



An innovative approach to the synthesis of sorbent materials for metal fixation

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Abstract

A new approach has been developed for the synthesis of wastewater treatment materials from calcareous substrates *via* the process of accelerated carbonation. This paper presents results from an investigation of the characterization and performance testing of carbonated ordinary Portland cement (CASM) as a sorbent for metal removal. CASM was synthesized by exposing cement to carbon dioxide gas, at a pressure of 2 bar, in the presence of moisture. The resulting product had funnel-shaped pores of 30–40Å and a specific surface area of 49m²g⁻¹. The main phases of CASM were crystalline polymorphs of calcium carbonate, amorphous silica/alumina and unreacted mineral phases. In a sessile kinetic sorption study CASM demonstrated the following trend in metal uptake (in mg/g): Pb(185) > Cd(180) > Cr(175) > Mo(106) > Co(69) > Ni(65) > Cu(59) > Cs(37). The fate and speciation of the immobilized metals were determined by the analysis of metal-bearing CASM specimens. Cadmium, lead and copper formed carbonate-based species, whereas molybdenum and chromium formed scheelite CaMoO₄ and the amorphous analogue of bracewellite CrO(OH), respectively. Sorption, ion-exchange and (co-)precipitation were suggested to be the mechanisms of nickel and cobalt fixation, whereas cesium was exclusively associated with anhydrous silica. The results indicate that accelerated carbonated may be used to produce new sorbent materials.

1 Introduction

Aqueous streams contaminated with hazardous metals, including radionuclides, are primarily generated by mining operations, industrial and nuclear processes, and waste disposal sites. Unlike many other pollutants, metal ions are not degradable, hence remediation and treatment methods for metal-bearing matter

are based on removal, changes in speciation or the formation of insoluble and less toxic compounds [1,2]. The treatment of radioactive isotopes primarily involves their concentration into residues, which then can be isolated for specific decay periods [2–4].

The choice of treatment technology depends on a number of factors relating to effluent characteristics and the ultimate disposal scenario. Removal of heavy metals from industrial wastewaters can be accomplished *via* numerous treatment regimes, including; chemical precipitation, complexation, adsorption, ion-exchange, oxidation/reduction, membrane processes, etc.. Despite currently available treatment technologies for the exclusion of metals from wastewater, there are economic and environmental incentives to seek alternative, more efficient and cheaper treatment techniques & materials.

International agreements are directed at reducing net emissions of all greenhouse gases, particularly carbon dioxide [5,6]. The mitigation options for CO₂ pollution include both source-oriented measures by energy conservation, efficiency improvement, fossil fuel switching, renewable energy sources and increasing CO₂ sequestration.

In developing strategic measures for CO₂ recycling and disposal, researchers have been exploring the benefits of controlled carbonation processes [7–9]. The process of ‘accelerated carbonation’ (during which, matter is exposed to a CO₂-rich atmosphere in the presence of moisture) has previously been found to alter properties of mineral phases, aluminous and silicate cement pastes, wastes [7–19]. It has been reported that, in some instances, carbonation can induce changes in the chemical and physical properties of waste forms, leading to the enhanced retention of certain metals [20–23].

The present work documents an investigation of a novel approach to the synthesis of heterogeneous sorbents, having multi-mechanistic potential to remove metals and radionuclides from concentrated effluents. The synthesis procedure employed in this work involved the exposure of a calcium aluminosilicate-based material, namely Portland cement, to a CO₂-rich atmosphere under controlled conditions. The product was characterised and examined for its ability to remove a range of metals from synthetic wastewaters.

2 Materials and methods

The parent reagent used to synthesise the carbonated aluminosilicate sorbent material, CASM, was ordinary Portland cement, OPC, (supplied by Blue Circle Cement, UK), a multi-phase system primarily comprising; tricalcium silicate, Ca₃SiO₅ (C₃S), dicalcium silicate Ca₂SiO₄ (C₂S), tricalcium aluminate, Ca₃Al₂O₆ (C₃A) and tetracalcium aluminoferrite, Ca₂AlFeO₅ (C₄AF). The oxide and Bogue analyses of the OPC are given in Table 1.

Prior to carbonation OPC was intimately blended with de-ionised water at a water:solid ratio of 0.1 (on a mass basis) and immediately placed into a purpose-built reaction chamber. A supply of CO₂ gas of 99.99% purity was then introduced such that a constant pressure of 0.2MPa was maintained within the chamber. The sample remained in the vessel for up to 12 hours whereupon it was

removed and ground with a Siebtechnik tema mill for 3 minutes. The ground sample was then oven-dried at 60°C to constant mass, re-moistened and again subjected to CO₂-exposure (as described above). The carbonation process, which was adapted from previous studies, was repeated four times [13]. The carbonated product, CASM, was characterised by X-ray diffraction XRD (Siemens D5 100), scanning electron microscopy SEM (JEOL JSM- 5310LV scanning electron microscope), nitrogen gas sorption (Quantachrome Autosorb Automated Gas Sorption System AS-6), differential thermal analysis DTA (Redcroft STA 780 Simultaneous Thermal Analyzer) and magic angle spinning nuclear magnetic resonance spectroscopy MAS NMR (Bruker AC 300 multinuclear spectrometer).

Table 1: Chemical and phase composition of OPC.

% Phase composition					
C ₃ S	C ₂ S	C ₃ A	C ₄ AF	CaSO ₄	
45	27	11	8	3.1	
% oxide content					
SiO ₂	Fe ₂ O ₃	Al ₂ O ₃	CaO	MgO	SO ₃
22	4	7	61	1	2

The leaching of calcium, magnesium, aluminium, silicon, potassium and sodium from CASM as a function of pH and time was examined. Experiments were set up in which 5g CASM were contacted with 1 litre deionised water. The pH levels were varied from 2 to 12 at 2 unit intervals, and the pH was maintained by appropriate additions of NaOH or HCl. The contact times were 6, 24, 48, 72, 120, 200, 600 hours. Each experiment was conducted in triplicate. An Iris simultaneous inductively coupled plasma analyser (ICP-OES) was used to measure the concentrations of calcium, magnesium, aluminium, silicon, potassium and sodium in the leachates obtained. An examination of microstructural changes due to dissolution as a result of exposure to acidic or basic conditions was carried out by SEM and XRD analysis.

Kinetic sorption studies were conducted using sessile batch experiments with single metal solutions of cobalt, lead, copper, chromium, molybdenum, cadmium, nickel, and cesium-134 (which is reported to behave similarly to the radioisotope cesium-137 [4]). Solutions were prepared from analytical reagent grade nitrate salts. The dosage of CASM and the concentration of metals were fixed at 5 g/l and 1000mg/l, respectively, whereas contact time and initial pH levels of solutions varied. The supernatant liquors from centrifuged suspensions were collected, acidified and analysed for Ca, Al, Si, Na, Mg, K and the relevant heavy metal by ICP-OES. Cesium concentrations were measured using atomic emission spectroscopy (Philips PYE UNICAM SP9-AAS). The influence of pH on metal uptake by CASM was also evaluated for molybdenum and cesium, nickel, and cobalt.

SEM, DTA and XRD analyses of the metal-bearing CASM specimens were used to determine the fate and speciation of the immobilised metals. For this purpose, metal solutions (1000 mg/l [500mg/l for cesium]) were contacted with the CASM (10g/l) for 72 hours, prior to recovery, freeze-drying and analyses.

3 Results and discussion

Examination of CASM in comparison with the OPC parent material enabled the textural, morphological and structural changes induced by accelerated carbonation to be characterised. The specific surface area of CASM was found to be $49 \text{ m}^2\text{g}^{-1}$ and the structure of the material was mesoporous with a predominance of funnel-shaped pores in the 30–40 Å diameter range. XRD analysis indicated incomplete carbonation of the original mineral phases of OPC and the formation of the crystalline product phases calcite and aragonite (both polymorphs of calcium carbonate).

The ^{29}Si MAS NMR spectrum of anhydrous OPC indicated the presence of Q^0 silicon environments assigned to C_3S and C_2S (-71ppm), whereas a signal arising from Q^4 amorphous silica (-103ppm) predominated in the spectrum of CASM [24]. Both octahedral (8ppm) and tetrahedral (81ppm) coordination sites were noted in the ^{27}Al NMR spectrum of the OPC. In contrast, the ^{27}Al NMR spectrum of CASM showed a 4-coordinate aluminium environment at 53 ppm.

Back-scattered SEM images of OPC and CASM particles (Fig. 1) show, calcium carbonate precipitation (grey-scale) adjacent to a 'decalcified' silica phase (dark-scale) and unreacted minerals (i.e. tetracalcium aluminoferrite having high atomic density and consequently represented by brighter fractions).

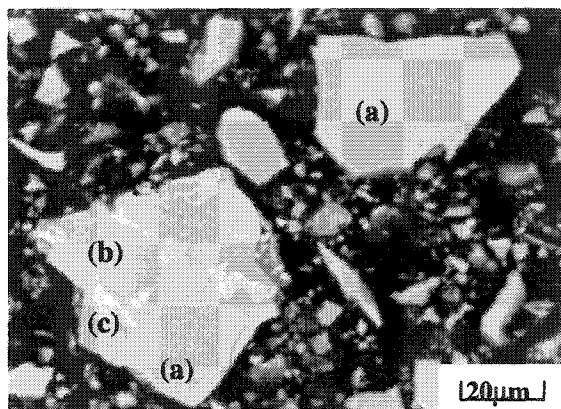
The rate and extent of dissolution of the constituents of CASM varied as functions of pH and time. It should be emphasised that CASM has a high acid buffering capacity by virtue of its calcium carbonate content, and consequently significant volumes of acid were required to maintain the pH at below 7 units. Most of the alkali metals leached extensively at pH values between 2 and 4 units. A comparison between maximum leaching concentrations of Ca, Al, Fe, K, Si and Mg from the CASM matrix during the initial 120 hours at pH 6–10 and corresponding drinking water standards is given in Table 2. Solid phase analysis showed that highly acidic conditions (pH 2) were detrimental to the structure of CASM. Calcium carbonate was particularly vulnerable to dissolution at this pH in comparison with tetracalcium aluminoferrite and silica. Minimal leaching of the constituents of CASM leading to secondary pollution was achieved at pH values in excess of 6 units.

The metal uptake by CASM as function of time is presented in Figure 2. The following widely applied kinetic sorption models were used to analyse the experimental data:

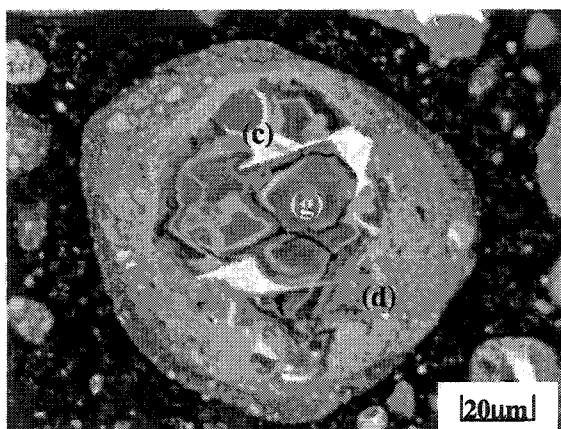
$$\begin{aligned}\text{Ln} [1 - (C_0 - C_t)/(C_0 - C_e)] &= -k/t \quad (\text{reversible first order}) \\ \text{Log} (q_e - q_t) &= \text{Log} (q_e) - k t/2.303 \quad (\text{pseudo-first order}) \\ t/q_t &= 1/(k q_e^2) - (1/q_e) t \quad (\text{pseudo-second order}) \\ q_t &= \ln(ab)/b + (1/b) \ln(t) \quad (\text{Elovich model})\end{aligned}$$

Table 2: Concentrations of dissolved alkali metals & corresponding drinking water standards.

	Ca	Al	Si	Mg	K	Fe
Max. concentration, (mg/l)	650	0.1	16.5	8.5	9	0.15
Drinking water standards, (mg/l)	100	0.1	NA	50	12	0.3

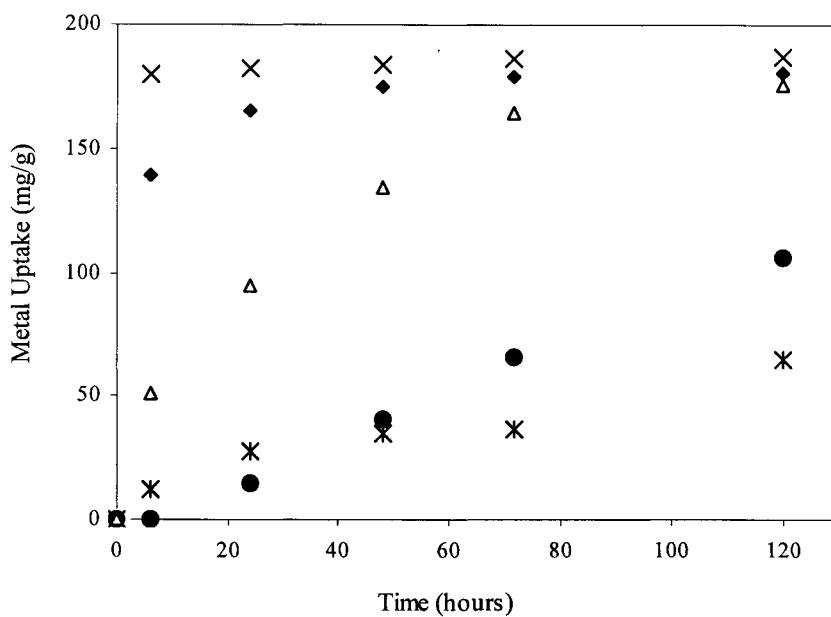


(1)

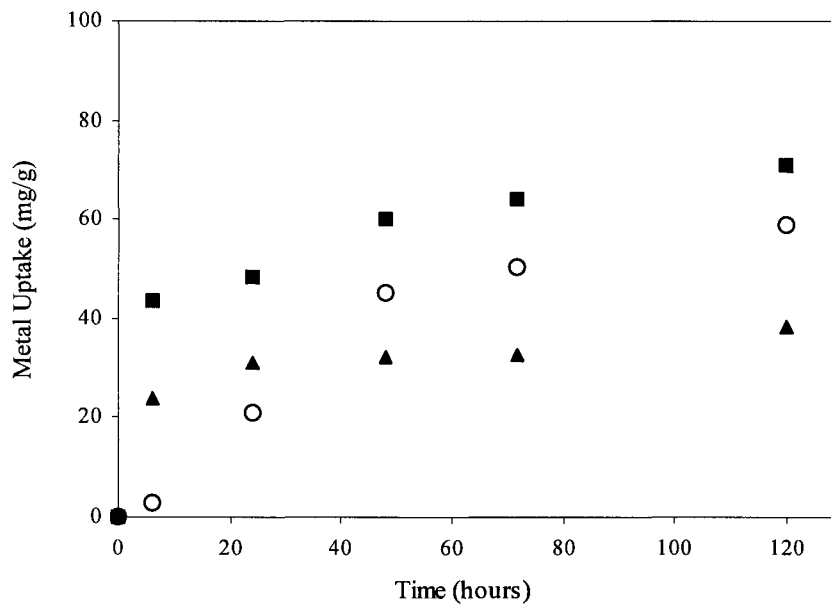


(2)

Figure 1: SEM back scattered electron images of OPC(1) and CASM (2). According to EDAX analysis the following phases are assigned a) C_3S & C_2S ; (b) C_3A ; (c) C_4AF ; (d) $CaCO_3$; (g) amorphous silica.



✖ Lead ◆ Cadmium ● Molybdenum ✖ Nickel △ Chromium



○ Copper ▲ Cesium ■ Cobalt

Figure 2: The kinetics of metal removal.

(where: q_e and q_t are the amounts sorbed at the equilibrium and at time t , respectively; C_e , C_t and C_0 are concentrations of sorbate at equilibrium, at time t and $t=0$, respectively; k is the overall rate constant; a and b are constants related to the rate of chemisorption and surface coverage, respectively.)

The kinetics of the uptake of Cd, Cs, Co, Cr and Pb followed the second-order rate expression. It was found that the Elovich equation was consistent with the experimental data obtained for Cu. The correlation coefficients obtained (>0.93) for these data were relatively high, however, as equilibrium was not achieved for the Mo and Ni solutions the above mentioned models were not applied.

The influence of the initial pH of metal solution on the removal efficiency was largely insignificant, however, a very slight decrease in recorded values for Cs, Ni, Co uptake were obtained at lower pH values of 3–4 units [26]. The reverse trend was observed for molybdenum, which is in oxy-anionic form (in comparison with all other metal species employed in this study which are in simple cationic form).

Microstructural and differential thermal analyses of CASM showed that cadmium and lead formed the carbonate-sulphate-based crystallites: otavite (CdCO_3), cerussite (PbCO_3) and leadhillite ($\text{Pb}_4(\text{SO}_4)(\text{CO}_3)_2(\text{OH})_2$). Copper was present as malachite $\text{Cu}_2\text{CO}_3(\text{OH})_2$ and $(\text{Cu}_2(\text{OH})_3\text{NO}_3)$, whereas chromium precipitated as an amorphous gel (CrOOH). Molybdenum was found to have formed calcium molybdate (scheelite CaMoO_4). Electron probe microanalysis indicated that cesium was exclusively associated with the de-calcified silica structure. Nickel and cobalt also demonstrated affinity to amorphous silica phase, but their distribution suggested that they were also involved in the formation of surface complexes, surface precipitates or as adsorbed ions.

4 Conclusions

The present work has shown that accelerated carbonation technology can be used to convert Portland cement into a material with sorptive potential for heavy metal ions. The carbonated product, CASM, was largely comprised of calcium carbonate and amorphous silica and was successfully used to neutralize and treat concentrated hazardous metal-bearing aqueous liquors, including those containing cesium.

The potential application of accelerated carbonation to calcium silicate/aluminate minerals and by-products in the production of novel sorptive materials has thus been established.

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