

The Influence of Heavy Metals on the Hydration and Carbonation of Ordinary Portland Cement

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Background

The encapsulation of heavy metal waste in cements is an established technology, yet its wide adoption is often precluded by the formation of oxy-anions of amphoteric elements at high pH, which may be mobile species such as plumbate, zincate *etc.* In addition, the long-term stability of cements in the near-surface environment has been criticized, as their inherently high alkalinity may be neutralised by flowing groundwater, principally through reaction with dissolved CO₂.

Alternative solidification-stabilization technology has been developed, which obviates these limits, through rapid carbonation of cement-waste systems. In such systems, the encapsulation medium is dominated by carbonate minerals, in which transition metal ions are held by co-precipitation and (presumably) sorption and physical occlusion. The technology has developed rapidly in recent years and this project seeks to better understand the fundamental mechanisms by which specific elements are retained in carbonated media.

Experimental

Four elements are considered here; Chromium, Copper, Lead and Zinc. Each was prepared as an aqueous solution of its nitrate salt, such that the total metal concentration was 1%, 2.5%, 5% 10% and 15% by mass of solution. The work reported here concerns the 5% solutions and quantities are shown below:

Salt	M ^{Z+} cation / mol.dm ⁻³	Nitrate ion / mol.dm ⁻³	pH
Cr(NO ₃) ₃ .9H ₂ O	9.664e-2	2.899e-1	2.0
Cu(NO ₃) ₂ .3H ₂ O	7.908e-2	1.582e-1	1.6
Pb(NO ₃) ₂	2.425e-2	4.850e-2	4.6
Zn(NO ₃) ₂ .6H ₂ O	7.685e-2	1.537e-1	5.1

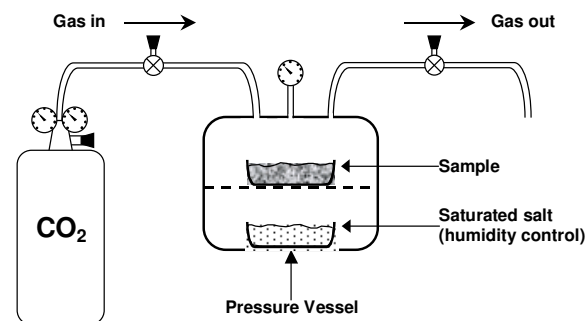
Pure cement minerals (C₃S, C₂S, C₃A, C₄AF, CA and C₁₂A₇) were synthesized from simple metal oxides and carbonates, by repeatedly intergrinding, pelletising and firing in platinum, until they were seen to be phase-pure by XRD analysis. Reactions

of these phases were compared with a Portland cement of the following composition:

SiO ₂	Fe ₂ O ₃	CaO	MgO	Na ₂ O	K ₂ O	Al ₂ O ₃	SO ₃
21.7	3.00	64.2	1.35	0.18	0.65	1.65	3.2

Three sets of experiments were performed, to follow the hydration, aerial carbonation and rapid carbonation of the pure phases and the reference OPC in the presence and absence of the heavy metal solutions.

The solids and liquids were mixed by low-shear mixing, with either deionised water or the metal nitrate solutions. The pure phase pastes were mixed at a water: liquid ratio of 0.4 and a cement slurry was produced at a higher w:s ratio of 1:3. The samples were divided and stored in sealed plastic vessels, a CO₂-filled glove bag for slow hydration and carbonation or rapidly carbonated at high pressure. Each experiment was performed at 17°C. The reaction chamber for the rapid carbonation treatment consists of a pressure vessel through which CO₂ may be passed, prior to closing the exit valve and pressurizing the chamber to 3 Bar. This pressure was held for the duration of the experiment and approximately 50% RH was maintained by a saturated sodium chloride bath below the sample. The apparatus is shown schematically below:



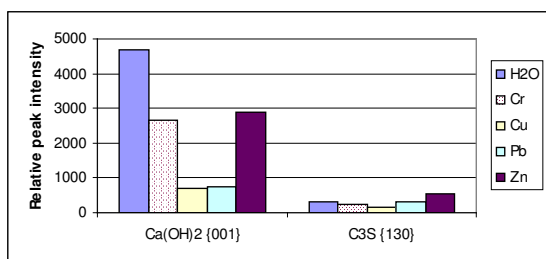
The rapidly carbonated samples, were removed after 30 minutes of carbonation, ground to < 30µm particle size, a sub-sample taken for XRD analysis and the remainder returned to the chamber. The cycle was repeated until non of the anhydrous

phase was detected; between seven and eight cycles.

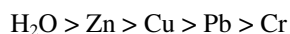
Results

N.B. Only results for tricalcium silicate and tricalcium aluminate are reported here

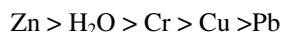
Tricalcium silicate. The hydration of C_3S is well documented and other than minor carbonation of the sample (presumably due to aerial carbonation) X-ray diffraction showed progressive dissolution of C_3S and formation of crystalline portlandite. Copper and chromium appear to accelerate the early dissolution of C_3S , whilst lead and zinc retard the process. This is illustrated after one month in the figure below:



After one year, the relative intensity of the {001} reflection of portlandite is in the following order:



Combined hydration and slow carbonation of C_3S was followed by the growth of calcite, followed by its strong {104} and {110} reflections, which showed the following relative order of carbonation rate after 1 year:

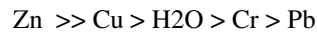


In addition to calcite, the copper-doped samples show some aragonite to have formed, whilst the chromium system contains vaterite.

By comparison, the rapid carbonation experiments show these two meta-stable carbonate phases dominate the system. The samples containing lead and zinc show similar crystalline product as the undoped system, calcite being the dominant crystal phase. The system containing copper however, is dominated by aragonite, whilst that containing chromium shows vaterite to be the most stable carbonate.

Tricalcium aluminate: The C_3A system was treated similarly. After 28 days of hydration, the major products were hydrogrossular (C_3AH_6) the calcium aluminate hydrates (C_2AH_8 , $C_4A_3H_3$, C_4AH_{13} , C_4AH_{19}) and minor quantities of the hemihydrate and monocarbonate ($C_4A\bar{C}H_{11}$ and $C_4A\bar{C}_{1/2}H_{12}$),

showing that the system had partially carbonated. The relative rate of C_3A consumption was in the following order:



It was noted that in the metal-doped systems, the C_4AH_{19} and C_2AH_8 phases persisted whilst re-crystallisation to C_3AH_6 was inhibited.

The hydration and slow carbonation experiments on C_3A , show that after one year, the bulk of the aluminate hydrates had carbonated to calcium hemi- and mono- carbonate.

Accelerated carbonation of C_3A without metal ion addition showed similar reaction products to those of slow carbonation, but with the addition of vaterite. In the presence of the transition metals, the relative rate of carbonation was markedly different, suggesting that metal nitrates promote natural carbonation, but impede rapid carbonation. The reaction of C_3A during rapid carbonation was in the following order:



As with the C_3S system, both aragonite and vaterite were products of rapid carbonation, vaterite being the dominant reaction product. Re-examining the samples for one year after rapid carbonation, shows gradual recrystallisation of both aragonite and vaterite to form calcite.

Discussion

It would appear that rapid carbonation of calcium silicates and aluminates results in the formation of aragonite and especially vaterite in favour of the more stable polymorph, calcite. Incorporation of transition metal ions as calcium substitution in carbonates is to be expected from analogues of natural minerals. Incorporation of zinc into calcite is to be expected, despite their differing ionic radii, and partial solid solution between trigonal calcite and smithsonite ($ZnCO_3$) is seen in nature, an intermediate phase minrecordite $CaZn(CO_3)_2$ though not common, is well documented. Similarly, incorporation of lead (as Pb^{2+}) into the orthorhombic aragonite lattice is seen and tarnowitzite ($CaPb$) CO_3 describes compositions in the aragonite - cerussite ($PbCO_3$) solid solution series.

Curiously, little evidence is seen of lattice-strain associated with these phases was seen during the experiments. The dominance of vaterite in the metal-doped systems is perplexing; its relatively open structure (Hexagonal $P6_3/mmc$) may be capable of incorporating interstitial ions in addition to direct substitution. It is hoped that further experiments will reveal the fate of transition metals in these systems.