

Laboratory carbonation of artificial silicate gels enhanced by citrate: implications for engineered pedogenic carbonate formation

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Abstract

Carbon dioxide sequestration through carbonation of calcium or magnesium-rich silicate materials is a geoengineering technology that could mitigate a substantial proportion of anthropogenic emissions. Contemporary mineral carbonation research considers optimising this process to overcome energy requirements for mineral pre-treatment and reactor operation. This paper compliments previous studies in this area by demonstrating enhanced weathering through the action of organic acids including those exuded by plant roots. Batch weathering experiments, conducted as part of this study, with hydrated cement gels have shown that up to 80-85 % of calcium is leached from the material in 5 hours when exposed to solutions containing citrate anions, at an approximate log weathering rate between -8.26 to -6.86 molCa cm⁻² sec⁻¹, which is much more rapid than observed carbonate precipitation rates in previous studies for urban soils that contain cement-derived minerals. Thus Ca availability is not rate limiting. Coupled silicate-dissolution/carbonate precipitation reactions provide a carbon sequestration function that can be designed into soils specifically engineered to facilitate carbon capture.

Keywords: Mineral carbonation, enhanced weathering, organic acid, geoengineering,

1. Introduction

There is a growing body of research investigating the accelerated carbonation of silicate minerals as an emission mitigation strategy. The global maximum potential of carbon capture through carbonation of artificial silicates may be as much as 192-333 MtC a⁻¹, which is equivalent to other emissions mitigation technologies (Renforth et al., 2011). Early work (Lackner et al., 1997; Lackner et al., 1995) investigated the carbonation of olivine and serpentine at high pressure and temperature. This 'reactor' method for accelerating carbonation has been applied to numerous artificial materials including slag (Lekakh et al., 2008; Huijgen et al., 2005), cements (Huntzinger et al., 2009; Fernandez Bertos et al., 2004) and ashes (Montes-Hernandez et al., 2009; Fléhoc et al., 2006; Rendek et al., 2006). An alternative, with minor energy input, is to use enhanced mineral weathering processes in soils (particularly taking advantage of the action of low molecular weight organic acids released from plant roots; Renforth et al., 2009; Manning, 2008; Schuiling and Krijgsman, 2006). Artificially enhanced pedogenic (soil formed) carbonate formation provides a complimentary strategy of carbon sequestration.

There are four regularly quoted mechanisms of silicate mineral dissolution (see White and

Brantley, 1995), which include protonation of the bridging oxygen between the Si and Al tetrahedra, protonation/deprotonation of dangling surface oxygen atoms, hydrogen exchange with surface cations, and complexing of anionic ligands with cations at the surface (particularly those that are multi-valent, primarily Al³⁺ and Ca²⁺). This paper addresses the net effects of all four mechanisms in the presence of an organic acid buffer solution, simply from the perspective of release of Ca and formation of carbonate precipitates.

In general, mineral weathering is accelerated in soils through a number of processes. First, physical processes (equivalent to mechanical activation) including freeze-thaw, wetting-drying, and mechanical grinding and compaction (through anthropogenic activity) facilitate weathering. Second, biochemical activity in soils including CO₂ production from respiration, and exudation of protons and organic anions from plant roots, microbes and fungal hyphae accelerate weathering particularly for nutrient acquisition; this is equivalent to chemical activation. In general, the rates of these processes are thought to be too slow at a catchment scale to sequester carbon on a human time scale. However, weathering rates similar to those determined in the laboratory may be substantially enhanced in an engineered soil (i.e. designed to optimise carbon capture using a

chosen combination of specific soil mineral components and specific planting schemes) to precipitate carbonate (Figure 1). Investigation of organic acid-mineral interaction has traditionally been focused on soil formation (Lundström and Öhman, 1990) or diagenesis of organic matter (Pittman and Lewan, 1994; Manning et al., 1992). More recent studies have investigated organic acid-mediated weathering in the context of mineral carbonation (Krevor and Lackner, in press; Teir et al., 2007b). In its focus on carbonate precipitation, this paper compliments contemporary research that investigates weathering dynamics of artificial silicates influenced by organic acids.

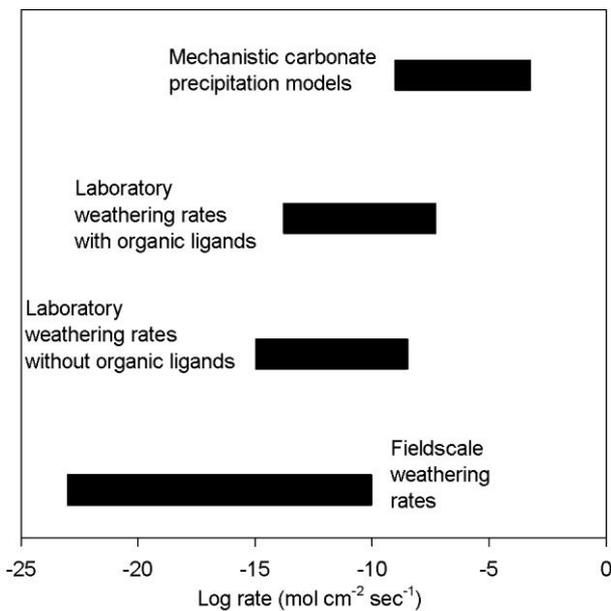


Figure 1: Typical weathering rates of silicate minerals (White and Brantley, 1995; and references therein) compared to carbonate precipitation rates calculated from mechanistic thin film models at ambient temperatures and pressures (e.g. Compton and Daly, 1987; Inskip and Bloom, 1985)

There is a large disparity between mineral weathering rates estimated from laboratory experiments compared with those calculated from cation flux in catchment scale experiments; field data indicate rates often several orders of magnitude lower than laboratory-determined rates. White (1995) suggests this to be an artefact of a number of properties including soil temperature, soil thickness, the composition of the parent material, vegetation type and density, and precipitation (rainfall) frequency and intensity. However, the work reported in this paper suggests that in an engineered soil system weathering rates can approach those determined in the laboratory, and can be sufficient to

precipitate carbonate and sequester carbon from the atmosphere on a human timescale.

1.1 Artificial Silicates

Artificial silicate-rich materials produced from high temperature processes are usually associated with (or wholly consist of) amorphous gels or glasses. Glasses and gels are composed of poorly crystalline or amorphous material, and are typically described using the crystalline mineral counterpart. For example, calcium silicate hydrate (C-S-H) gels found in cement are often regarded as ‘tobermorite-like’ or ‘jennite-like’ (e.g. Chen et al., 2004), jennite ($\text{Ca}_9\text{Si}_6\text{O}_{18}(\text{OH})_6 \cdot 8\text{H}_2\text{O}$) and tobermorite ($\text{Ca}_5\text{Si}_6\text{O}_{16}(\text{OH})_2 \cdot 4\text{H}_2\text{O}$) being the crystalline mineral counterparts. A study comparing the weathering rate of an albite ($\text{NaAlSi}_3\text{O}_8$) glass to its crystalline counterpart has demonstrated enhanced cation leaching from the surface layer by 2-3 orders of magnitude greater in the glass (Hamilton et al., 2000), suggesting that the poorly defined structural bonds in the amorphous silicate framework are readily broken in solution.

Laboratory X-ray powder diffraction (XRD), a standard mineral identification technique, is usually inappropriate when routinely analysing amorphous material (as the glasses and gels appear as a poorly defined ‘hump’ on the spectra distribution). Thus mineral identification is problematic when considering the varying weathering characteristics of a range of glasses or gels. However, XRD has been successfully employed to investigate the structure of hydrothermally formed crystalline phases in cements (Shaw et al., 2000a) which are chemically related to the C-H-S gels but are stable at different temperatures.

Small/wide angle X-ray scattering coupled with thermogravimetric (TG)/differential scanning calorimetry (DSC) has been used to characterise the breakdown of hydrated minerals under varying thermal conditions (Shaw et al., 2000b). The results demonstrate dehydroxylation and water loss from the hydrated minerals (Table 1) and subsequent re-crystallisation during a TG heating cycle to form low temperature wollastonite at approximately 750-800°C.

Mineral	CaO %	Ca/Si	H ₂ O %	Dehydroxylation temperature (°C)
Xonotilite	46.9	1.0	2.5	750-800
Tobermorite	35.2	0.8	12.2	20-320

Hillebrandite	58.7	2.0	9.5	450-650
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Table 1 – Thermogravimetric analysis of calcium silicate hydrate minerals. Source: Shaw et al. (2000b).

While silicate glasses and gels are the largest component of some human material streams, they are often associated with other minerals. Free lime (CaO) and portlandite (Ca(OH)₂) are typical constituents of cements, slags and fly ashes, and readily carbonate in the presence of dissolved CO₂. Ca(OH)₂ dissolves in water with a solubility constant of approximately 5.19 (Duchesne and Reardon, 1995) and buffers the pH to approximately 12. Reardon and Fagan (2000) suggest that portlandite placed in subsurface environments will convert to calcite acting as a sink for gaseous CO₂. Gypsum (CaSO₄·2H₂O) is added to cement clinker during production and reacts with Ca(OH)₂ and alumina during hydration to form ettringite (Ca₆Al₂(SO₄)₃(OH)₁₂·26H₂O). Ettringite is stable at pH>10.7, below which it dissolves to form gypsum and aluminium hydroxides (Myneni et al., 1998).

Cement is a complex mixture of unhydrated cement clinker, poorly crystalline C-S-H gels, portlandite, gypsum and ettringite. Furthermore, iron, aluminium and magnesium may be incorporated into the silicate framework. For simplicity, solubility characteristics have been previously determined for pure C-S-H minerals (Chen et al., 2004; Rothstein et al., 2002; Jennings, 1986). Solubility is considered a function of the Ca/Si ratio in the solid, which is related to mean chain length in a silicate (Figure 2). A comprehensive study of the solubility of a range of cement minerals is presented in Matschei et al. (2007). The calcium contents in Figure 2 are those from pore fluids in equilibrium with cement minerals, and do not relate to the rate of weathering.

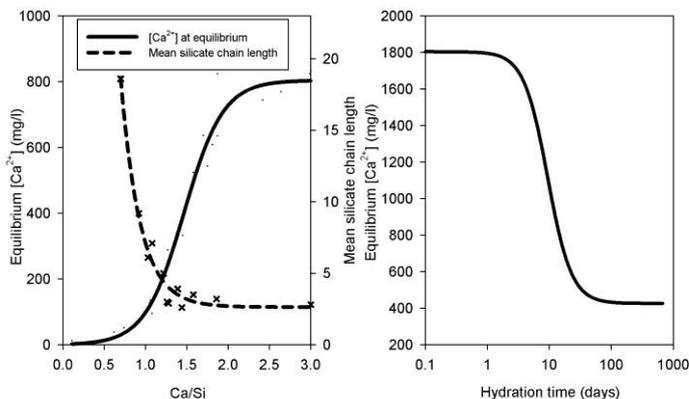


Figure 2 – Solubility of C-S-H as a function of Ca/Si ratio in the solid and hydration time,

Source: adapted from Chen et al. (2004) Rothstein et al. (2002).

Previous work has investigated the impact of artificial silicate weathering on the environment (e.g. Mayes et al., 2006; Krishnamurthy et al., 2003; Manning, 2001; Rochelle et al., 1998) and the solubility characteristics of individual cement minerals (Chen et al., 2004; Jennings, 1986), but there are no data that express the kinetics of these processes in terms of the weathering rates as a function of surface area. To this end, the experiments described in this paper used methodologies developed to investigate weathering of natural silicates for the determination of cement weathering rate. The approach taken is similar to that presented by Dijkstra et al. (2006) who investigated the leaching behaviour of municipal solid waste bottom ash. Using partially characterised material these authors provide data that connects theoretical individual phase dynamics (presented in earlier papers) with real environmental conditions.

In this paper, we present the results of investigations that provide estimates of the weathering rates of hydrated cements as bulk materials, without full characterisation of individual phases in the material.

2. Material and Methods

To simulate the enhanced weathering conditions in soils, a citric acid - sodium citrate pH buffer was used, citrate being a common organic acid in soils and plant root exudates with typical concentrations in the $\mu\text{mol l}^{-1}$ to mmol l^{-1} scale (Bylund et al., 2007; Strom et al., 2005). XRD, TG and bulk chemical analysis by X-ray fluorescence are used as part of this study to aid in the description of the material and its weathering properties.

2.1. Experiment A

OPC clinker (Lafarge Cement UK) was hydrated in controlled conditions to limit the formation of free lime/portlandite and subsequent carbonation of these materials. Deionised water was boiled for 30 minutes to remove dissolved CO₂ and allowed to cool in a reduced-pressure desiccator (approximately 0.7-0.8 atm). 36.9-57.5 g of OPC cement clinker were mixed with 42.5-63.1 g of oven dried powdered silica fume (Tarmac Ltd.) to form three materials with varying calcium to silicon (Ca/Si) ratio (Table 2), and hydrated using 20 ml of CO₂-stripped deionised water.

The resulting mixtures were cured at ambient laboratory temperatures (~20°C) over 14 days in a desiccator containing a NaOH trap to minimise exposure to atmospheric CO₂, crushed using a Siebtechnik Tema mill (20 seconds), rehydrated with an additional 10 ml of CO₂-stripped deionised water, and left for 10 days in the depressurised desiccator. The cured material was hand crushed using a pestle and mortar, oven dried to constant weight and sieved between 150 µm < Φ < 212 µm. The surface area of this size fraction was determined by the BET method using a Micromeritics Gemini Surface Area Analyser (0.05 and 0.3 atm) at the University of Reading. Bulk chemical compositions of the OPC, silica fume and hydrated cement pastes were determined using a PANalytical Axios Advanced XRF spectrometer at Leicester University, Department of Geology, and carbonate content was determined using acid digestion in an Eijkelkamp calcimeter with reproducibility better than ± 0.6 %CaCO₃. Free lime in the cement and untreated calcium silicate hydrate gels was determined in accordance with the methods in Swendon and Throvaldson (1950) and Lerch and Bogue (1930).

0.2 g of each hydrated cement sample were measured into 250 ml centrifuge bottles and 150 ml of 10 mmol l⁻¹ citric acid - sodium citrate solution buffered to pH 5, or deionised water (as a control), were added. The mixture was shaken and aliquots were taken after 1, 2, 3, 4 and 5 hours following centrifuging at 9000 rpm for 15 minutes wholly replacing the solution at each interval. Samples were filtered using 0.2 µm cellulose nitrate syringe filters; 5 ml of filtrate was measured into 25 ml glass volumetric flasks containing 0.1 % lanthanum (lanthanum chloride; Spectrosol) and acidified using concentrated nitric acid. Solutions were diluted to 25 ml and analysed for calcium by atomic absorption using a Varian SpectrAA 400 with reproducibility ±1.74 mg l⁻¹ when accounting for a dilution factor of 5. pH of the solution during the experiment was measured using a Jenway 3020 pH meter.

2.2. Experiment B

A further experiment was undertaken to determine the change in solid material composition as a result of weathering. 10 g of each material were immersed in 150 ml of sodium citrate buffer solution for 1 week. The solution was centrifuged, filtered, acidified, diluted and analysed for calcium concentration using AAS. The material was oven dried at 80 °C overnight and analysed for calcium carbonate.

XRD analysis was conducted on the OPC clinker, untreated cement pastes and weathered material using a PANalytical X'Pert Pro Multipurpose Diffractometer fitted with an X'Celerator and a secondary monochromator, operating with a Cu anode at 40 kV and 40 mA. Spectra were acquired for Cu Kα (λ = 1.54180 Å) or Cu Kα1 (λ = 1.54060 Å) radiation over 2-70°2θ with a nominal step size of 0.0167°2θ and time per step of 100 or 150 seconds. All scans were carried out in 'continuous' mode using the X'Celerator RTMS detector.

Images were taken of the treated and un-treated cement pastes using a FEI XL series environmental scanning electron microscope, using a 20 kV electron beam voltage. The pressure inside the chamber was controlled at 1.8 x 10⁻³ atm, flushed with nitrogen gas. Characteristic X-ray spectra were determined using X-ray spectroscopy.

2.3. Experiment C

Finally, an investigation was undertaken to determine the effect of silica fume on the hydration of cement paste. OPC and silica fume were mixed in varying quantities to create desired Ca/Si ratios. The material was hydrated with 15 ml of CO₂ stripped deionised water, and cured over 20 days in a reduced pressure desiccator. The solid material was powdered using a Siebtechnik Tema mill. A Netzsch TG209 thermogravimetric analyser, purged with He_{80%}O_{20%}, was used to investigate the transformation of hydrated cement paste in a 0-900 °C heating regime.

3. Results

XRF analyses of the cement clinker, silica fume and hydrated cement pastes are presented in Table 2. Plotting the hydrated cement paste as a proportion of un-hydrated cement clinker, silica fume and theoretical tobermorite (Ca₅Si₆O₁₆(OH)₂.4(H₂O)) in a ternary diagram suggests that there is approximately 0-28 % un-hydrated cement clinker in the sample (Figure 3).

	Un-reacted hydrated cement			OPC	Silica fume	Tobermorite ($\text{Ca}_5\text{Si}_6\text{O}_{16}(\text{OH})_2 \cdot 4(\text{H}_2\text{O})$)
	Ca/Si 0.54	Ca/Si 0.66	Ca/Si 1.03			
SiO ₂	60.41	56.41	46.64	26.91	94.23	49.32
TiO ₂	0.15	0.15	0.19	0.31	0.00	-
Al ₂ O ₃	4.12	4.42	5.33	7.60	0.90	-
Fe ₂ O ₃	1.92	2.02	2.48	3.92	0.21	-
MnO	0.07	0.07	0.07	0.09	0.04	-
MgO	1.53	1.55	1.82	2.62	0.68	-
CaO	21.39	24.46	31.45	53.23	0.35	38.36
Na ₂ O	0.33	0.32	0.28	0.31	0.38	-
K ₂ O	0.86	0.816	0.676	0.837	1.131	-
P ₂ O ₅	0.12	0.129	0.144	0.204	0.063	-
SO ₃	1.16	1.316	1.539	2.041	0.078	-
LOI	8.24	8.50	9.45	1.85	1.58	12.33
Total	100.31	100.17	100.06	99.93	99.65	100.00
% CaCO ₃	2.23	2.66	2.88	0.90	0.10	-
% H ₂ O weight loss	7.23	7.33	8.18	1.46	1.54	12.33
% Free lime	0.04	0.04	0.09	0.86	-	-
BET surface area (m ² g ⁻¹)	29.10	20.39	14.76	-	-	-

Table 2 – Data from XRF analysis, carbonate content, free lime (wt %) and BET analysis of cement clinker (giving Ca/Si mass ratios), silica fume and unreacted cement pastes. Tobermorite composition calculated from formula.

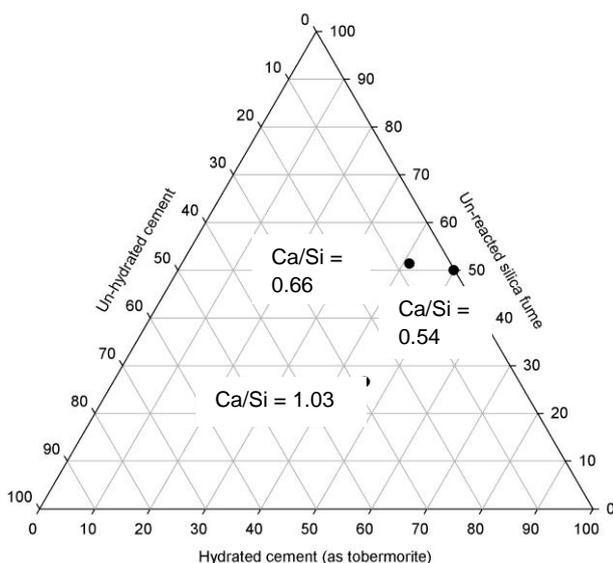


Figure 3 – Composition of un-treated cement pastes.

The calcium content of the solutions (Figure 4a) in Experiment A decreased with each successive sampling to 129.6 ± 1.7 to 3.2 ± 1.7 mg l⁻¹ over the 5 hour experiment (a significant difference ($P < 0.001$) compared with the deionised water control which decreased from 17.8 ± 1.7 to 6.4 ± 1.7 mg l⁻¹). The material with Ca/Si ratio = 1.03

leached significantly more calcium into solution ($P = 0.006$), with no discernable difference between results for starting materials with the other two Ca/Si ratios. pH was successfully buffered between 5.01 and 5.60 over the 5 hours of the experiment (the control was not buffered and fluctuated between 9.7 and 10.5; Figure 4b).

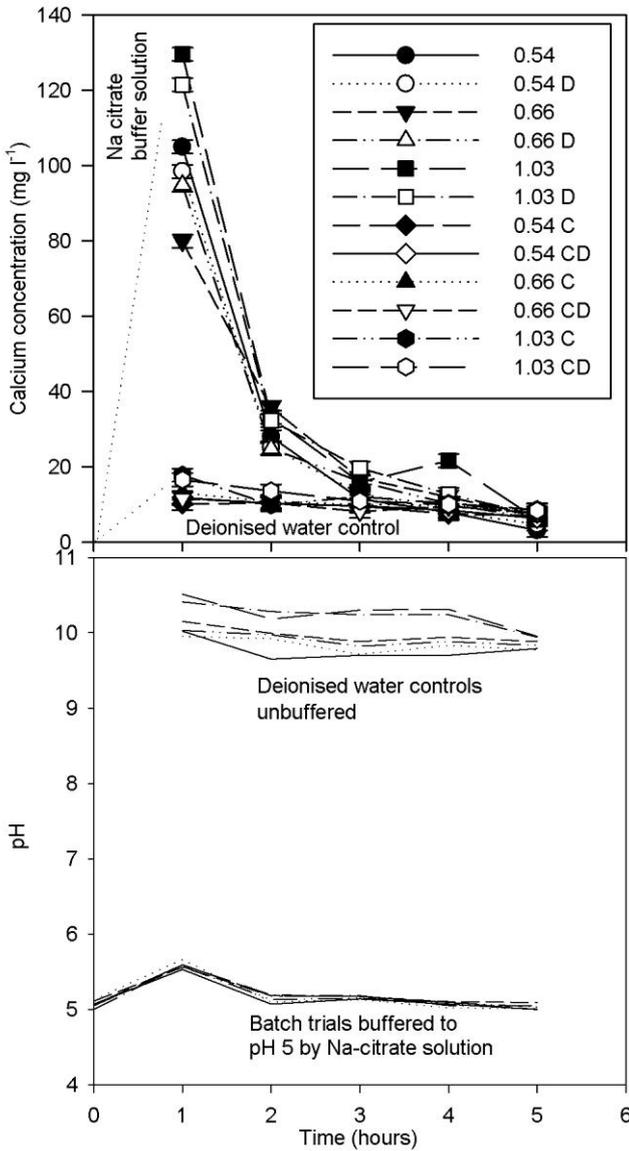


Figure 4 – Calcium content and pH of solutions during batch weathering in Experiment A. D – duplicate trial, C – deionised water control. 0.54, 0.66 or 1.03 denotes the Ca/Si ratio of the solid phase. Note reproducibility error bars for calcium concentration are within the size of the data points.

The carbonate content of the solid increased over the week-long Experiment B (mean = 4.21 %, s = 1.1), and was confirmed to be calcite using XRD analysis, which also detected the cement minerals larnite/belite (Ca_2SiO_4) and brownmillerite ($\text{Ca}_2(\text{Al,Fe})_2\text{O}_5$), a calcium magnesium aluminium silicate, JCPDS reference no. 00-013-0272), and quartz (SiO_2 ; Figure 5). As expected, a broad peak was detected between 16 and 26 $^{\circ}2\theta$ during XRD analysis which confirmed the presence of amorphous or poorly crystalline silicate materials. Interestingly, the intensity of the peak appears to decrease with decreasing Ca/Si. The same mineral assemblage was detected in the cement clinker and un-

treated hydrated cement pastes. XRD analysis of the weathered minerals shows systematic variations in mineralogical composition (Figure 6), particularly the increased intensity and the appearance of additional calcite peaks, the reduction in larnite peak intensity and the increased intensity of the amorphous hump. Furthermore, weathering appears to have had little effect on the brownmillerite peak, suggesting varying stability of the mineral phases. The calcium concentration of the solutions overall ranged from 204.7 to 326.2 \pm 5.2 mg l^{-1} , and were 210.0, 220.2 and 324.2 mg l^{-1} for Ca/Si ratios of 0.54, 0.66 and 1.03 respectively.

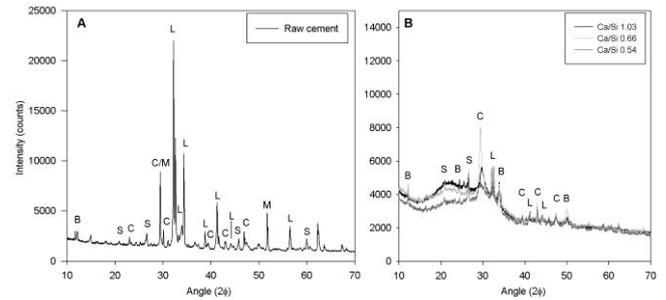


Figure 5 – X-ray diffractogram of cement clinker (A) and the un-weathered hydrated cement paste (B). B – brownmillerite ($\text{Ca}_2(\text{Al,Fe})_2\text{O}_5$) C – calcite (CaCO_3) L – larnite/belite (Ca_2SiO_4) M – calcium, magnesium, aluminium silicate S – quartz (SiO_4).

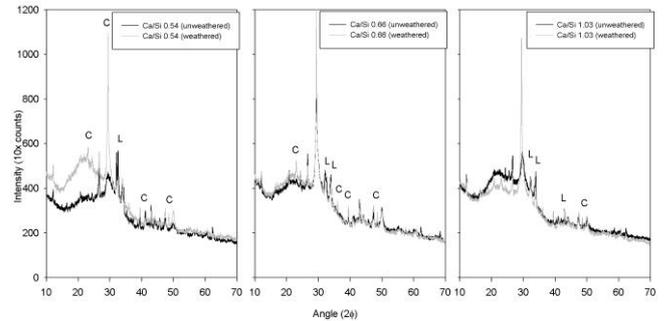


Figure 6 – Comparison of diffractograms from weathered and un-weathered materials. L – larnite (Ca_2SiO_4) C – calcite (CaCO_3).

SEM investigation showed small (~10-20 μm) particles attached to the surface of the weathered and un-weathered grains (Figure 7). Using X-ray spectroscopy (coupled with SEM), the elemental composition of the particles was semi-quantitatively determined. The characteristic X-ray spectra suggest that the particles are concentrated relatively in Ca, Mg and Al, compared to the background matrix (Figure 8). Investigation of surface layers in polished thin sections of grain mounts was not carried out.

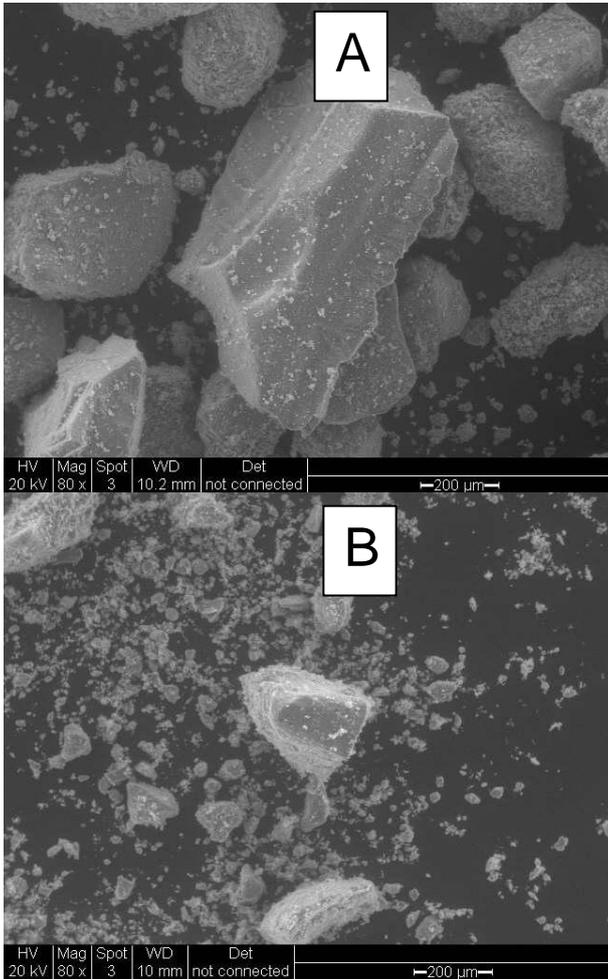


Figure 7 – Scanning electron microscope images of un-weathered (A) and weathered (B) cement minerals.

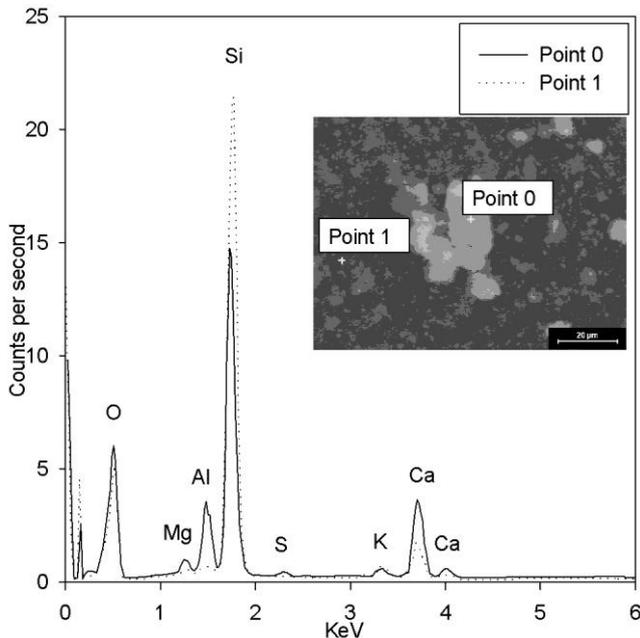


Figure 8 – Characteristic X-ray spectra of surface anomaly compared with the background material.

The hydration of cement paste as a function of Ca/Si in Experiment C (Table 3) was investigated using thermogravimetric analysis. There was a discrete mass loss between 200 and 300 °C in all

samples, most likely representing the dehydroxylation or water loss from a semi-crystalline hydrated mineral (although this was not detected in the XRD spectra, see below). Mass loss between 650-750 °C represents the loss of CO₂ from carbonate minerals (0.64-0.81 wt% as CO₂) probably formed by unintentional dissolution of CO₂ during cement curing or clinker carbonation with ambient CO₂ during manufacturing (Figure 9).

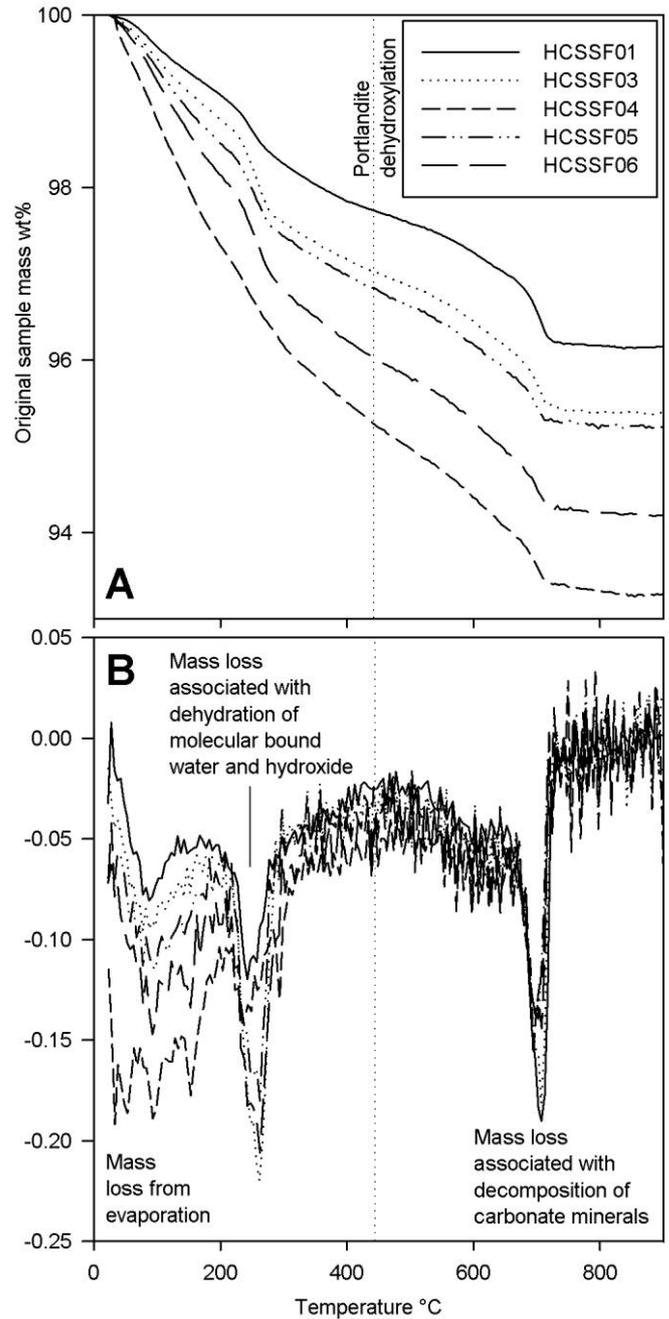


Figure 9 – (A) Mass loss of hydrated cements during thermal analysis and (B) differentiated mass loss.

Sample	Ca/Si	Mass loss 200-300°C (%)	Mass loss 0- 600°C (%)	Mass loss 650-750°C (%)
HCSSF 1	3.03	0.79	2.77	0.81
HCSSF 3	1.26	1.20	3.56	0.75
HCSSF 4	0.98	1.16	5.60	0.69
HCSSF 5	0.80	1.07	3.83	0.64
HCSSF 6	0.67	1.32	4.71	0.71

Table 3 – The effect of the calcium/silicon ratio on cement hydration.

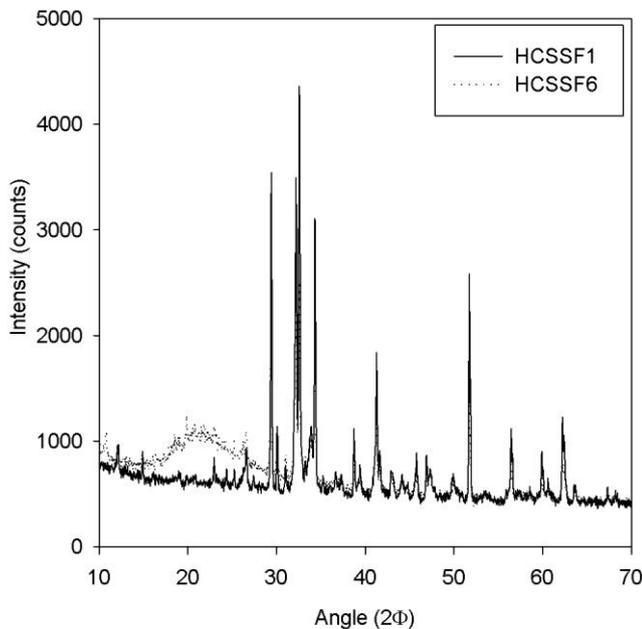


Figure 10– XRD diffractogram of hydrated cement in Experiment C. C – calcite (CaCO_3), L – larnite/belite (Ca_2SiO_4), M – calcium, magnesium, aluminium silicate, S- quartz (SiO_4).

The XRD diffractograms of the hydrated cement minerals are similar to that in Experiment B, where the minerals calcite, quartz, larnite and a calcium magnesium aluminium silicate were identified. However, Figure 10 identifies the variation in amorphous material as a function of Ca/Si ratio. HCSSF 6 (Ca/Si = 0.67) has the larger amorphous hump compared with HCSSF 1 (Ca/Si = 3.03).

4. Discussion

Using a BET determined surface area between $14.76\text{--}29.19\text{ m}^2\text{ g}^{-1}$, the log rate of weathering is calculated between $-8.23\text{ to }-7.85\text{ molCa cm}^{-2}\text{ sec}^{-1}$ over the 5 hour experiment (30-40% greater than this in the first 3 hours), which is similar to the rate calculated from results published in previous work investigating the degradation of cylindrical cement columns using 6 mol l^{-1} ammonium nitrate at elevated water pressure ($\sim 8.0\text{ mol cm}^{-2}\text{ sec}^{-1}$; Galle et al., 2004). Expressing the weathered calcium as a percentage of the initial total calcium in the material it can be estimated that between 62.7 and 75.5 wt% Ca is leached out within the 5 hour trial, compared to the deionised water control which leached 19.1 and 22.9 wt% (Figure 11). This is less than that recorded in a previous study investigating the weathering of calcium from slag in acetic acid solution, which recorded 80 – 100 % of Ca removal from the material in 2 hours weathering (Teir et al., 2007a), highlighting potential variability between organic acids as well as differences in the behaviour of different solids. The rate of calcium weathering is several orders of magnitude greater than those reported for natural silicates in the laboratory (See Figure 1).

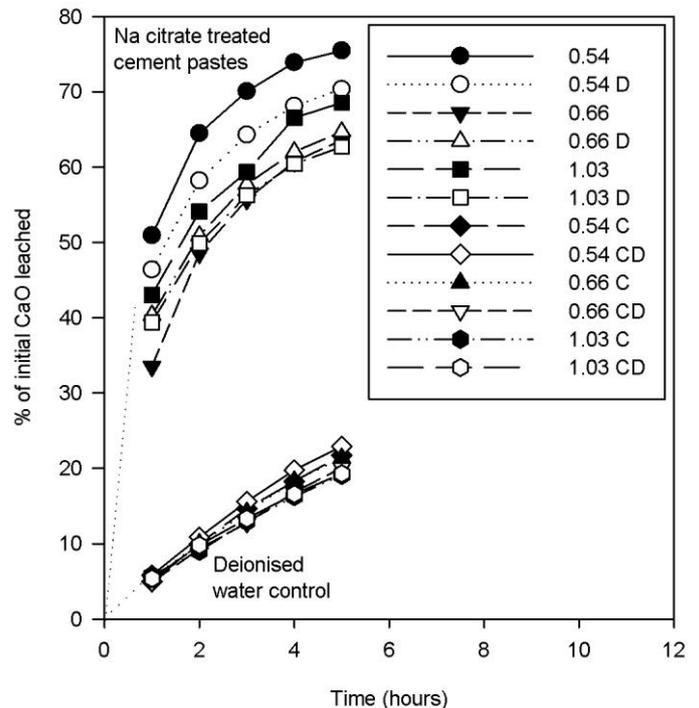


Figure 11 – Calcium weathered as wt% of the total calcium in the initial material in Experiment A. D – duplicate trial, C – deionised water control. 0.54, 0.66 or 1.03 denotes the Ca/Si of the solid phase.

The experimental results suggest that C-S-H gels are highly soluble and rapidly equilibrate with the surrounding solution, which is supported by the solubility data presented in Chen et al. (2004) that predicts calcium solution concentrations of 15.6-108.7 mg l⁻¹ for Ca/Si ratios of 0.54 – 1.03. Interpretation of the maximum weathering rate potential leads to the following possibilities:

- The upper limit of calcium weathering (62.7 % and 75.5 %) is controlled by the mineralogy of the cement. The calcium weathered in this experiment originated in a soluble phase and the remaining calcium is fixed in less soluble minerals representing 25-35 % of the initial CaO content. This is supported by SEM images which possibly show the presence of crystalline calcium silicate hydrate minerals on the surface of the weathered material, and XRD spectra which confirm the presence of stable calcium-containing phases.
- Alternatively, the observed upper limit may be a function of the depth of a weathered surface layer, in which the underlying calcium-rich core is protected from further weathering by a silica-rich outer layer. The depth of the surface layer can be estimated between 11-17 µm calculated geometrically (for a normally distributed particle size between 150 < θ < 212 µm), which is 2 orders of magnitude greater than that reported by Nesbitt and Skinner (2001) for natural silicates.
- Secondary minerals have precipitated on the outer surface of the cement grains and reduced the active surface area available for weathering (supported by XRD analysis and carbonate concentrations). Furthermore, precipitation of calcite would subsequently remove solute from solution. A 2 % increase in calcite concentration equates to 10-15 % of the calcium content of the initial material. Given that carbonate precipitation was recorded in experiment B, it is assumed that the original carbonate content in the hydrated cement raw material contributed little to the measured calcium concentration of the solution.

The results of the experiments reported here, especially Experiment A, shows that cement-based minerals readily weather when crushed

and exposed to continually replaced solutions. The presence of an organic acid enhances the weathering rate by half an order of magnitude, although this could be attributed to a buffered pH in the sodium citrate trial, compared to that in the control. Experiment B clearly demonstrate that calcite precipitation has taken place from solution with pH 5.

In the context of carbon sequestration, this study supports the use of cement-derived materials in soils, where plant root exudation involves addition of multidentate organic acid anions such as citrate to the soil solution (Jones, 1998). Such anions are known to be effective complexing agents that accelerate the dissolution of aluminosilicate minerals (Manning et al., 1992). It also provides kinetic data that are vital to predict carbonation rates, so that soil treatments can be designed to maximise carbon capture within a given period of time. Work based on cement-bearing urban soils developed on demolition sites of known age (Renforth et al., 2009), has shown that as much as 30 kg C m⁻³(soil) can accumulate in 10 years (based on two time points), representing a minimum log accumulation rate of -16 molC cm⁻² sec⁻¹ (assuming a surface area of 20 m² g⁻¹ or 3 x 10⁷ m² m⁻³), which is within the range for dissolution rates based on field weathering experiments (Figure 1). Combining the field observations with the laboratory experimental results, it seems clear that Ca supply from artificial silicates is not limited by dissolution rate, and is capable of capturing substantial quantities of carbon in the soil as carbonate minerals. Importantly, this work shows that the predicted dissolution rate for cement-derived minerals and the precipitation rate for calcite under laboratory conditions fall within the range observed for the carbon accumulation rate in urban soils as calcium carbonate. This confirms one mechanism by which calcium carbonate is formed in urban soils (i.e. carbonation of cement minerals within soil as a consequence of plant root exudation), and permits predictive modelling of the performance of soils expressly designed for carbon capture. According to Renforth et al. (2011), the carbonation potential globally of calcium silicates that arise from industry is of the order of 192-333 MtC a⁻¹; these materials represent a significant resource for carbon sequestration through the use of specifically designed soils.

Extrapolation of the results of this work to natural soil systems requires a thorough understanding of soil solution chemistry in each specific case. However, the precipitation of calcite in soils that contain cement-derived materials is widely

observed within urban soils, and is known to be rapid (up to 300 T C/ha within 10 years; Renforth et al., 2009). In general, comparison of weathering rates determined in the laboratory with those determined at field scale shows that laboratory experiments tend to underestimate reaction rates by a factor of 10^2 (White, 1995). Nevertheless, the results reported in this paper demonstrate that carbonation rates observed from investigation of urban soils in the field are compatible with rates determined for the dissolution of calcium silicate minerals representative of cement-derived materials.

A further consideration is soil pH. In Experiments A and B, pH was buffered at pH 5, and this was maintained as the reactions proceeded, with calcite as an observed product (Figure 4). Given that calcite precipitation takes place at pH values as low as 5.6 in sanitary landfills (Manning and Robinson, 1999; Manning, 2001), it can be expected that calcite will form in soils over a wide range of pH. The key factor is not the pH alone of the soil solution. Calcite saturation is governed by the bulk chemistry of the solution, and requires the product of the activities (thermodynamic concentrations) of Ca^{2+} and carbonate to be sufficient. In certain circumstances, such as very high concentrations of Ca^{2+} , this can be achieved at low pH. Empirical studies of calcite dissolution over a range of pH values confirm its stability under certain conditions at low pH. Niemann and Hatheway (1997) reported moderate dissolution of limestone in model landfill leachates (solutions whose composition may resemble soil solutions in their complexity) at pH 3 (12 wt %), and negligible dissolution at pH 6 - 6.5. In any case, the pH of soils that contain cement-derived materials is consistently higher than this, influenced by the presence of portlandite ($\text{Ca}(\text{OH})_2$) which can control pH to as high as 12 in the absence of organic matter, or by calcite, which buffers pH to approximately pH 8.

5. Conclusions

The research presented in this paper compliments existing mineral carbonation research by demonstrating organic-acid mediated weathering of artificial silicates. This develops further the potential of mineral carbonation in soils as an alternative to high pressure/temperature based technologies.

Between 62.7 and 75.5 % (up to 85% when considering secondary mineral precipitation) of the calcium in artificial cement pastes was leached out over the 5 hours of the batch

weathering trial containing citrate anions, which is comparable to a previous study using acetic acid. The log weathering rate was between -8.23 to -7.85 $\text{molCa cm}^{-2} \text{sec}^{-1}$, which is several orders of magnitude greater than laboratory determined weathering rates reported for natural silicates, but comparable to a previous study investigating the degradation of concrete. Calcite was observed as a precipitate in experimental solutions buffered to pH 5. The results highlight that in ambient, organically influenced, conditions such as those found in soil, cement minerals readily weather and carbonate. This paper compliments existing mineral carbonation research investigating enhanced weathering of natural silicates, and demonstrates the potential value of designing soils expressly for carbon sequestration.

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