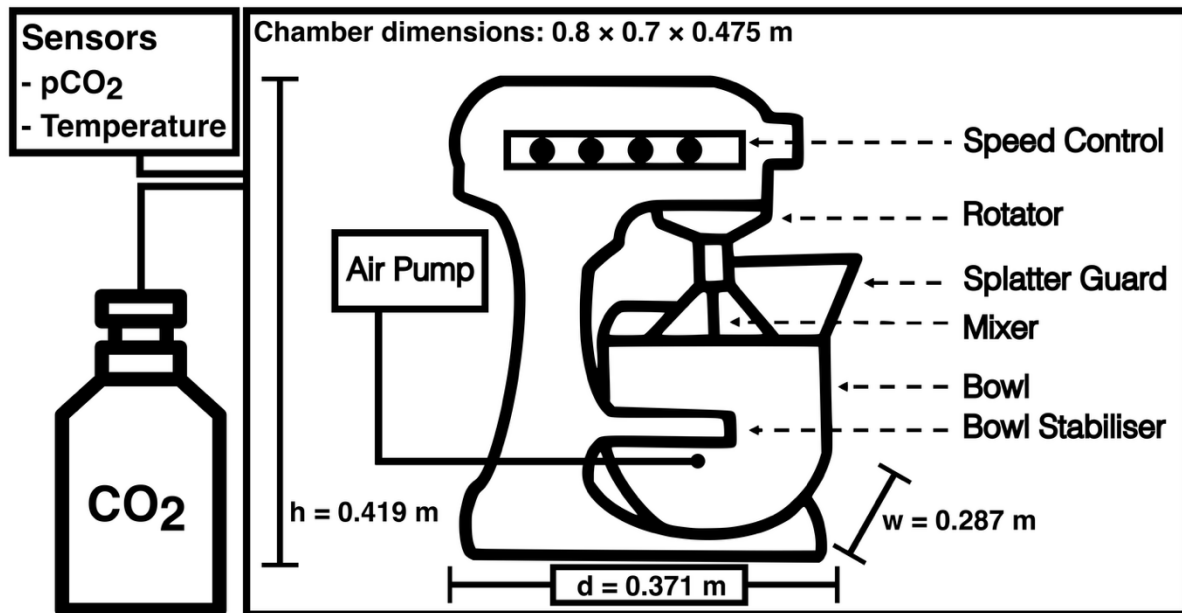


Figure 1 Schematic of the experimental setup: a modified KitchenAid in a sealed chamber with sensors continuously monitoring pCO₂ and temperature. An air pump connected to the bottom of the bowl optimised gas circulation and agitation into the mixture.

The experimental setup was based on the KitchenAid machine (Heavy Duty-5KSM7591X, USA), modified for direct aqueous carbonation through mechanical mixing and CO₂-enriched air bubbling (**Figure 1**). The mixing bowl was equipped with two gas inlet ports connected to an air pump (Fedour 10W–1200 L/h, China), circulating the CO₂-enriched air within the chamber to the mixture, allowing continuous CO₂ bubbling and enhancing gas-liquid transfer. The initial pCO₂ in the chamber was set at 25% ± 1.5% and monitored continuously with gas sampling and multi-sensors (GasLab Pro, USA). The splatter guard entirely covered the bowl, reducing splashes

while maintaining vent holes to prevent overpressure during bubbling. A flat beater was used for continuous mixing at 90 RPM. The rotor voltage was monitored to ensure the rotational speed (RPM) remained consistent throughout the experiments.

Ultrapure water (MQ, 18.2 M Ω) and natural seawater (NSW; from the North Sea, German Bight, 54.93 °N 6.43 °E; practical salinity $\approx$ 35.02, PSS-78 scale, TA_{initial} = 2310.57 $\pm$ 1.93 μ mol kg⁻¹) were utilised as two distinct aqueous media. The natural seawater was filtered through a 0.2 μ m Whatman Polycap AS 36 encapsulated filter (Cytiva, USA) to remove suspended particulates, ensuring a controlled and reproducible aqueous medium. The use of different aqueous media facilitated a comparative evaluation of carbonate formation and CO₂ sequestration from steel slag carbonation among various water chemistries. The S/L ratio of 1:3 was consistent across all setups, with a fixed mass of 3 kg of liquid and no liquid replenishment during the experimental run, to simulate an operating system with a low water footprint.

Each experimental run was conducted over a period of 24 h. Two technical replicates were performed for each run using two methods: (1) discrete runs without intermediate sampling (e.g., 0-1, 0-4, 0-12, 0-24 h), and (2) a continuous run sampled at multiple time points over 24 h (e.g., 1, 4, 12, and 24 h). An additional sampling point at 8 h was included in the ultrapure water setup based on preliminary observations, to provide intermediate measurements between 4 h and 12 h.

Liquid-phase sampling was performed at the designated sampling time points throughout the experiment. The samples for hydrochemical analyses were collected using a pre-cleaned syringe (50 mL BD Plastipak, Spain) and filtered through 0.45 μ m polyether sulfone (PES) filters (Sartorius, Germany). The filtered samples were stored

in pre-cleaned polypropylene (PP) bottles (Kautex, Germany). Total alkalinity (TA) and physicochemical parameters (temperature, electrical conductivity, and pH) were measured immediately after the sampling procedure. For cation analysis, samples were acidified with 1 M HNO₃ (Suprapur 1.00441, Merck, Germany) until the pH reached ~2 and stored at 4 °C until further analysis.

Solid-phase sampling was exclusively conducted at the termination of each run. The settled solids were transferred into a pre-cleaned high-density polyethylene (HDPE) bottle (Kautex, Germany) after carefully decanting the supernatant. The samples were dried at a low temperature (≤ 40 °C) for at least 24 h to prevent mineral alteration. The dried sample was first divided into ten equal subsamples (~100 g each). Each subsample was then subjected to quartering and coning to obtain representative subsamples for subsequent solid-phase analyses¹⁷.

2.2. Slag Characterisation of Steel Slag

Steel slag produced from basic oxygen furnace (BOF) steelmaking was obtained from ThyssenKrupp (Germany). **Table 1** and **Table 2** present the mineralogical, chemical, and physical characterisation of the used steel slag. The specific surface area (SSA) was measured using the Brunauer-Emmett-Teller (BET) method with five-point determination and nitrogen (N₂) adsorption isotherms at 77 K (Quantachrome Autosorb iQ, USA), with at least three replicate measurements per sample to ensure reproducibility. A certified α -alumina powder (BAM-PM-102 – DIN ISO 9277, Germany) was used as a reference material to ensure measurement accuracy. The grain size distribution was measured using a laser particle size analyser (Symphatec

HELOS/KF Magic, Germany). An in-house grain size standard was used to ensure the reproducibility of the measurement.

The elemental composition of the steel slag was analysed using X-ray fluorescence spectroscopy (XRF) equipped with a Rh-tube (Panalytical Magix Pro), with detection limits <0.02 wt% for major elements and <0.01 wt% for others. Loss on ignition (LOI) was also conducted by heating the materials at ± 1050 °C for an hour¹⁸. Mineral phase identification was analysed using X-ray diffraction (XRD Bruker D8 Advance, XE-T detector, Cu-K α radiation). Microstructural features of the steel slag were examined using scanning electron microscopy coupled with energy-dispersive X-ray spectroscopy (SEM-EDX, HITACHI TM4000Plus).

Table 1 Chemical and physical characterisation of the steel slag

Material		Steel Slag
Type		BOF Slag
Source		ThyssenKrupp, DE
Carbonation Potential [kg CO₂ · t⁻¹ slag]		375 ± 7.5
Maximum Carbonation Potential Derived from Ca-(hydr)oxide minerals [kg CO₂ · t⁻¹ slag]		95
Specific Surface Area [m²·g⁻¹]		10.271 ± 0.339
Initial PIC [C %]		1.18 ± 0.26
Grain Size Distribution (µm)	D₁₀	78.6 ± 10.8
	D₅₀	357.8 ± 46.2
	D₉₀	1264.4 ± 98.3
Major Elemental Compositions (%)	SiO₂	11.26 ± 0.01
	TiO₂	0.52 ± 0.04
	Al₂O₃	3.21 ± 0.65

	Fe₂O₃	22.69 ± 3.89
	MnO	1.46 ± 0.05
	MgO	4.7 ± 0.25
	CaO	41.95 ± 0.63
	Na₂O	Below detection limit
	K₂O	Below detection limit
	P₂O₅	1.32 ± 0.01
	SO₃	0.1 ± 0.03
	LOI	12.59 ± 4.55

153 Note: The maximum carbonation potential derived from and Ca-(hydr)oxides, based
154 on the upper-bound fractions determined by XRD.

155 **Table 2** Mineralogical characterisation of the steel slag

Mineral Phase		Fraction [%]
Silicates	Beta C2S (Larnite)	4.3 ± 1.8
	Alpha C2S	1.8 ± 0.6
	Ellestadite/Apatite	0.8 ± 0.2
	Hydrogarnet	4.1 ± 0.8
	Melilite group	1.0 ± 0.2
	Wollastonite	1.6 ± 1.2
Carbonates	Calcite	7.6 ± 3.3
	Aragonite	1.4 ± 0.1
	Vaterite	1.9 ± 1.2
Oxides/Hydroxides	Spinel-type minerals	0.9 ± 0.3
	Wuestite	2.0 ± 0.6
	Nordstrandite	1.6 ± 0.7
	Lime	0.6 ± 0.5
	Portlandite	8.2 ± 4.7
	Periclase	0.8 ± 0.2
	Afm	0.7 ± 0.3

	Srebrodolskite	7.4 ± 1.7
	Mayenite	1.9 ± 0.3
Others	Amorphous	53.2 ± 2.5

Note: Amorphous content was estimated from residual background in Rietveld refinement, representing poorly crystalline or non-crystalline phases.

2.3. Hydrochemical Analysis

Physicochemical properties were measured using a digital multimeter (WTW MultiLine® 3630 IDS, Xylem, Germany) equipped with a conductivity cell (TetraCon 925) and a pH electrode (SenTix 940). Electrical conductivity (EC) was temperature-corrected to 25 °C using the instrument's internal non-linear correlation function. All probes were calibrated using certified standards: one single-point conductivity standard (PTB/NIST, 0.01 mol. L⁻¹ KCl, 1413 µS cm⁻¹ at 25 °C, Xylem) and four buffer standards for pH electrode (4.006, 6.865, 9.180, and 12.454; DIN/NIST, Xylem). The temperature of the liquid samples was recorded concurrently during pH measurements.

Total Alkalinity (TA) was determined by automated titration (Metrohm Titrando 888, Switzerland) with 0.02 M or 0.2 M hydrochloric acid (HCl), depending on the expected TA, using EC as a proxy. TA was calculated via Gran titration with four pH endpoints (4.5, 4.3, 4.0, 3.7), following Handbuch Forstliche Analytik¹⁹ and established protocols^{20,21}. TA calibration was performed using certified reference materials (CRM batches 190; Andrew Dickson, Scripps Institution of Oceanography, USA) and an internal North Sea standard. The major cations (Na, K, Ca, Mg) were determined using ICP-OES (Thermo Scientific iCAP 6500 dual view, USA) and the major anions (F⁻, Cl⁻, NO₂⁻, NO₃⁻, and SO₄²⁻) were determined using Ion Chromatography (IC; Metrohm

881 Compact IC Pro system, Switzerland). The calibration was conducted using an internal standard (IC; Carl Roth, Germany) and ISO 17304-certified single- and multi-element stock solutions (ICP-OES; Inorganic Ventures, New Jersey, USA).

2.4. Carbon sequestration potential

The CO₂ sequestration potential via the carbonation pathway (C_{pot}) was estimated via the elemental composition of the steel slag (**Table 1**). The C_{pot} in **Equation 4** only consider Ca²⁺ and Mg²⁺ for the complete carbonation due to the solubility and kinetics considerations for the carbonation process^{22,23}, whereas the alkali metals, e.g., Na⁺ and K⁺, are excluded due to their high solubility. The inclusion of sulphur and phosphorus fractions in **Equation 4** account for their potential roles as reducing agents, either bound to cations or acting as acidic species that influence the carbonate system¹⁵. The coefficients reflect the dominant charge of each species in the pH range 6 to 12 ($\alpha = 2$ for Ca²⁺, $\beta = 2$ for Mg²⁺, $\gamma = -2$ for SO₄²⁻, and $\delta = -3$ for PO₄³⁻), set conservatively from speciation diagrams in **Supplementary 1**. The ω denotes a conversion factor for the CO₂ sequestered²⁴. In this study, $\omega = 0.5$ was chosen to represent the stoichiometric balance typical of the carbonation pathway.

Equation 4
$$C_{\text{pot}} = \frac{M_{\text{CO}_2}}{100} \left(\alpha \frac{\text{CaO}}{M_{\text{CaO}}} + \beta \frac{\text{MgO}}{M_{\text{MgO}}} + \gamma \frac{\text{SO}_3}{M_{\text{SO}_3}} + \delta \frac{\text{P}_2\text{O}_5}{M_{\text{P}_2\text{O}_5}} \right) \cdot 10^3 \cdot \omega$$

2.5. Aqueous phase: CO₂ sequestration

CO₂ sequestration in the aqueous phase was determined from carbonate alkalinity (A_c), which was calculated from TA by subtracting the fraction of OH⁻, H⁺, and minor contributors (**Equation 5** and **Equation 6**).

198 **Equation 5** $TA = HCO_3^- + 2CO_3^{2-} + OH^- - H^+ \pm \text{minor contributors}$

199 **Equation 6** $A_c = HCO_3^- + 2CO_3^{2-}$

200 The speciation was determined using PHREEQC (v3.7.3; llnl.dat) for the ultrapure
201 water setup, with pH, temperature, TA, and ionic composition as input parameters,
202 and seacarb (v3.3.3) with TA, pH, temperature, and salinity as input parameters for
203 the seawater setup. The A_c concentration (c_{Ac} , in mol kg^{-1}) was multiplied by the mass
204 of the water (m_{water} , in kg) to obtain the alkalinity production (A_{produced} , in mol)
205 (**Equation 7**). The corresponding CO_2 mass (g) sequestered in the aqueous phase
206 was then calculated by multiplying A_{produced} by the molar mass of CO_2 (44.01 g mol^{-1})
207 (**Equation 8**).

208 **Equation 7** $A_{\text{produced}} = c_{Ac} \times m_{\text{water}}$

209 **Equation 8** $m_{\text{CO}_2} = A_{\text{produced}} \times M_{\text{CO}_2}$

210 **2.6. Gas Phase: CO_2 sequestration rate (R) and efficiency (η)**

211 The CO_2 sequestration rate (R, in g h^{-1}) was calculated by quantifying the mass of CO_2
212 (m_{CO_2} , in g) sequestered during the reaction time (t, in h).

213 **Equation 9** $R_{\text{CO}_2} = \frac{m_{\text{CO}_2(0)} - m_{\text{CO}_2(t)}}{t}$

214 The mass of CO_2 in the experimental chamber at a given point in time was estimated
215 using the ideal gas law:

216 **Equation 10** $m_{\text{CO}_2} = \frac{P_{\text{CO}_2} \times V}{R \times T} \times M_{\text{CO}_2}$

217 where P_{CO_2} is the partial pressure of CO_2 (in Pa), V is the volume of the chamber (in
 218 m^3), R is the universal gas constant ($8.314 \text{ J mol}^{-1} \text{ K}^{-1}$), T is the absolute temperature
 219 (in Kelvin), and M_{CO_2} is the molar mass of CO_2 (44.01 g mol^{-1}).

220 The sequestration efficiency metric was calculated to directly reflect the degree of CO_2
 221 removal attributed to mineral carbonation processes. The quantification of CO_2
 222 sequestration efficiency (η , in %) was based on the relative change in $p\text{CO}_2$ over a
 223 specific observation time. It is defined as:

224 **Equation 11** $\eta_{\text{CO}_2} (\%) = \frac{p\text{CO}_{2(o)} - p\text{CO}_{2(t)}}{p\text{CO}_{2(o)}} \times 100$

225 where $p\text{CO}_{2(o)}$ and $p\text{CO}_{2(t)}$ represent the initial and time-dependent partial pressure of
 226 CO_2 , respectively (here in %). Baseline measurements were conducted to validate the
 227 calculations by performing the experiment without slag in the chamber. No detectable
 228 CO_2 gradients were observed across multiple sampling points within the experimental
 229 chamber. The CO_2 loss was negligible and remained within the instrument's margin of
 230 error over 24 h (system stability = $98.63\% \pm 0.39\%$).

231 **2.7. Solid Phase: Particulate Inorganic Carbon**

232 The quantification of CO_2 sequestered in the solid phase was determined by
 233 particulate inorganic carbon (PIC) measurements, representing the formation of
 234 carbonate minerals during carbonation. First, the change in PIC (ΔPIC) over the
 235 experimental time was calculated:

Equation 12 $\Delta\text{PIC} = \text{PIC}_t - \text{PIC}_0$

The initial PIC content from the fresh slag (PIC_0) and PIC content after the specific reaction time (PIC_t) were measured using an elemental analyser (EA, Euro Vector EA-3000), reported as weight per cent of carbon (C wt%) with an analytical precision of 0.05% and ≥ 10 aliquots per sample. The measured change in PIC was then used to calculate the mass of CO_2 sequestered in the solid phase (m_{CO_2} as solid, in g):

Equation 13 $m_{\text{CO}_2} = \Delta\text{PIC} \times m_{\text{bulk}} \times \frac{M_{\text{CO}_2}}{M_{\text{C}}}$

where m_{bulk} is the mass of the slag (in g), M_{CO_2} and M_{C} are the molar mass of CO_2 (44.01 g mol⁻¹) and C (12.011 g mol⁻¹), respectively.

3. Results

3.1. Gas: CO_2 capture efficiency (η) and sequestration rate (RCO_2)

The CO_2 capture efficiency (η) from the ultrapure water setup reached approximately 90% within 24 h, while the natural seawater setup reached 60-80% over the same period (**Figure 2**). The reaction proceeded rapidly in the early stages across all setups. CO_2 sequestration rates were highest during the first hour, at 33.1 ± 1.6 and 33.2 ± 2.8 g CO_2 h⁻¹ for ultrapure water and seawater, respectively, and decreased progressively over 24 h to 4.4 ± 0.1 and 3.4 ± 0.2 g CO_2 h⁻¹ (**Supplementary Materials 2**). η peaked around 8 h in ultrapure water and 12 h in seawater, marked by a sharp decline in pCO_2 . CO_2 uptake subsequently levelled off at pCO_2 levels of 3.1 ± 0.5 % for ultrapure water and 10.5 ± 2.6 % for seawater as the reaction rate slowed, indicating a shift to a rate-limited phase.

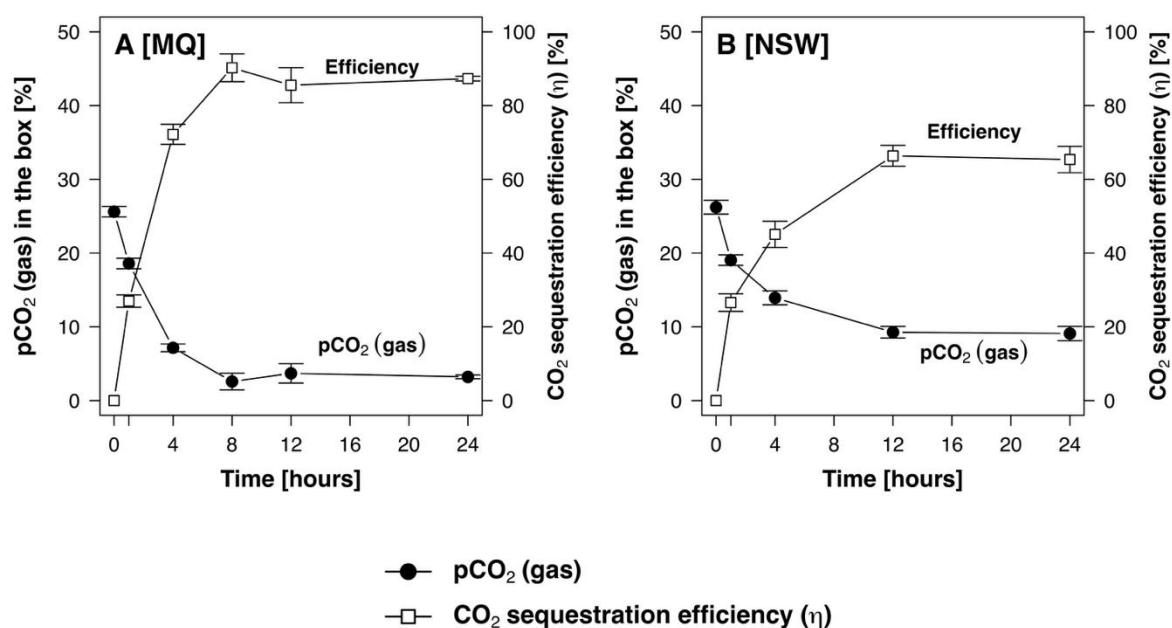


Figure 2 Time series of pCO₂ levels (in %) and CO₂ sequestration efficiency (η, in %) in (A) ultrapure water and (B) natural seawater setups. Error bars represent the standard deviation from two technical replicates and three analytical measurements at each sampling point.

3.2. Solid: Particulate Inorganic Carbon (PIC) and Carbonation Efficiency

The observed decline in pCO₂ levels from the gas data (**Section 3.1**) is corroborated by the corresponding increase in PIC across all setups, confirming adequate carbonation that sequestered CO_{2(g)} into the solid phase (**Figure 3A-B, Supplementary Material 3**). The ultrapure water setup showed a higher absolute increase in PIC, with an increase of 3.1 ± 0.6 percentage points, compared to a 2.3 ± 0.1 percentage points increase observed in seawater. These increases resulted

270 in a bulk carbonate fraction of approximately 30-40 wt% of the carbonated slag after
271 24 h.

272 The maximum carbonation potential of the slag was estimated at 375 kg CO₂ t⁻¹ of
273 slag, with Ca-(hydr)oxide species contributing 95 kg CO₂ t⁻¹ (**Table 1**; **Table 2**). The
274 net CO₂ uptake reached 105 ± 5 kg CO₂ t⁻¹ for ultrapure water, slightly exceeding the
275 theoretical hydroxide carbonation potential of the slag, and 78 ± 4 kg CO₂ t⁻¹ for
276 seawater. Consistent with gas-phase observations, the carbonation kinetics were
277 initially rapid, with near-maximal conversion by 8 h in ultrapure water and 12 h in
278 seawater, after which the rates substantially decreased (**Figure 3C-D**). This indicates
279 the onset of rate-limited kinetics and phases, potentially reflecting the depletion of
280 reactive species and reduced carbonate precipitation rates.

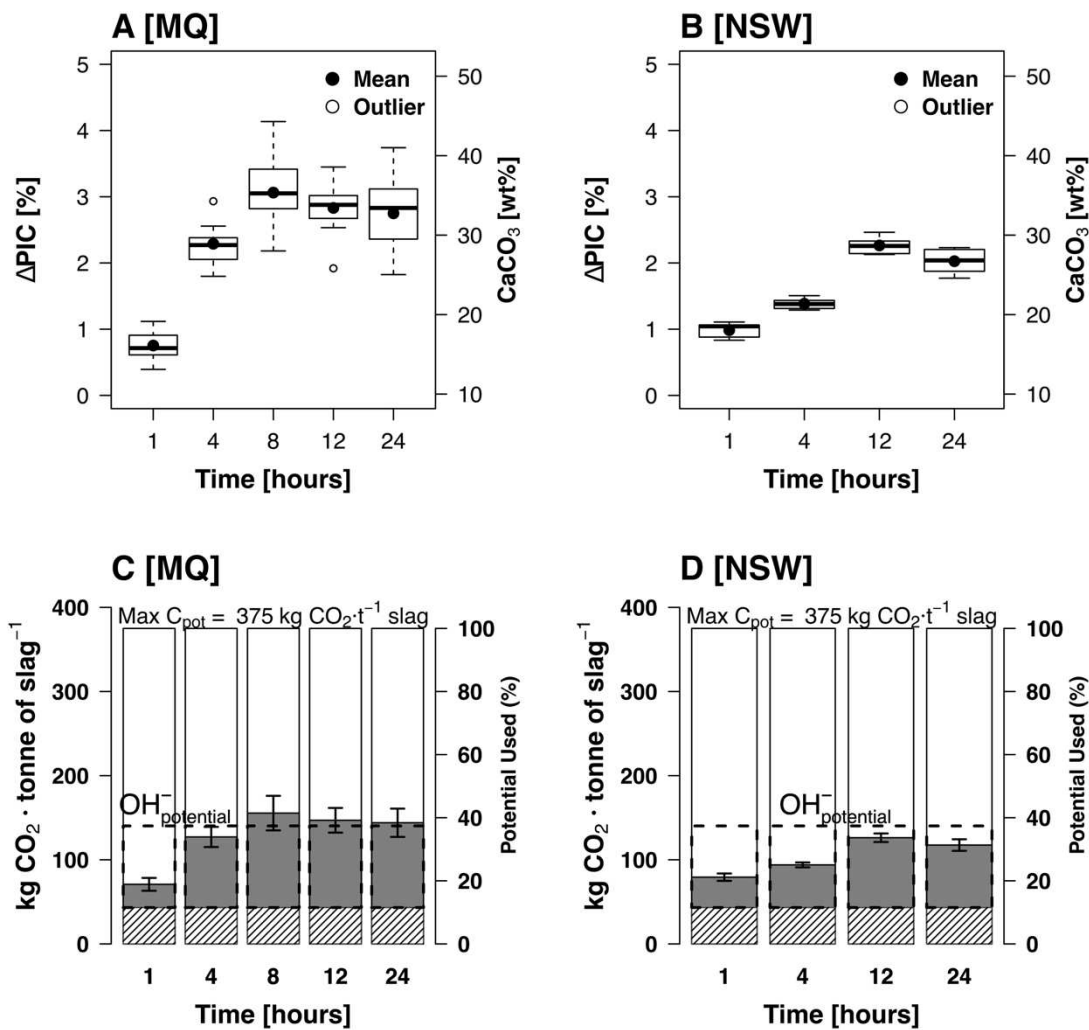


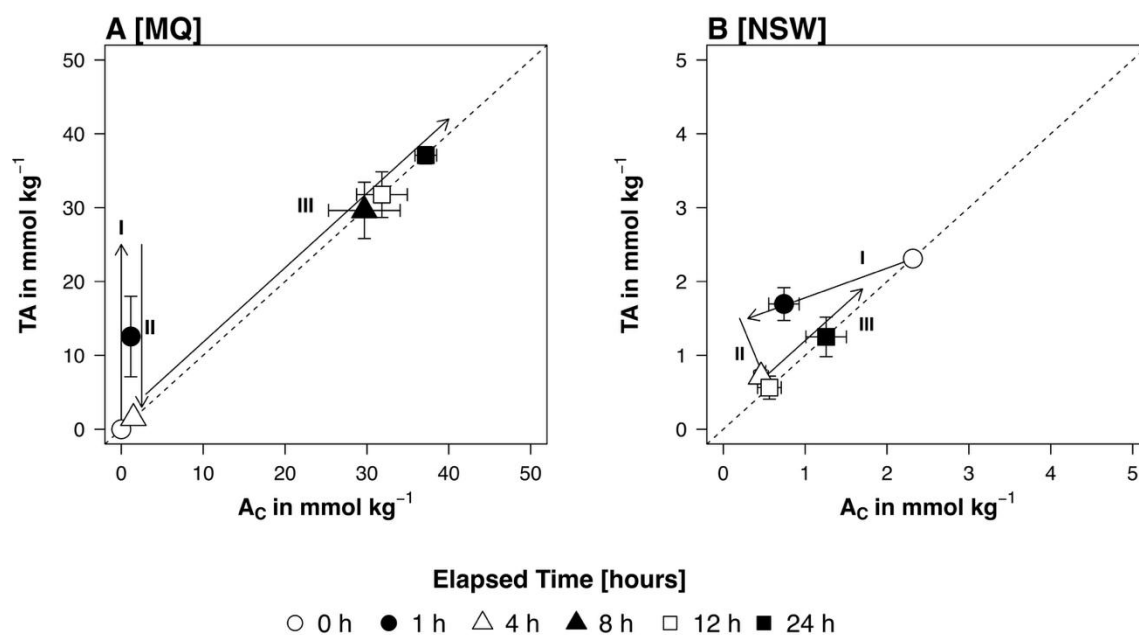
Figure 3 Changes in particulate inorganic carbon (ΔPIC) and CaCO_3 fraction in the bulk solid over time (A-B), and corresponding carbonation potential, solid-phase CO_2 sequestration, and proportion of potential used (C-D). “MQ” indicates the ultrapure water setup and “NSW” indicates the natural seawater setup. Error bars represent the standard deviation from replicate PIC measurements ($n \geq 10$). The diagonally hatched segment at the base of each bar represents the initial PIC present in the steel slag. The dashed outline bar marks the maximum carbonation potential from Ca-(hydr)oxides ($95 \text{ kg CO}_2 \text{ t}^{-1} \text{ slag}$).

3.3. Hydrochemical: Total Alkalinity, Carbonate Speciation, and Major Ions

Hydrochemical analyses revealed distinct TA and A_c evolution trajectories across experimental setups, reflecting divergent carbonation pathways governed by aqueous chemistry. In the low ionic strength matrix represented by the ultrapure water, TA surged to $12.5 \pm 5.4 \text{ mmol kg}^{-1}$ within the first hour, while A_c remained low at $1.2 \pm 0.1 \text{ mmol kg}^{-1}$ (**Figure 4A, Arrow I**). This surge coincided with an increase in pH from 4.30 ± 0.13 (initial ultrapure water at the elevated $p\text{CO}_2$) to 12.02 ± 0.16 , and hydroxide comprised over 90% of the TA fraction (**Figure 5**). A substantial TA decline was observed within 4 h (**Figure 4A, Arrow II**), decreasing by 88% to $1.5 \pm 0.2 \text{ mmol kg}^{-1}$, accompanied by a decrease in pH and the hydroxide fraction (**Figure 5A**). As the system evolved, TA and A_c increased and converged along the 1:1 line (**Figure 4A, Arrow III**) with pH around 7.25 ± 0.28 , indicating a shift toward carbonate-dominated alkalinity, particularly HCO_3^- . In the high ionic strength matrix represented by the natural seawater, TA and A_c decreased within the first hour by 27% and 68%, respectively (**Figure 4B, Arrow I**), causing TA to deviate from A_c . pH increased from 5.59 ± 0.14 (initial natural seawater at elevated $p\text{CO}_2$) to 10.94 ± 0.14 (**Figure 5B**). Subsequently, TA returned toward A_c (**Figure 4B, Arrow II**), accompanied by a decrease in pH, eventually aligning closely with the 1:1 trajectory (**Figure 4B, Arrow III**).

The cation fraction from the ultrapure water setup was dominated by divalent species, with Ca^{2+} accounting for 87% of total cations within the first 4 h (**Figure 6A**). Mg^{2+} progressively increased thereafter, shifting the $\text{Ca}^{2+}:\text{Mg}^{2+}$ ratio to 1:2.5 by 24 h. In the natural seawater setup, divalent cations changed from initial Mg^{2+} dominance to Ca^{2+}

314 (Figure 6B). The $\text{Ca}^{2+}:\text{Mg}^{2+}$ molar ratio shifted from 1:5.2 to over 25:1 by the end of
 315 the experiment. Mg^{2+} dropped from 17% of total cations to less than 1% ($<1.8 \text{ mmol}$
 316 L^{-1}), while Ca^{2+} rose to $\sim 17.4 \pm 0.4\%$ of total cations ($48.64 \pm 2.61 \text{ mmol L}^{-1}$) within 4
 317 h and then stabilised.



318
 319 **Figure 4** Partitioning of total alkalinity (TA) into carbonate alkalinity (A_c) from (A)
 320 ultrapure water (MQ) and (B) natural seawater (NSW) setup. Both TA and A_c are
 321 reported in mmol kg^{-1} . Arrows labelled with Roman numerals indicate the chronological
 322 measurement points, showing how alkalinity speciation changed during the reaction
 323 time. Error bars (both horizontal and vertical) represent the standard deviation from
 324 analytical and technical replicates.

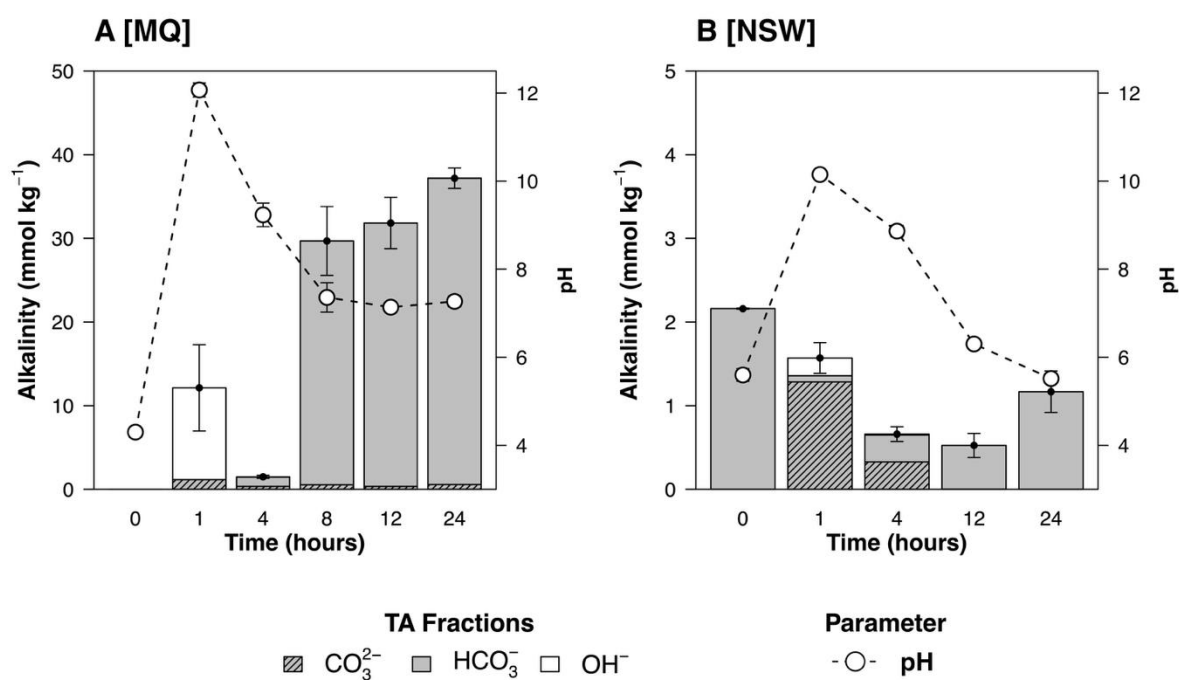


Figure 5 Shifts in total alkalinity (TA) speciation and pH over time. Bars represent the fractional contribution of OH⁻, HCO₃⁻, and CO₃²⁻ to TA (in mmol kg⁻¹), shown across time points for (A) ultrapure water (MQ) setup and (B) natural seawater (NSW). The dashed line shows pH levels. Error bars represent the standard deviation from analytical and technical replicates.

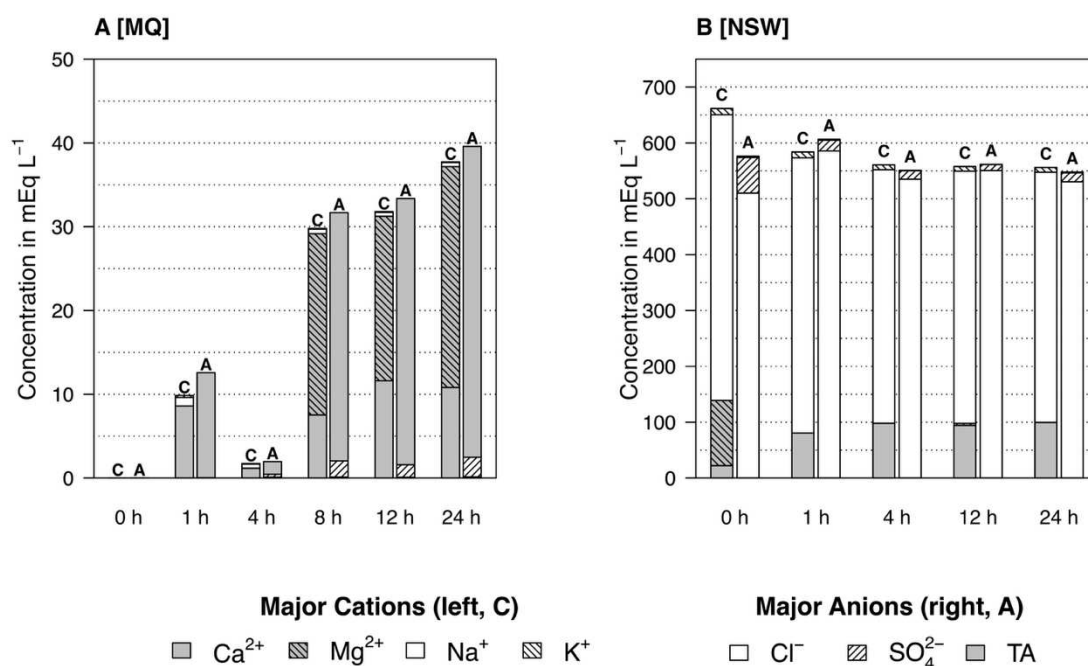


Figure 6 Concentrations of major cations and anions in (A) ultrapure water (MQ) and (B) natural seawater (NSW) setups in milliequivalents (mEq L⁻¹; molarity × ion charge). “C” denotes cations and “A” denotes anions. The charge balance error (CBE) remains below 10%.

4. Discussion

The experiments reveal that carbonation of alkaline synthetic materials, such as slag, occurred rapidly in the first phase, but the finite availability of oxide-hydroxide minerals constrained this rate. The carbonation levelled off once the fraction of oxide-hydroxide minerals had been transformed into carbonate polymorph minerals, as reflected by the increase in PIC in the bulk (**Figure 3**). Data from the experiments demonstrate that the first carbonation phase was characterised by the high solubility and reactivity of oxide-hydroxide minerals, defined here as the slaking stage. This phase was driven by the hydration of lime (CaO), which produced slaked lime (Ca(OH)₂)²⁵, and simultaneously by the dissolution of slaked lime and preexisting hydroxide minerals in the slag, such as portlandite⁶. The dissolution released a large amount of hydroxide, resulting in high initial TA that promoted rapid carbonation. However, it was observed that the magnitude of TA produced was heavily influenced by the composition of the aqueous matrix, reflecting distinct carbonation trajectories driven and impacted by the aqueous matrix.

In a low ionic strength matrix (ultrapure water), Ca²⁺ and OH⁻ released from the slag increased without competition from preexisting ions, raising TA up to 12.5 ± 5.4 mmol kg⁻¹, before full carbonation occurred. In contrast, the TA was much more constrained in the high ionic strength matrix (natural seawater), where TA even dropped to 1.7 ±

0.2 mmol kg⁻¹ and shifted into the hydroxide-dominated fraction (**Figure 4B, Arrow 1**). This contrasting trajectory aligns with the observation that Ca(OH)₂ dissolves more quickly at low salinity²⁶, highlighting the influence of the aqueous matrix on controlling reaction kinetics. In the context of CDR applications, mineral carbonation in reactors using high ionic strength matrices, particularly seawater, may limit CO₂ uptake and require longer reaction times to achieve comparable performance to the low ionic strength matrices.

Thermodynamically, carbonation of slaked lime ($\Delta H^\circ \approx -93.54 \pm 1.99$ kJ mol⁻¹) is more favourable than the slaking of lime ($\Delta H^\circ \approx -65.17 \pm 1.57$ kJ mol⁻¹)^{27,28}. However, it was observed that the carbonation was controlled by kinetics rather than thermodynamics, as shown by the continued dominance of the hydroxide fraction in the TA (**Figure 5**). The diffusion of CO₂ into the mixture seems to be the main kinetic barrier here, despite continuous agitation and the absence of CO₂ limitation. The rapid slaking reactions elevated TA concentration, particularly the hydroxide fraction. This slightly increased the viscosity of the mixture due to an increase in ion concentration, which reduced CO₂ solubility and hindered diffusion in the liquid phase (salting-out effect)²⁹. In contrast to solid-gas systems, such as CaO carbonation in fluidised beds, where once CO₂ supply is sufficient, the intrinsic reaction steps of carbonation and decarbonation become rate-limiting, particularly at low temperatures³⁰.

The completion of the slaking stage, indicated by the near-complete conversion of CaO and Ca(OH)₂, marked a shift in which carbonation became limited by slower processes. The depletion of CaO and Ca(OH)₂ triggered a cascade reaction that impeded carbonation: hydroxide ions (OH⁻) decreased, the pH fell, and carbonate speciation shifted, collectively hindering carbonation (**Figure 5**). The carbonate ions

(CO₃²⁻) dominated the A_c fraction during the slaking stage (~99%), while the hydroxide (OH⁻) fraction remained a major fraction of the TA. Once the slaking stage was nearly complete, the carbonate system shifted to a bicarbonate-dominated fraction (HCO₃⁻) as pH declined and gradually approached equilibrium state. This shift occurred approximately 4 h for both setups, associated with a deceleration of carbonation rate.

Ionic inhibitors may have further decelerated the carbonation rate following the slaking stage. Substantial concentrations of Mg²⁺, which notably inhibit CaCO₃ nucleation^{31,32}, seem to maintain Ca²⁺ and TA in the aqueous phase despite the thermodynamic conditions favouring precipitation, reflected by the positive value of saturation level (**Supplementary Material 4**). In the low ionic strength matrix (ultrapure water), Mg-bearing solid phases remained largely undissolved during the slaking stage, thereby enabling carbonation to progress rapidly without significant inhibitors. The dissolution started during the late slaking stage, releasing significant Mg²⁺ and coinciding with the slowdown in the carbonation rate. In the high ionic strength matrix (natural seawater), Mg²⁺ was depleted following slag addition, likely due to the precipitation of brucite once pH rose above 10.6 and oversaturation was reached during the slaking stage^{33,34}. Carbonation in natural seawater did not occur as rapidly as in the ultrapure water because the high initial Mg²⁺/Ca²⁺ ratio (~5) in the natural seawater might have diverted the pathway toward Mg-bearing carbonate phases, such as amorphous Mg-carbonates and/or Ca(Mg)CO₃ precursors^{35,36}. The incorporation or adsorption of Mg²⁺ onto growing carbonate nuclei then inhibited nucleation and crystal growth, acting as a rate-controlling step^{37,38}. Nevertheless, when Mg²⁺ concentrations were substantial in both setups, carbonation was likely inhibited because Mg²⁺ competed for adsorption sites at step edges and occupied key growth sites on the surface of the crystal,

affecting CaCO_3 nucleation and growth, consistent with thermodynamic predictions of Mg^{2+} -induced growth inhibition³⁹.

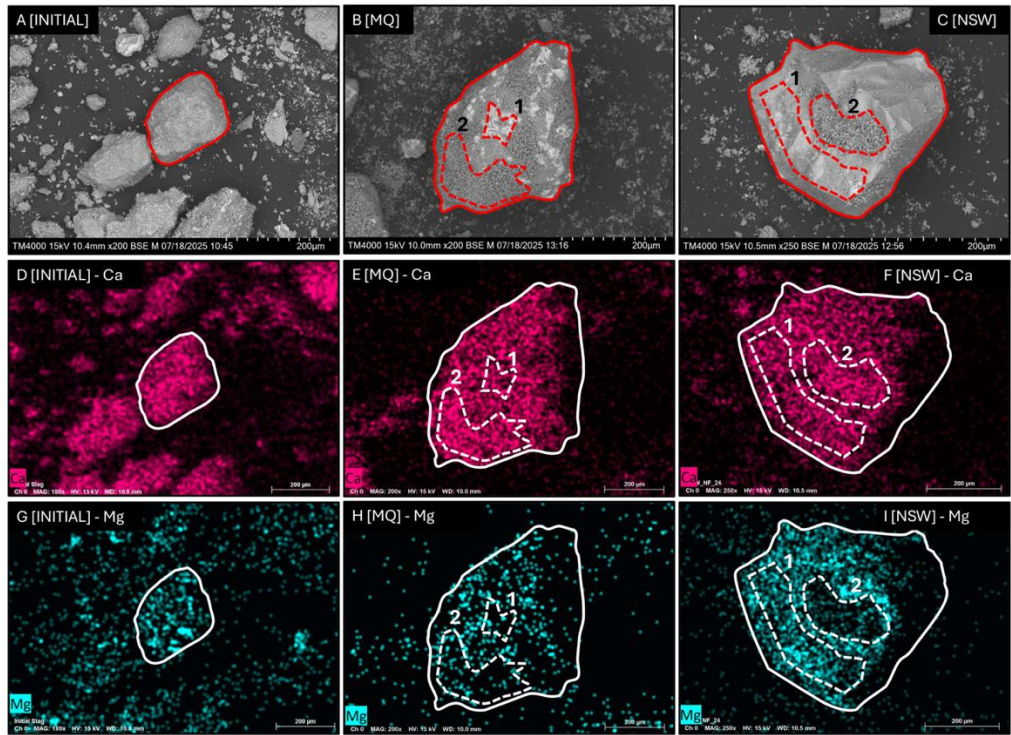


Figure 7 SEM-EDX mapping of Ca^{2+} (Panels D-F) and Mg^{2+} (Panels G-I) on grain surfaces at the microscale. MQ and NSW represent carbonated slag from ultrapure water and natural seawater setups, respectively, post-experiment (24 h). The bold line delineates the observed grain, whereas the dashed line delineates the region of interest (ROI). Region 1 corresponds to the bare site, and region 2 corresponds to the carbonate-rich site.

Table 3 Surface divalent elemental composition (Ca^{2+} and Mg^{2+}) of reference carbonate minerals, initial slag, and carbonated slag after 24 h from the experimental setups, expressed as atomic concentration [%], ratios, and molar fractions (X_{Ca} and X_{Mg}).

Spectrum	Atomic concentration [%]		Ca/Mg	X_{Ca}	X_{Mg}
	Ca	Mg			
Pure Minerals					
- CaCO_3	20	0	-	1	0

- CaMg(CO ₃) ₂	10	10	1	0.5	0.5
- MgCO ₃	0	20	0	0	1
Initial Slag	6.81 ± 0.27	0.56 ± 0.13	12.27 ± 3.57	0.92 ± 0.02	0.08 ± 0.02
Ultrapure Water Setup					
- Bare site	10.2 ± 0.80	0.59 ± 0.09	17.29 ± 1.85	0.95 ± 0.01	0.05 ± 0.01
- CaCO ₃ -rich site	10.04 ± 0.87	0.1 ± <0.01	98.9 ± 12.3	0.99 ± <0.01	0.01 ± <0.01
Natural Seawater					
- Bare site	4.86 ± 0.54	1.93 ± 0.25	2.52 ± 0.06	0.72 ± 0.01	0.28 ± 0.01
- CaCO ₃ -rich site	8.43 ± 0.75	2.13 ± 0.25	3.96 ± 0.16	0.80 ± 0.01	0.20 ± 0.01

416

417 Mineralogical analysis of the carbonated slags indicates that the aqueous matrix also
418 controlled the type of precipitated carbonate minerals. The distinction in the surface
419 composition between the matrices was apparent (**Figure 7 and Table 3**). The
420 carbonated slag derived from ultrapure water setups was primarily composed of
421 calcium-rich carbonates ($X_{Ca} \approx 0.95$ at bare sites and >0.99 at carbonate-rich sites).
422 This aligns with the limited involvement of Mg^{2+} during the carbonation phase. In
423 contrast, the carbonated slag from natural seawater setups was notably marked by
424 the inclusion of Mg^{2+} into the carbonate structure ($X_{Mg} \approx 0.28$ at bare sites and ≈ 0.2
425 at carbonate-rich sites). The high initial Mg^{2+} concentration in natural seawater
426 facilitated this inclusion into the carbonate structure, particularly during the carbonation
427 stage.

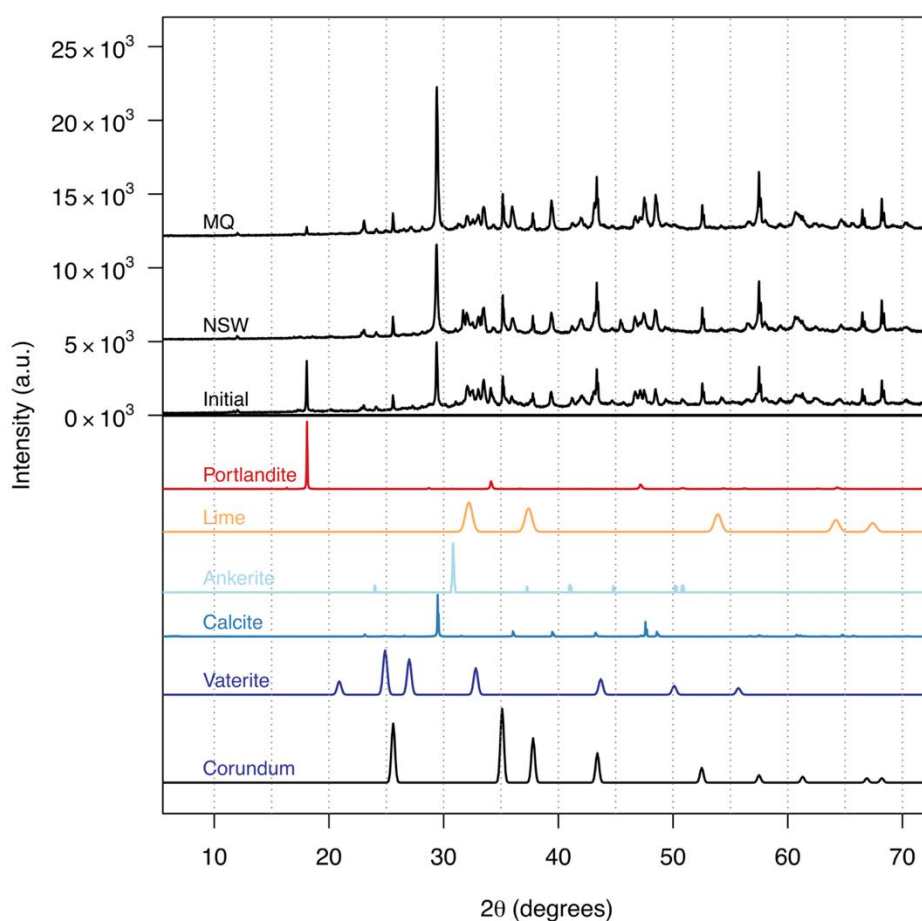


Figure 8 X-ray diffraction (XRD) patterns of the slags. Diffraction patterns are shown for the initial slag (pre-experiment) as well as for the post-experiment slag from the Milli-Q (MQ) and natural seawater (NSW) setups after 24 h. Reference patterns for portlandite, lime, ankerite, calcite, and vaterite are included for comparative purposes. The addition of corundum was carried out as an internal standard. For the quantitative values, see **Supplementary Materials 5**.

According to the diffractograms, calcite was the dominant form of carbonate polymorphs in the carbonated slag for both setups (**Figure 8**). Ankerite was also detected in the carbonated slag from both setups. Mg-bearing calcite and/or ankerite were most likely present, as indicated by the Mg atomic fraction in CaCO_3 -rich regions of the carbonated slag (**Table 3**). In natural seawater, these minerals likely formed during the slaking stage, whereas in ultrapure water it appeared later, when Mg-bearing phases began dissolving. The formation of these minerals could occur either

through direct primary precipitation or secondary transformation of CaCO_3 . The secondary transformation mechanism concurs with the prior observation that the transformation of the CaCO_3 structure into $\text{Ca}(\text{Mg})\text{CO}_3$ is facilitated by a sufficient presence of Mg^{2+} , postulated either through the diffusion into the CaCO_3 lattices (solid-state diffusion) or via Ca^{2+} replacement due to partial dissolution at the surface and subsequent rapid precipitation with Mg^{2+} incorporation into the structure (coupled dissolution-reprecipitation)⁴⁰. Vaterite was found exclusively in the ultrapure water setup. It most likely formed during the carbonation stage when Mg^{2+} was low or absent. No pronounced vaterite peaks were detected in the natural seawater setup. This finding aligns with the observation that ions like Mg^{2+} suppress metastable vaterite formation, instead forming a more stable polymorph such as calcite^{41,42}.

In addition to the crystalline carbonates observed in the carbonated slag, residual carbonate phases may also have been incorporated into the amorphous fraction. The fraction of non-crystalline phase was higher in the natural seawater setup, which had up to 20% more amorphous phase than the ultrapure water setup. This is because of the presence of Mg^{2+} during the slaking stage, which stabilises the amorphous calcium carbonate (ACC) and significantly retard its transformation into crystalline polymorphs⁴³. This may account for the slight discrepancy in carbonate content (%), with the elemental analyser reporting higher carbon fractions than XRD, which quantifies only the crystalline carbonate minerals (the amorphous fraction is inferred), although the values remain within analytical uncertainty (**Supplementary 5**).

In the context of carbon sequestration, rapid carbonation mainly occurred during the slaking stage, driven by reactions of Ca-(hydr)oxide phases that produced Ca-carbonate polymorphs. The substantial formation of crystalline Mg-carbonates was not

detected, indicating that the kinetics of Mg-carbonate phases are slow⁴⁴. Instead, Mg²⁺ was partly integrated into the CaCO₃ and the amorphous structure and/or remained in the aqueous phase. Therefore, it may be necessary to refine the assessment of mineral carbonation in slag or other alkaline materials, especially the effective or real carbonation capacity as previously discussed by Doucet⁴⁵. C_{pot} in **Equation 4** calculates the maximum CO₂ sequestration by assuming full utilisation of Ca²⁺ and Mg²⁺ to form solid carbonates. A more realistic estimation can be obtained by focusing on the reactive Ca-bearing phases, namely lime (free CaO) and portlandite (Ca(OH)₂), as indicated by their pronounced decrease in the carbonated slag (**Figure 8**). C_{eff} (**Equation 14**, in kg CO₂ t⁻¹ material) can be calculated from the weight fractions of free CaO and Ca(OH)₂ minerals (in %) and normalised by their molar masses (in g mol⁻¹) to determine the corresponding CO₂ sequestered, assuming that one mole of each mineral binds one mole of CO₂.

Equation 14
$$C_{\text{eff}} = \frac{M_{\text{CO}_2}}{100} \left(\frac{\text{free CaO}}{M_{\text{CaO}}} + \frac{\text{Ca(OH)}_2}{M_{\text{Ca(OH)}_2}} \right) \cdot 10^3$$

The C_{eff} of the used slag was 95 kg CO₂ t⁻¹, substantially lower than the theoretical C_{pot} of 375 kg CO₂ t⁻¹ (**Figure 3**). The proximity of C_{eff} to the carbonation achieved in this study implies that only a fraction of the reactive Ca-(hydro)oxide phases was converted under the experimental conditions. Moreover, C_{eff} provides a more realistic measure of the rapid and effective sequestration phase than C_{pot}. This distinction is critical for techno-economic models and assessments, which frequently extrapolate short-term carbonation rate (e.g., <24 h) linearly to C_{pot}. Here, the reaction rate levelled off once C_{eff} was reached, meaning that such extrapolations can substantially overstate sequestration efficiency and realistic slag utilisation, as further carbonation

beyond this point would require disproportionate time relative to the CO₂ gained and yield only marginal additional uptake.

In principle, maximum slag utilisation could be reached. The challenge lies in incomplete elemental extraction from minerals, which limits the carbonation rate from reaching the theoretical maximum capacity (C_{pot}). The remaining elements are bound within silicates, cement phases, or complex oxide phases, such as α -/ β -C₂S, hydrogarnet, or srebrodolskite (**Table 2**), constraining their reactivity⁴⁶. Further, maximising carbonation potential requires precipitating the dissolved cations, with Mg²⁺ posing a particular challenge due to its dual role as a potential carbonate-forming species and as an inhibitor of CaCO₃ nucleation. The precipitation of Mg-carbonates is complex and has been widely discussed^{47,48}. Intermediate precursors, notably hydromagnesite, control the formation of stable Mg-carbonate phases, such as magnesite. These phases require supersaturation with respect to these minerals, and elevated CO₂ pressures (>>3 bar) and temperatures (120 °C). Even under these conditions, Hänchen, et al.⁴⁷ argued that the precipitation kinetics remain slow for practical application in industrial mineral processing, particularly for carbonation.

Following the assessment of the mechanism and extent of mineral carbonation from this work, subsequent considerations are the prospective applications of mineral carbonation and the potential advantages that carbonated slag may confer for the sustainable management of this by-product. Apart from sequestering CO₂ in solid form, carbonated slag acquires added value through enhanced material properties that facilitate its sustainable reuse in environmental and engineering applications. Carbonated steel slag can be utilised in the production of bricks, supplementary cementitious materials, and aggregates, as carbonation enhances its stability and

mechanical performance¹⁶. The formation of CaCO_3 densifies the paste microstructure by filling pores and providing nucleation sites, thereby improving durability and strength^{49,50}. These enhancements improve compressive and flexural performance, providing additional co-benefits for sustainable concrete uses and enhancing the economic value of carbonated slag as a supplementary cementitious material.

Integration of a controlled reactor system coupled with industrial flue gas streams is one approach to use the existing excess CO_2 and heat streams. Flue gas in Europe typically contains 10-15% of CO_2 , and it can be higher in some industries, such as in biogas, cement, iron, and steel production, ranging from 15% to 45%^{51,52}. The temperature varies depending on the heat recovery stages, ranging from over 70 to 260 °C, or even higher⁵³⁻⁵⁶. Under this condition, the carbonation degree can be enhanced, with the possibility of MgCO_3 formation, as observed by Hänchen, et al.⁴⁷. Further, harnessing excess heat and CO_2 streams from industrial processes can optimise the degree of sequestration through mineral carbonation and offer a localised carbon management pathway that integrates waste volatilisation with decarbonisation.

Alternatively, mineral carbonation can be conducted in reactor systems that dynamically control temperature and pressure to maintain optimal conditions, enabling a high degree of carbonation within a short period. The main trade-off, however, lies in the balance between enhanced carbonation efficiency and the additional energy required to operate such reactors, which can substantially increase capital and operating costs⁵⁷. At the opposite end of the spectrum, carbonation at ambient temperature and pressure with elevated $p\text{CO}_2$ remains attractive for local and low-energy deployment. As in this study, the rapid uptake of CO_2 can still be achieved for both aqueous matrices, though the long-term kinetics of substantial Mg-carbonate

precipitation remain sluggish. Future endeavours should the cost and energy efficiency of technological pathways to optimise the feasibility of mineral carbonation reactors at both local and industrial scales.

Another key aspect for future investigation is reducing the water footprint, which is a major concern for most CDR technologies. The setup in this study used an S/L ratio of 1:3 without any water replenishment during the carbonation process, corresponding to ~ 0.3 gram of CO_2 kg^{-1} of water or ~ 30 t water t^{-1} CO_2 from the CO_2 sequestration achieved. This water consumption is relatively high compared to direct air carbon capture and sequestration (DACCS) systems, which typically require 3-30 t water t^{-1} CO_2 ^{58,59}. However, the water consumption in this study falls within the range reported for CCS technologies (0.74–575 t water t^{-1} CO_2)⁵⁹. Reducing the S/L ratio might not be a practical way to decrease water use, as it has been reported that an S/L ratio below 1:2 leads to inefficient mixing and limited CO_2 gas-liquid and solid-liquid mass transfer⁶. One potential strategy to further suppress water consumption is recycling processed water across multiple carbonation cycles. Recycling processed water into a new cycle with fresh alkaline by-products might be beneficial because it can lower the water footprint and promote further carbonation. The reactive hydroxide and oxide minerals from fresh feedstock will raise the pH towards alkaline, shift the system back into CO_3^{2-} , and may promote carbonate precipitation. Therefore, it is important to further investigate the efficiency and reaction rate of carbonation under these recycling conditions, as well as the thresholds at which water replenishment becomes necessary.

5. Conclusions

Direct aqueous carbonation of slag, driven by CO₂-enriched air bubbling and mechanical mixing, reached effective carbonation in less than 24 h through rapid dissolution and reaction of oxide-hydroxide minerals, demonstrating efficient CO₂ sequestration even under ambient temperature and atmospheric pressure. Ca-(hydr)oxide phases drove a rapid carbonation rate, while further CO₂ uptake was constrained once these phases were fully utilised. The depletion of oxide-hydroxide phases following the slaking stage initiates a cascade reaction that decelerates the kinetic and carbonation processes, particularly due to the depletion of the OH⁻ fraction. Carbonation is often presumed to follow a smooth trajectory toward maximum slag utilisation. The effective carbonation occurred predominantly during the slaking stage, when oxide-hydroxide phases govern reactivity. This aligns with concerns that a realistic assessment of CO₂ sequestration should be based on the effective capacity of the material rather than the maximum theoretical⁴⁵.

The aqueous matrix strongly influenced both the carbonation rate and the resulting carbonate polymorphs, highlighting the kinetic control of the process. The Mg concentration is relevant for the efficiency of CO₂ capture. The dissolution of Mg-(hydr)oxide phases inhibited carbonation, decreasing both the reaction rate and CO₂ sequestration efficiency, instead of producing stable MgCO₃. The solution might involve promoting the formation of Mg-hydrocarbonates and related phases through low-energy semi-drying of the material after carbonation in the reactor, by driving the remaining porewater into high supersaturation to trigger the precipitation of the related phases.

Future work should explore strategies for the carbonation pathways: (i) promoting the dissolution of residual Ca- and Mg-silicate minerals to increase the carbonation degree, preferably under ambient temperature and atmospheric pressure to minimize energy demand, enabling scalable and low-tech application; or (ii) accepting that carbonation may be limited to the effective degree (C_{eff}), yet the carbonated slag still contained a substantial bulk carbonate fraction of approximately 30–40 wt%, providing a co-benefit for sustainable concrete applications as a supplementary cementitious material and enhancing its economic value^{49,50}. Additionally, reducing the water footprint by reusing process water in subsequent cycles should be evaluated, e.g., its impact on carbonation rate and the resulting carbonate polymorphs. These offered pathways must be assessed for trade-offs between maximising CO₂ sequestration, preserving the functional properties and co-benefits of carbonated slag for feasibility and economic viability.

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610 **Competing Interests**

611 The authors declare that the research was conducted without any commercial or
612 financial relationships that could potentially create a conflict of interest.

613 **Author Contributions**

614 **R.P.** and **J.H.** conceptualised the experiment with input from **C.A.M.** **R.P.** and **I.S.N.**
615 conducted the experiments and performed the hydrochemical analyses. **R.P.**, **I.S.N.**,
616 and **C.A.M.** performed the solid phase analyses. **R.P.** performed the formal data
617 analysis, with input and interpretation support from **M.H.**, **J.H.**, **C.A.M.**, and **L.R.** **R.P.**,
618 **J.H.**, and **M.H.** prepared the original draft and data visualisations. **All authors**
619 contributed to reviewing and improving the manuscript. **J.H.** and **M.H.** secured project
620 funding.

621 **Appendix: Supplementary Materials**

622 Supplementary materials to this article are provided in the accompanying document.

623 **Data availability**

624 Data availability is provided in the main manuscript and in the supplementary
625 materials. Should any raw data files be needed in another format they are available
626 from the corresponding author upon reasonable request.

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