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Production of low-carbon amorphous SiO_2 for use as a supplementary cementitious material and nesquehonite from olivine

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ABSTRACT

Amorphous silica and hydrated magnesium carbonate (nesquehonite, $MgCO_3{\cdot}3H_2O$) have been produced by acid dissolution of olivine ($(Mg,Fe)_2{\cdot}SiO_4$). The amorphous silica is a viable supplementary cementitious material, and the formation of nesquehonite by carbonation, results in a carbon negative process. Using the amorphous silica as a supplementary cementitious material produces low-carbon cement. The global reserve of olivine makes this a viable route to producing low-carbon concrete.

1. Introduction

There is an urgent need to transform concrete from a material associated with for over 2 billion tonnes of CO_2 per year, to a carbon negative material [1]. The emissions associated with concrete are from the production of Portland cement, global production of which was 4.2 billion tonnes in 2021, with cement plants producing ~842 Kg CO_2 tonne^{-1} of cement clinker [2].

The cement and concrete industry have produced a road map to achieve net zero concrete by 2050 [3] that highlights the role of cement clinker substitution. This occurs when supplementary cementitious materials (SCMs), such as ground granulated blast-furnace slag (GGBS), coal fly ash and silica fume, replace Portland cement. However, the amounts available and their distribution, mean these cannot be a viable global solution for low-carbon concrete. Magnesium silicate minerals are available in enormous quantities. Although not as widely distributed as limestone and clays, magnesium silicate rocks such as olivine ($(Mg,Fe)_2\ SiO_4$) represent an industrially interesting raw material for low-carbon SCM production.

Fig. 1 shows a process for producing SiO_2 and nesquehonite ($MgCO_3{\cdot}3H_2O$) from olivine [4]. The olivine is dissolved in sulphuric acid, and SiO_2 and magnesium/iron sulphate solutions are separated. Dried SiO_2 forms an SCM, while carbonation of magnesium sulphate solution produces hydrated magnesium carbonate (nesquehonite). Experiments to optimise this process are reported.

2. Experiments

2.1. Materials and methods

Olivine ($(Mg,Fe)_2\ SiO_4$, Sibelco Nordic AS) with a particle size <180 μm was analysed by X-ray diffraction (XRD, Malvern Panalytical Empyrean diffractometer over a scanning range from 5 to 75° 2θ, with Ni-filtered CuKα radiation, at a scanning rate of 0.1° 2θ s^{-1}). X-ray fluorescence (XRF, Malvern Panalytical Zetium) of olivine samples prepared as fused beads at 1050 °C using lithium borate flux, showed ~93 % of metal ions (M^{2+}) in olivine were Mg^{2+}.

Sulphuric acid (H_2SO_4, 96–98 wt%, Merrick), NH_4OH (35 wt%, Sigma-Aldrich), $MgSO_4{\cdot}7H_2O$ (≥98 wt%, ACS reagent, Sigma-Aldrich) and isopropyl alcohol (99 wt%, Sigma-Aldrich) were used as chemical grade reagents. Erichrome® Black T (ACS reagent, indicator grade), ethanol (99.95 wt%, Sigma-Aldrich), $MgCl_2{\cdot}6H_2O$ (99.0–100.0 wt%, ACS reagent), NH_4Cl (≥99.5 wt%, Sigma-Aldrich) and disodium EDTA (≥99 wt%, ACS reagent, Arcos) were used in titration experiments.

2.2. Dissolution

H_2SO_4 solutions (500 mL) with concentrations of 1.0, 1.5, 2.0, 2.5 and 2.75 M, were placed in 1 L beakers containing a Teflon coated metal stirring bar at 70 °C. Olivine was added as a 10 % molar excess and stirred for 120 min. The slurry initially contained aqueous magnesium, iron sulphates, and dissolved silica monomers (Eq. (1)).

$$(Mg,Fe)_2SiO_4 + 2H_2SO_4 \rightarrow 2(Mg,Fe)SO_{4(aq)} + H_4SiO_{4(aq)} \quad (1)$$

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SiO_2 was precipitated as a hydrogel through a condensation polymerisation reaction (Eq. (2)).

$$H_4SiO_{4(aq)} \rightarrow SiO_{2(gel)} + 2H_2O \quad (2)$$

The final slurry consisted of silica gel, (Mg, Fe).SO_4 solution and residual olivine. Reaction progression was monitored by extracting a slurry sample, and the M^{2+} ion concentration was determined by EDTA-M^{2+} titration [5].

2.3. Separation

The silica gel was separated from the (Mg, Fe).SO_4 solution using isopropyl alcohol (IPA). Water and IPA are miscible at ambient temperature and pressure, but in a ternary system containing a salt, the mix exhibits liquid–liquid phase separation. An organic-rich upper layer contained the non-polar silica gel, and this was separated using a syringe, and dried at 60 °C to remove excess IPA. The amorphous precipitated silica (APS) formed was washed in tap water, filtered, and dried at 60 °C. The lower solution contained aqueous (Mg, Fe)·SO_4.

2.4. Carbonation

The M^{2+} concentration of the (Mg, Fe).SO_4 from olivine was determined using EDTA-M^{2+} titration. Synthetic 0.4 and 0.5 M $MgSO_4$ solutions were also prepared to match the olivine-derived solution by dissolving reagent grade epsomite ($MgSO_4{\cdot}7H_2O$) in distilled water. Carbonation of the three sulphate solutions and characterisation of the carbonate products allowed the effect of Fe impurities to be determined. The pH of the sulphate solutions was increased to 9.5 using NH_4OH. In the case of the sulphate solution derived from olivine, this caused the formation of $Fe(OH)_{2\ (s)}$ (Eq. (3)).

$$FeSO_{4(aq)} + 2NH_4OH_{(aq)} \rightarrow Fe(OH)_{2(ppt)} + (NH_4)_2SO_{4(aq)} \quad (3)$$

99.8 % CO_2 was bubbled through the $MgSO_4$ solution at ~250 mL.min^{-1}. The pH was maintained at 9.5 ± 0.2 by addition of NH_4OH solution, causing the formation of $MgCO_3{\cdot}3H_2O$ (Eq. (4)).

$$MgSO_{4(aq)} + CO_{2(g)} + 2NH_4OH_{(aq)} + 2H_2O \rightarrow MgCO_3.3H_2O_{(ppt)} + (NH_4)_2SO_{4(aq)} \quad (4)$$

The extent of carbonation was determined from the Mg^{2+} concentration, using EDTA-M^{2+} titration on extracted samples. The carbonate precipitate was separated by vacuum filtration, washed in tap water, and dried at 40 °C for 24 h.

3. Results

3.1. Dissolution

The as received olivine sample contained >80 % fosterite (Mg_2SiO_4), ~7 % of chabazite ($(Ca,K_2,Na_2,Mg)Al_2\ Si_4O_{12}{\cdot}6H_2O$), ~6 % lizardite ($Mg_3(Si_2O_5)(OH)_4$) and ~3 % vermiculite ($(Mg,\ Fe^{2+},\ Fe^{3+})_3\ [(Al,\ Si)_4O_{10}]$). The M^{2+} concentration in the slurry produced by acid dissolution of olivine, as a function H_2SO_4 concentration and time is shown in Fig. 2. Dissolution rate was initially high, but this decreases as reactants are consumed and increases with increasing acid concentration. The relationship between the concentration of M^{2+} ions and time for each acid concentration and olivine content is given by $\mathbf{C = C_m(1\text{-}e^{-t/\tau})}$, where C is the M^{2+} concentration at time t, C_m is the maximum theoretical concentration at complete dissolution, and τ is a constant determined from regression analysis.

Reaction completion times were determined from the best-fit exponential equation, as the time when the [M^{2+}] was equal to 99 % of the theoretical maximum concentration C_m. This is when ~99 % of olivine dissolution has occurred and when the time elapsed is 5τ. For all initial acid concentrations, M^{2+} extraction reached over 99 % of the theoretical maximum. The time to completion ranged from 50 to 110 min and was inversely proportional to the initial acid concentration.

3.2. Separation

XRD data of silica samples dried at 60 °C is shown in Fig. 3a. The washed sample (i) has a hump centred around 22° 2θ characteristic of amorphous SiO_2. The unwashed sample in (ii) shows crystalline peaks identified in (iii) as $MgSO_4{\cdot}H_2O$ Fig. 3b shows SEM-BSE images of washed amorphous SiO_2, showing agglomerated micron-sized SiO_2 particles with rough, microporous texture, and high surface area.

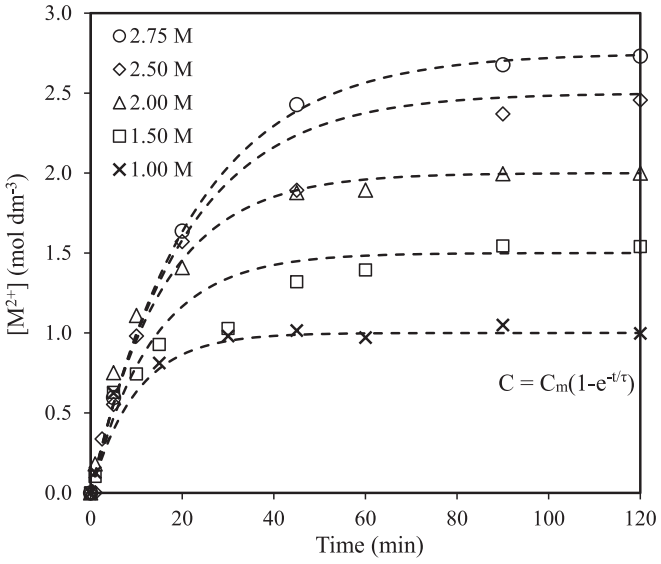

Fig. 2. Concentration of M^{2+} ions produced from acid dissolution of olivine as a function of acid concentration and time. All samples achieved >99 % theoretical maximum dissolution.

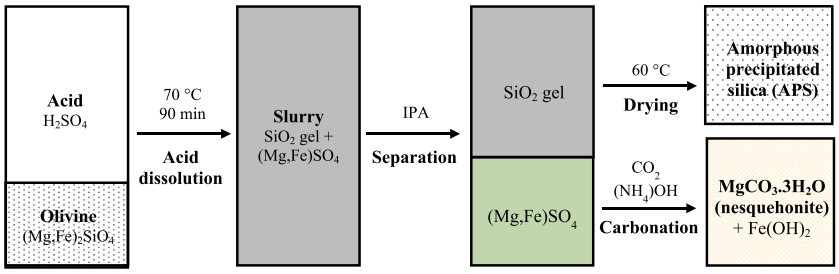

Fig. 1. Flowchart showing the production of amorphous precipitated silica (APS) and hydrated magnesium carbonate (nesquehonite) from acid dissolution of olivine followed by IPA separation and carbonation.

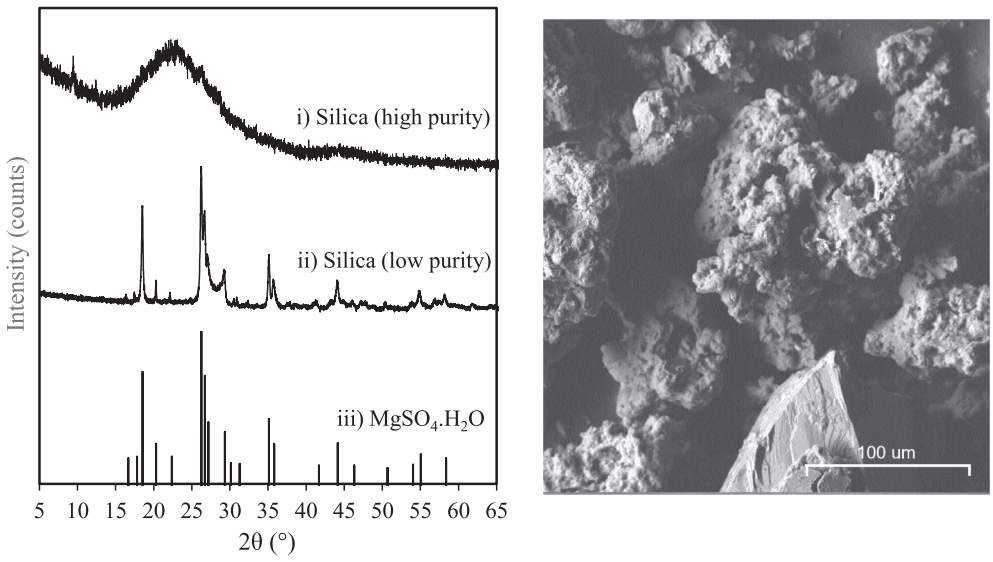

Fig. 3. a) XRD data showing i) an amorphous hump at around ~22° 2θ in washed, high-purity silica, ii) unwashed, low-purity silica containing impurities of iii) $MgSO_4{\cdot}H_2O$ b) SEM-BSE image of the amorphous precipitated silica.

3.3. Carbonation

Fig. 4a shows that carbonation occurs in 3-stages for both synthetic $MgSO_4$ solutions and for slurry samples of (Mg,Fe).SO_4 obtained from olivine. Initial incubation of ~15 min occurs, where the Mg^{2+} concentration remains constant. It takes time for the HCO_3^- saturation required to form $MgCO_3{\cdot}3H_2O$ Precipitation occurs when HCO_3^- concentrations reaches the saturation limit, and steady state precipitation occurs (stage 2) with a linear rate of Mg^{2+} removal. The third stage is associated with reduced Mg^{2+} consumption, as the concentration of Mg^{2+} ions control the rate, rather than the [HCO_3^-] ions. Fe impurities did not influence carbonation reactions.

XRD data confirmed that carbonate precipitates were nesquehonite ($MgCO_3{\cdot}3H_2O$) and Fig. 4b shows ~100 μm needle-like structures, characteristic of nesquehonite. XRF of precipitates extracted from the carbonation of olivine derived (Mg,Fe).SO_4 and synthethic $MgSO_4$ showed trace SO_3, due to incomplete washing. The carbonates derived from olivine contain low SiO_2, indicating the efficiency of the separation process. There was increased Fe_2O_3 content in the carbonate formed from olivine extracted solutions compared to the carbonate from reagent grade epsomite, and this oxidises into various ferrous oxides.

4. Discussion

This process uses acid dissolution of olivine to form amorphous SiO_2 and nesquehonite ($MgCO_3{\cdot}3H_2O$). Both products have potential uses in construction materials. The amorphous SiO_2 is a highly reactive cement replacement material and can be used to form carbon negative cement and low-carbon concrete. Previous research has shown that the phase transition from nesquehonite to hydromagnesite

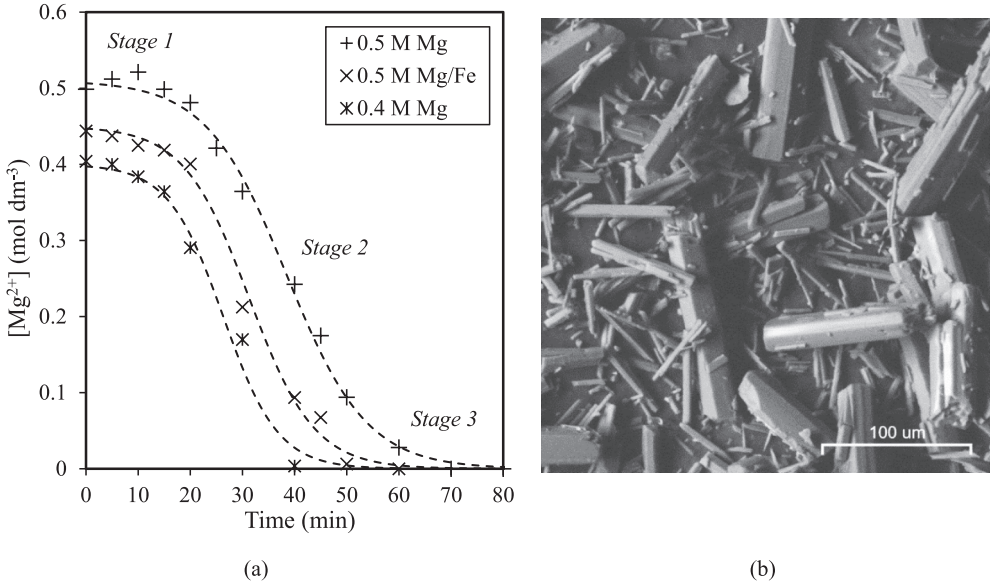

Fig. 4. a) Carbonation of the synthetic $MgSO_4$ solution (0.4 and 0.5 M), and the 0.5 M (Mg,Fe).SO_4 solution obtained from olivine dissolution. b) SEM-BSE image of hydrated magnesium carbonate with needle-like structures (nesquehonite).

($Mg_5(CO_3)_4(OH)_2{\cdot}4H_2O$) can be used to form construction products [6] including low-carbon blocks, bricks, and boards [6]. This low-cost carbon capture process therefore generates two end products with commercial value and sequesters carbon into the built environment. No alternative carbon capture, utilisation and storage (CCUS) method currently provides these benefits.

The European standard for cementitious materials (EN 197-1) [7], defines pozzolanic SCMs as materials containing a minimum of 25 wt% reactive SiO_2, with limits on other metal oxide, including MgO, and the loss on ignition. By removing carbonate and other impurities via an efficient separation process to increase the wt.% of SiO_2, the olivine-derived silica product conforms to EN 197-1. The process described can have a major role in emission mitigation strategies.

Limitations of this work are the use of pure CO_2 in the carbonation stage and the spent reagents are not recycled. Ongoing research is establishing the effects of gas purity, flow rate, gas–liquid contact area and verifying the effectiveness of CO_2 capture. Current research is also optimising a regeneration step to achieve circularity and ensure the technology is viable at scale.

5. Conclusions

A process for producing precipitated amorphous silica and nesquehonite from olivine is reported. The silica is a supplementary cementitious material (SCM) and the nesquehonite formation sequesters carbon. The process involves acid dissolution using H_2SO_4 at 70 °C. An efficient separation of dissolution products uses isopropyl alcohol (IPA). Impurities in the silica and magnesium carbonates can be controlled by altering process variables. High purity amorphous silica is produced from optimised separation, washing, and drying. The presence of Fe in olivine has no influence on nesquehonite. The processing method reported produces carbon negative amorphous SiO_2 and nesquehonite for use in low-carbon construction.

CRediT authorship contribution statement

Barney Shanks: Conceptualization, Investigation, Writing – original draft. **Caitlin Howe:** Formal analysis, Investigation. **Sam Draper:** Formal analysis, Investigation, Writing – original draft. **Hong Wong:** Formal analysis, Resources, Supervision, Writing – review & editing. **Christopher Cheeseman:** Formal analysis, Funding acquisition, Project administration, Supervision, Writing – review & editing.

Declaration of competing interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: Sam Draper, Barney Shanks, Hong Wong, Christopher Cheeseman has patent #International Patent Application No. PCT/GB2023/050085 pending to Assignee. None If there are other authors, they declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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