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Modification of low-pH calcium aluminate cement to enhance stability for immobilisation of metallic wastes

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ABSTRACT

Cementing systems based on calcium aluminate cement (CAC) have been studied as an alternative cement matrix for the encapsulation of intermediate level wastes (ILW) arising from the nuclear industry. CAC-based systems have great potential for the incorporation of aluminium containing ILW owing to the near-neutral internal pH of these binders. However, CAC-based binders usually undergo phase conversion from the metastable hydration phases C_3AH_{10} and/or C_2AH_8 to the stable CAH_6, resulting in strength regression and dimensional instability. The present study investigates the feasibility of CAC modification to prevent this detrimental process of phase conversion. Two different types of sodium phosphates are used to modify a CAC system, and the setting behaviour and the mineralogy of the binder products studied. It is shown that it is possible to avoid the conventional phase conversion of CAC hydrates due to the formation of an amorphous aluminate phase in place of the metastable hydrates, leading to the production of a phase assemblage which is stable for at least 180 days.

Keywords : Calcium aluminate cement, Phosphate, Conversion, Inhibition, TGA, XRD.

1. INTRODUCTION

Cement encapsulation has been identified as a suitable treatment for intermediate level waste (ILW) arising from the UK nuclear industry[1]. Generally, an ordinary Portland cement (OPC) composite system is favoured, with blast furnace slag (BFS) and pulverized fuel ash (PFA) being common additional components due to the improved material properties achievable[2]. OPC-based encapsulation matrices, with highly alkaline internal environments, reduce the solubility (and hence mobility[3]) of many radionuclides through their precipitation as hydroxides[4]. However, such systems can cause corrosion of aluminium metal found in ILW[5], originating from MAGNOX fuel cladding[6] and reactor components[2]. At high pH, the passivation layer on the surface of the aluminium dissolves (equation 1), revealing fresh sites for corrosion and resulting in hydrogen gas production and expansion (equation 2). This reduces the integrity of the wasteform and can also cause explosion hazards in a repository environment[7].

$$Al_2O_3 + 2OH\ \ + 3H_2O \rightarrow 2Al(OH)_4 \qquad (1)$$

$$Al + 2OH\ \ + 2H_2O \rightarrow Al(OH)_4 + H_2 \qquad (2)$$

Calcium aluminate cements (CACs) have been identified as promising waste encapsulants[3], with some potentially highly desirable properties as a wasteform matrix[1]. In particular, CAC has a lower pH pore solution than pure OPC[8] (where the pH can exceed 13 in a pure OPC system[9]), and hence may be valuable in encapsulating aluminium-containing wastes with minimal aluminium corrosion. However, monocalcium aluminate (CA), the main reactive phase in CAC, hydrates to give various metastable phases, depending on the temperature and chemical environment prevailing during initial mixing and curing, which could reduce the integrity of the material[10]. As shown in equations 3-6, hexagonal crystalline metastable phases (CAH_{10} and C_2AH_8) transform to cubic hydrogarnet (CAH_6) and gibbsite ($Al(OH)_3$). This conversion causes loss of strength, increase in porosity and eventually increases the susceptibility to failure of CAC[10-14]. In addition to the crystalline phases there is also likely to be an amorphous alumina-rich gel phase formed[11, 13, 15].

$$CA + 10H \rightarrow CAH_{10} \tag{3}$$

$$2CA + 11H \rightarrow C_2AH_8 + AH_3 \tag{4}$$

$$2CAH_{10} \rightarrow C_2AH_8 + AH_3 + 9H \tag{5}$$

$$3C_2AH_8 \rightarrow 2C_3AH_6 + AH_3 + 9H \tag{6}$$

Calcium aluminophosphate systems based on modified CACs have also been investigated[14, 16, 17]. As an acidic or near-neutral soluble sodium phosphate is usually combined with CAC, the internal pH of such systems could be lower than that of the unmodified CACs, which may be advantageous for the encapsulation of aluminium-containing wastes. Swift et al.[16] investigated combinations of CAC and various phosphate solutions with the aim of encapsulating Al-containing ILW, and reported marked differences between CACs blended with mono- and poly-phosphates in terms of setting behaviour and hydration products.

This study investigates the feasibility of CAC modification by addition of single or mixed sodium phosphates, to produce a stable CAC-based system. Sodium phosphates with different phosphate chain lengths are used to modify a CAC system, and their setting behaviour, product phases and phase stability analysed in the context of binder design for encapsulation of aluminium-containing ILW.

2. EXPERIMENTAL

Secar 51 CAC (Al_2O_3 ≥50 wt.%, CaO ≤39.5 wt.%, SiO_2 ≤6.0 wt.% and TiO_2 < 4.0 wt.% according to supplier data), supplied by Kerneos, was used as the basis of the binders studied, combined with reagent grade sodium polyphosphate ($(NaPO_3)_n$, 97%, Acros Organics), sodium dihydrogen phosphate dihydrate (monophosphate, $NaH_2PO_4.2H_2O$, 99%, Acros Organics), and distilled water. The water to cement ratio (w/c), excluding the mass of phosphate additions, was maintained at 0.35. The sodium monophosphate to cement ratio (m/c) and polypolyphosphate to cement ratio (p/c) were varied to assess their effect on the cement produced (Table 1). Samples are named according to their p/c and m/c ratios, for example sample 0.4p0.175m has p/c 0.40 and m/c 0.175.

Table 1. Sample formulations for the single and mixed phosphate series analysed, defined according to polyphosphate/CAC (p/c) and monophosphate/CAC.(m/c) mass ratios

	p/c	**m/c**	**w/c**	**Curing temperature**
Unmodified CAC	0	0	0.350	20℃
Single phosphate series	0.40	0		
	0	0.025		
Mixed phosphate series (denoted 0.2p and 0.4p series)	0.20	0.050 - 0.250		
	0.40	0.050 - 0.250		

Monophosphate and/or polyphosphate powders were premixed with the distilled water on roller mixers for 24 h at room temperature. The phosphate solution was then added to the cement during initial hand mixing for 30 seconds, followed by shear mixing using a Silverson L4RT high shear mixer for 120 seconds at 2500 rpm to form a homogeneous paste. The total mass of each batch was 800 g.

After mixing, a 300 g sample of the slurry was tested to assess the setting behaviour using a MASTRAD Vicat penetration apparatus. The error associated with measurements was calculated as ±15 mins via multiple replicate measurements for each formulation. The remaining slurry was cured in sealed plastic centrifuge tubes at $20^{o}C$ for 28, 120 and 180 days. After curing, the hydration process was arrested by crushing the samples into pieces <1 cm^3 and then immersing them in acetone for 2 days. Samples were then dried at room temperature for 24 hours, followed by vacuum dessication at ~50 Torr to prevent carbonation. Samples were further ground and sieved to <63 μm for X-ray diffraction (XRD) analysis with a Siemens D500 Diffractometer (Cu Kα radiation). Thermogravimetric analysis (TGA) was also carried out, with powdered samples heated from room temperature to 1000 ℃ at 10℃/min in an N_2 atmosphere, using a PerkinElmer TG Analyser.

3. RESULTS AND DISCUSSION

3.1. PHASE EVOLUTION IN SINGLE-PHOSPHATE SYSTEMS

After 28 days of curing, all samples produced hard monolithic products. Figure 1 shows XRD data for the single phosphate formulations together with unmodified CAC. As the unmodified CAC showed little difference at the two curing ages, only the data for samples cured for 180 days are shown. The unmodified CAC shows well-defined intense peaks for the conventional stable hydration products hydrogarnet and gibbsite. The metastable hexagonal CAC hydration phases~~,~~ CAH_{10} and C_2AH_8, are not observed after either 28 or 180 days, suggesting that they had already converted to the stable hydrogarnet (C_3AH_6) and gibbsite. In addition, the phases in the remnant anhydrous CAC, being CA, C_2AS and CT, are also detected.

The monophosphate-only sample, 0p0.025m, does show the presence of metastable hexagonal CAC hydration phases~~,~~ CAH_{10} and C_2AH_8, together with the stable C_3AH_6 and gibbsite and CAC clinker phases, after 28 days of curing. After 180 days, the intensities of the peaks attributed to the stable C_3AH_6 and gibbsite increase significantly, while the metastable phases and unreacted CA precursor decrease. These results indicate that the monophosphate was retarding both the conventional hydration and conversion of CAC, maintaining the metastable phases beyond the timescale on which they are detected in the unmodified system.

On the other hand, the sample with only polyphosphate, 0.4p0m, shows neither the conventional CAC hydration products nor any other crystalline hydration products. This is a radical modification of CAC hydration, as previously reported in a similar system after 7 days, where the phosphate addition results in the formation of amorphous binding phase[18]; these results show that this modification extends to a curing duration of 180 days. This amorphous phase must be responsible for the hardening of the paste, and is identifiable through the broad humps in the diffractogram of this sample in Figure 1 at 25-35° 2θ. The polyphosphate appears to have inhibited the formation of crystalline hydration products, including the metastable ones, for 180 days by forming an amorphous phase that appears to be stable on this timeframe. Thus, the introduction of polyphosphate to the CAC may allow the system to limit the conversion process observed in unmodified CAC, and the associated issues of dimensional instability.

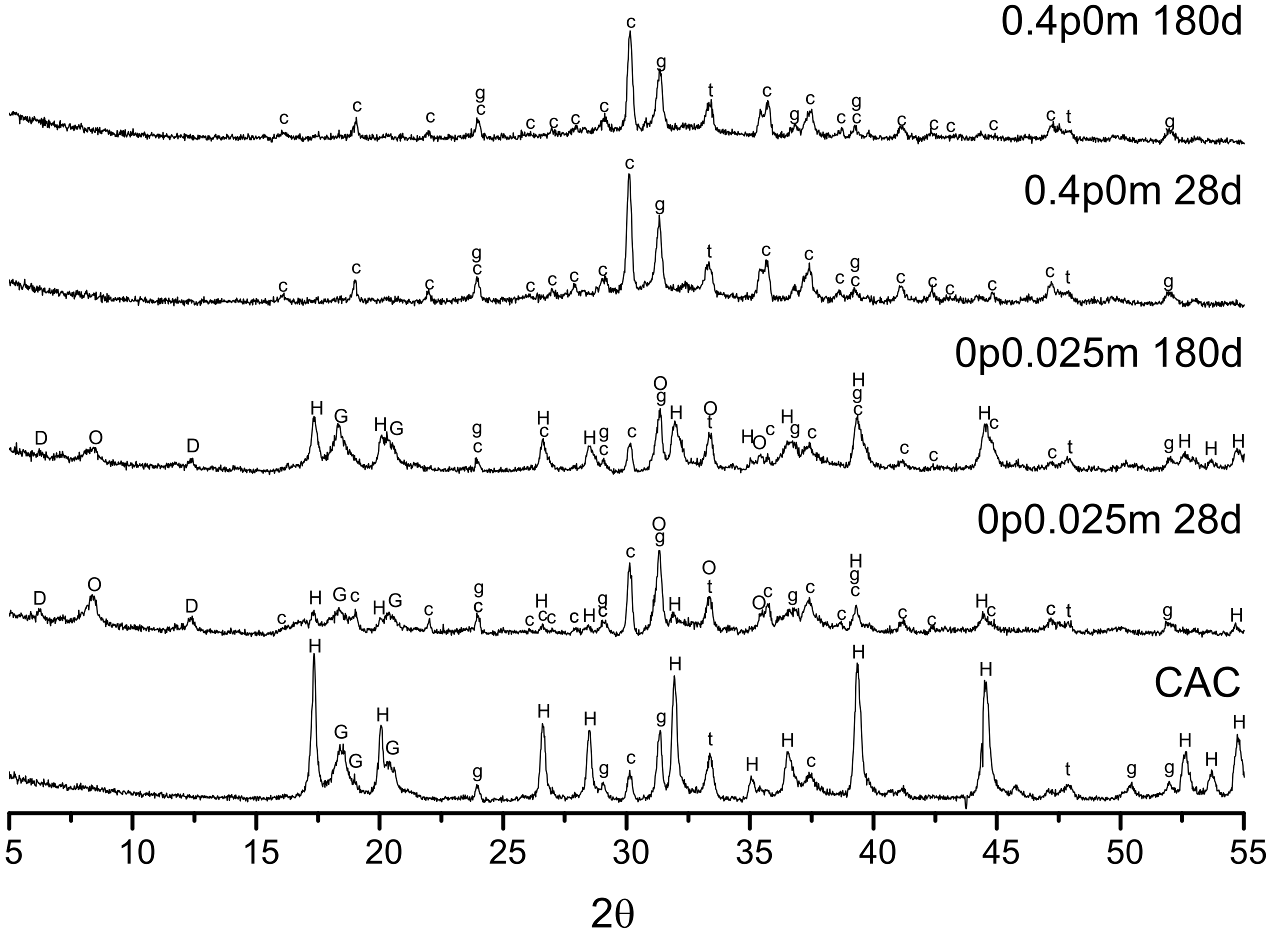

Figure 1. XRD data for single phosphate samples, 0.4p0m and 0p0.025m, at 28 and 180 days of curing, compared against unmodified CAC after 180 days curing. Letters indicate monocalcium

aluminate (CA, c), gehlenite (C_2AS, g), calcium titanate (CT, t) and CAC hydration phases CAH_{10} (D),C_2AH_8 (O), hydrogarnet (C_3AH_6, H), and gibbsite (AH_3, G).

Figure 2 shows the weight loss as a function of the temperature obtained via TGA, and the first derivative of this (DTG), for single-phosphate formulations cured for 28 and 180 days, as well as data for unmodified CAC. The results for the unmodified CAC sample indicate very little change in the products between 28 and 180 days, in accordance with the diffraction data. Therefore, only the 180 days data are shown for the unmodified CAC.

The two weight loss events observed for the unmodified CAC sample, in the ranges 275-300℃ and 300-315℃, are attributed to the presence of AH_3[17] and C_3AH_6[18] respectively. The minimal weight loss in the range 80-125℃ indicates the absence of loosely bound water.

The monophosphate-containing formulation 0p0.025m shows a weight loss at 75-110℃, in the region relating to loosely bound water, with an additional weight loss in the range of 125-170℃, which corresponds to the presence of CAH_{10},[13] as confirmed by XRD. The weight losses associated with AH_3 and C_3AH_6 are also present in this sample, confirming the observations from XRD.

The polyphosphate-containing sample 0.4p0m shows a broad weight loss peak at low temperatures at both ages studied. As this does not correlate to the dehydration of any known CAC hydration products, this weight loss may relate to the dehydration of the amorphous phase formed in the system. This sample also shows another weight loss event in the range 250-280℃ which appears to increase over the curing time. Although this could be assigned to the dehydration of AH_3, this phase was not identified in the XRD results, which indicates that the amorphous phase is likely to contain Al and hydroxyl groups in environments resembling those of AH_3. The low-temperature peak assigned to the dehydration of the amorphous phase becomes more distinctive as the curing time increases. Since the total weight loss up to ~200°C did not change significantly, this phase appears to retain the same amount of water while evolving a more ordered local structure over the curing period of 180 days, as a more-ordered phase is expected to show a more distinctive TG response compared with a highly disordered structure.

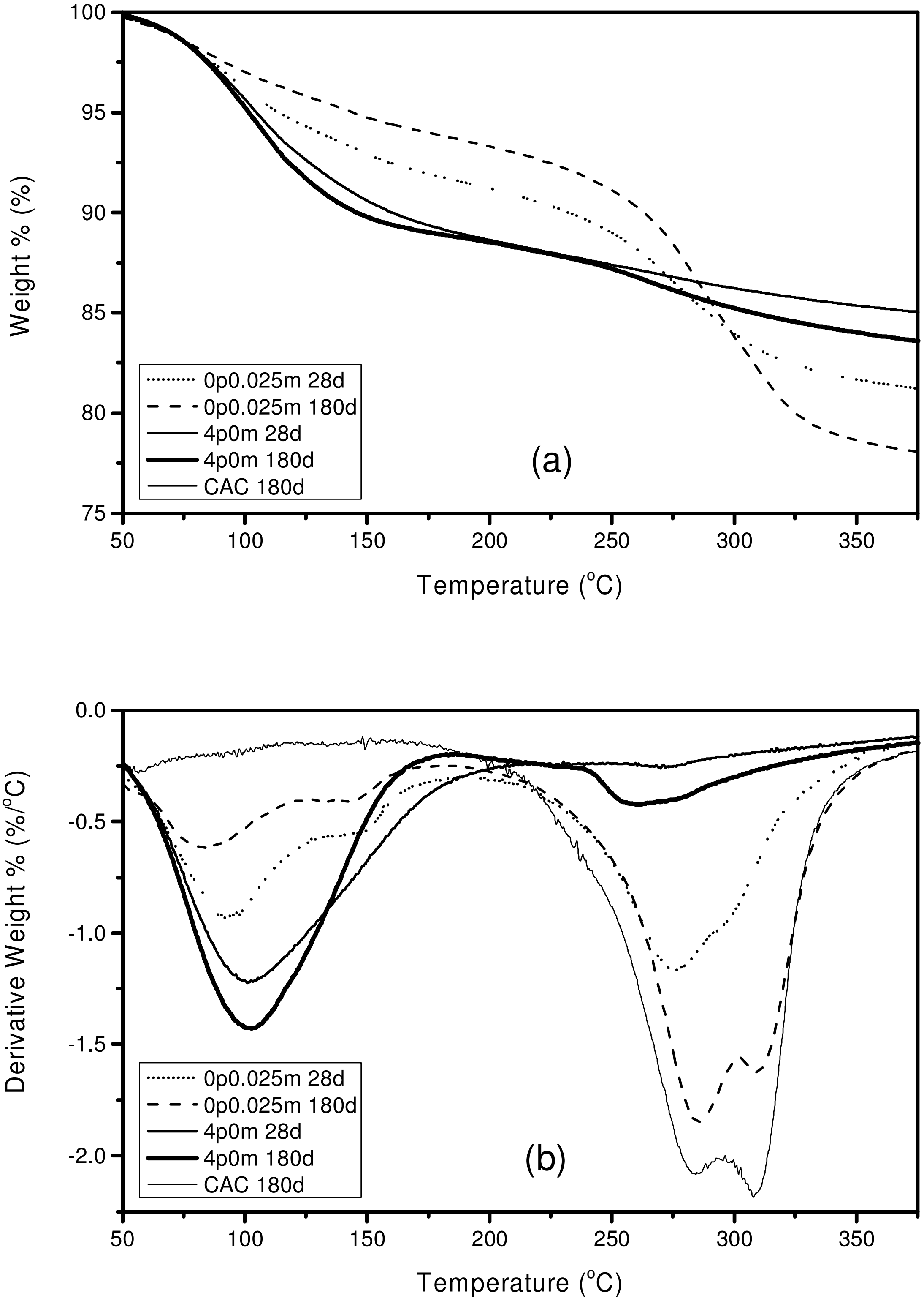

Figure 2. (a) TGA and (b) DTG data for the single phosphate samples cured for 28 and 180 days, compared with unmodified CAC cured for 180 days.

3.2. SETTING BEHAVIOUR OF MIXED-PHOSPHATE SYSTEMS

All samples with addition of mixed mono- and poly-phosphates hardened; Vicat initial and final setting times for both the 0.2p and 0.4p series are shown in Figure 3. Both the initial and final setting times depend strongly on the monophosphate content, but the effect was not monotonic. The 0.2p series generally had much shorter initial and final setting times than 0.4p. The use of sodium monophosphate as a setting retarder for CAC has been documented previously[10], but it is seen here that excess doses of this additive cause the loss of this retarding effect. The maximum initial and final setting times were achieved at slightly different m/c ratios in the two series. For the 0.2p series, m/c ratios of 0.075 and 0.1 were identified as giving the maximum initial and final setting times, respectively, whereas ratios of 0.05 and 0.075 were identified as giving these maxima for the 0.4p series. The greatest extent of retardation of the initial or final sets for the two series did not occur at the same m/c ratio, but the ratio between mono- and poly-phosphates (m/p) at the longest setting time for the 0.2p series coincides with the second retardation peak for the 0.4p series, suggesting that the retardation may be related to some extent to the interaction between mono- and poly-phosphates.

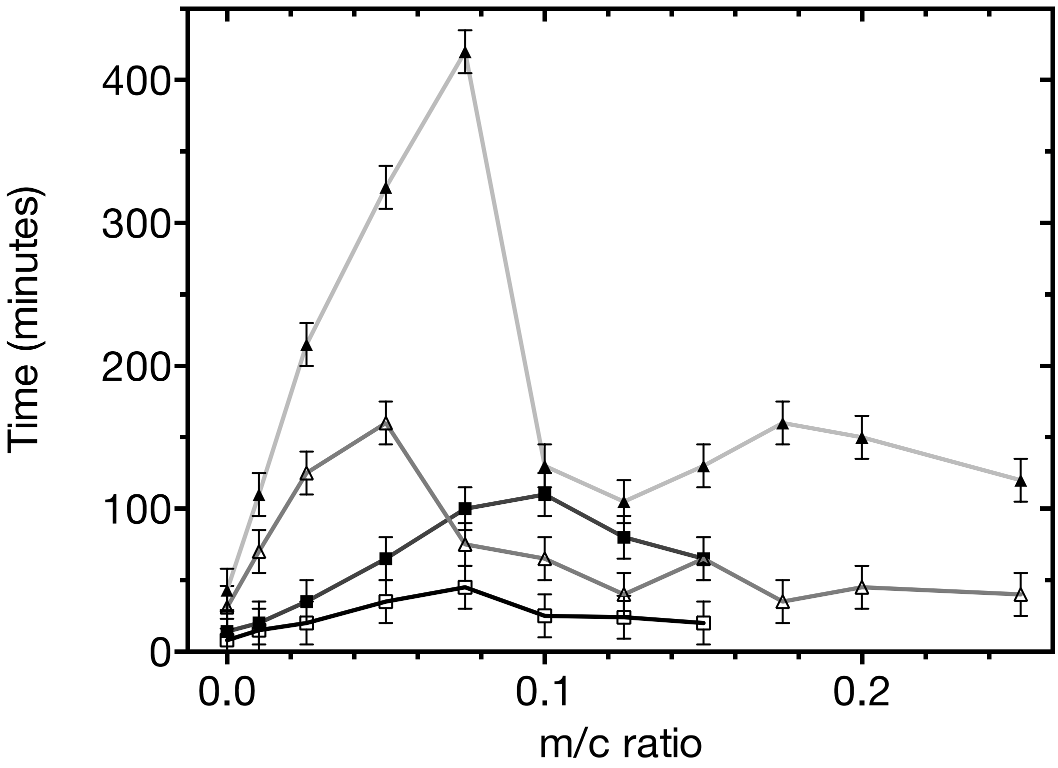

Figure 3. Vicat setting data showing 0.2p series initial (□) and final (■) setting times, and 0.4p series initial (∆) and final (▲) setting times.

3.3. PHASE EVOLUTION IN MIXED-PHOSPHATE SYSTEMS

Typical examples of the XRD data for the 0.2p0.075m and 0.4p0.075 formulations at two different ages are shown in Figure 4. Very little difference was noted in the diffraction data with different monophosphate contents.

At 28 days, the data for the 0.2p samples show that the conventional hydration of CAC has been altered considerably, with a high prevalence of unreacted clinker phases and only a small amount of AH_3 formation. The identification of hydrogarnet (C_3AH_6) was inconclusive, as the peaks are of similar intensity to the background. After 180 days, the formation of the conventional CAC hydration products AH_3 and C_3AH_6 was pronounced, with a reduction in the proportion of unreacted clinker phases. It must be noted that the unreacted clinker phases persist up to 180 days, whereas the unblended CAC system showed the significantly less presence of these phases even after 28 days. These data indicate the mixed effects of mono- and poly-phosphates discussed in the previous section. The conventional CAC hydration process was inhibited initially, but the conventional stable phases were eventually formed over time.

The XRD results for the 0.4p mixed-phosphate series were significantly different, and resembled the 0.4p single-phosphate samples. The 28 day sample indicates no formation of conventional crystalline CAC hydration products, although the Vicat data showed that the material had hardened at within the first four hours after mixing. The absence of these phases persisted to 180 days of curing. The absence of the peaks for conventional hydration products indicates either (i) a retarding mechanism similar to that in 0.2p series, but to a much greater extent, or (ii) that a different mechanism is inhibiting the conventional hydration process. The latter seems much more likely, because the additional setting retardation in the 0.4p series was not significant enough to cause such a dramatic difference after 180 days of curing in a hardened binder. The presence of one or more amorphous phases, formed as a result of the phosphate modification, can be corroborated by a region of diffuse scattering in XRD data in the range of 25-35° 2θ as noted above for the polyphosphate-only systems. As no crystalline compounds containing sodium and/or phosphorous were identified, this amorphous phase may be identified as being rich in these elements in addition to Ca and Al supplied by the CAC.

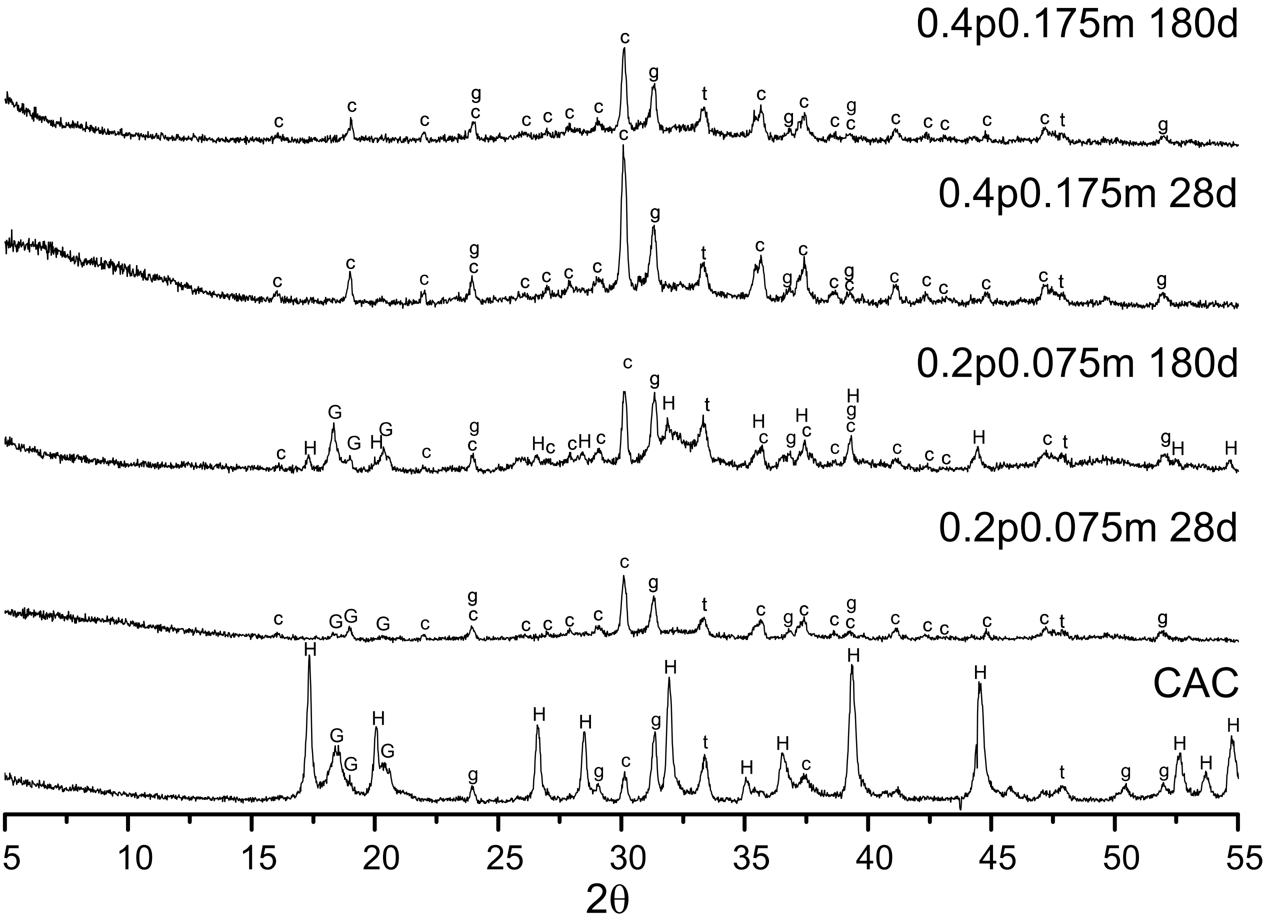

Figure 4. XRD data for mixed-phosphate samples 0.4p0.175m and 0.2p0.075m at 28 and 180 days of curing, compared to unmodified CAC after 180 days of curing. Letters indicate monocalcium aluminate (CA, c), gehlenite (C_2AS, g), calcium titanate (CT, t) and CAC hydration phases hydrogarnet (C_3AH_6, H), and gibbsite (AH_3, G).

Similar to the XRD results, the TGA data (Figure 5) show the mixed effects of mono- and polyphosphate in the 0.2p samples. Although hydration was inhibited at first, a significant formation of AH_3 and CAH_6 was observed over the longer curing period of 180 days, consistent with XRD data. The apparent reduction in the amorphous phase content (low temperature mass loss) could be related to the formation of AH_3 or C_3AH_6. These results suggest that a polyphosphate to cement ratio of greater than 0.2 is required to inhibit AH_3 and C_3AH_6 phase formation for 180 days.

The TGA results for the higher polyphosphate content samples, as exemplified by the 0.4p0.025m sample in Figure 5, are very similar to those for the polyphosphate-only sample shown in Figure 2. This suggests that the effect of polyphosphate is dominant in this system. The 0.4p mixed-phosphate samples showed an increase in the amorphous phase content, from 28 to 180 days, which is different from the trend in the 0.4p single phosphate sample, suggesting that the retarding effect of monophosphate also contributes to the formation of this phase.

For the case of the low temperature amorphous phase dehydration event, the relative weight loss between 0.2p and 0.4p samples of the same age is determined by the phosphate content, supporting the basis for the identification of this peak as the dehydration of an amorphous phosphate phase. In unblended CAC systems it may also be attributed to the dehydration of CAH_{10}[13] or the presence of alumina gels[11], but CAH_{10} was not observed by XRD. The 0.2p mixed phosphate series did show a small difference in the amount of amorphous phase detected between the two ages, but there was a marked increase in the gibbsite and hydrogarnet phases, consistent with the XRD data. However, this does not necessarily imply that there is no conversion from the amorphous phase into gibbsite or C_3AH_6, because the formation of the amorphous phase may also be ongoing to replace any material which is converted.

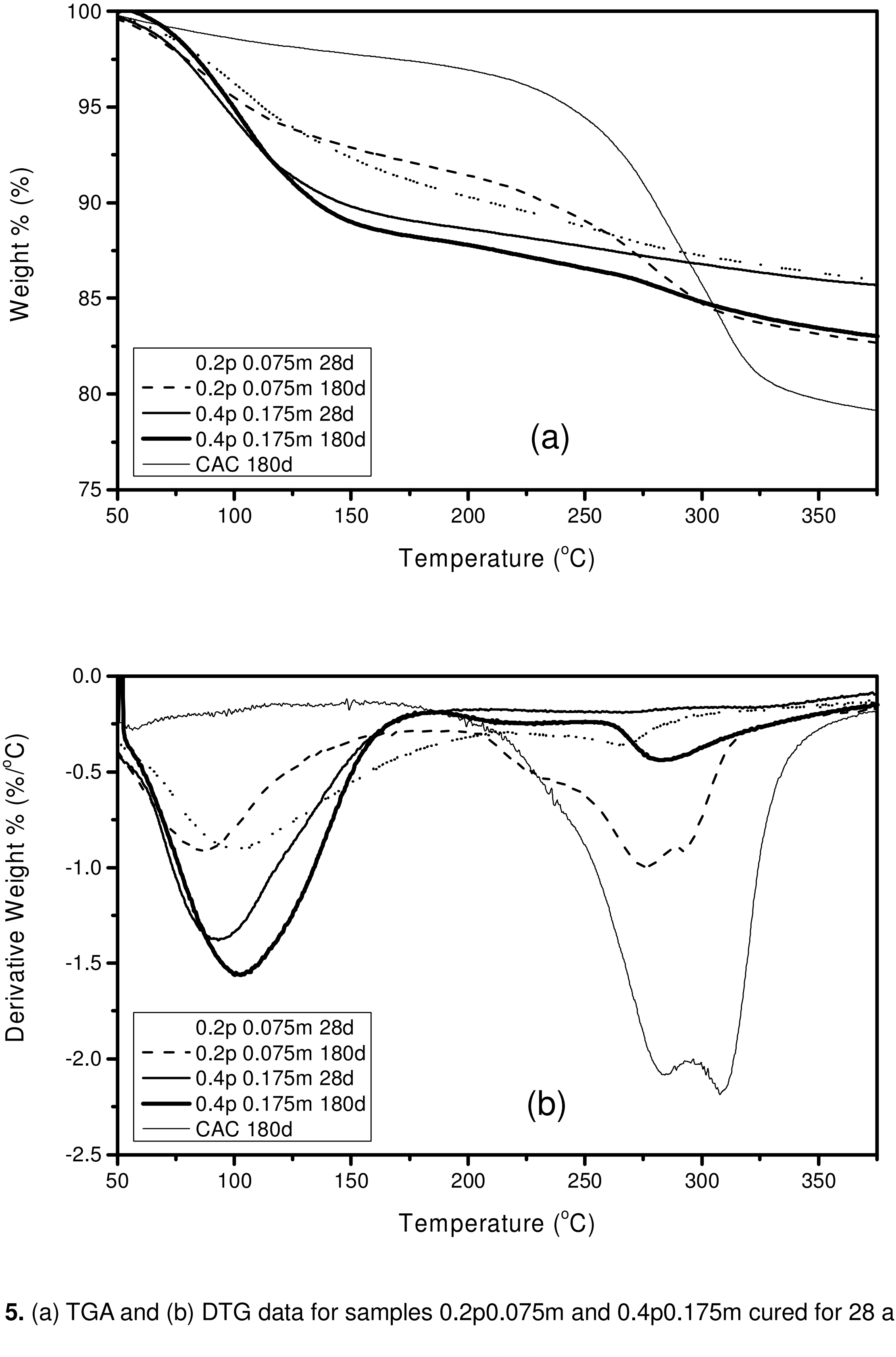

Figure 5. (a) TGA and (b) DTG data for samples 0.2p0.075m and 0.4p0.175m cured for 28 and 180 days, compared with unmodified CAC cured for 180 days.

3.4. DISCUSSION AND IMPLICATIONS OF RESULTS

Ma and Brown[19] have previously discussed the possibility of formation of an amorphous C-A-P-H gel phase with loosely bound water in phosphate-modified calcium aluminate binders; such a phase may be the amorphous phase identified from the DTG and XRD data here. With the absence of the conventional strength-providing CAC hydrate phases such as CAH_{10} and C_2AH_8, this amorphous phase must be the primary binding phase when phosphate is introduced. The effect of phosphate content on Vicat setting time measurements also indicates that this amorphous phase may be a product of the phosphate modification, consistent with the fact that the weight loss at approximately 100°C is greater with increasing phosphate content.

The retarding mechanism of inorganic salt admixtures, as described by Thomas et al.,[20] is based on the precipitation of a gelatinous colloidal material between cement grains (probably containing phosphate in this case), which restricts diffusion of the calcium and aluminium from the surface of the cement particles. However, this phase does allow some diffusion, and so the hydration process is retarded rather than entirely inhibited. At higher monophosphate contents, a sharp decrease in the setting times is observed (Figure 3).

The inhibition by the polyphosphate, however, is likely to follow a different mechanism. Rather than the formation of a diffusion barrier on and around the surface of the cement particles, there is also likely to be phosphate complexation of the calcium[21] and/or aluminium[22] ions that diffuse from the cement particles into a gel phase, preventing the expected calcium aluminate hydrates from forming. This gel phase must also act as a diffusion barrier, and may be similar to the amorphous C-A-P-H gel of Ma and Brown[19]. The formation of this phase is rapid, as seen in the Vicat testing, and hence sodium polyphosphate appears to act as a setting accelerator but also modifies the products of standard CAC hydration.

4. CONCLUSIONS

Phosphate-modified CAC samples with varying sodium monophosphate and sodium polyphosphate contents can set and attain hardness. One or more amorphous phases result from phosphate modification of CAC, potentially including a C-A-P-H gel, which is believed to be responsible for strength development in the mixed mono-/poly-phosphate samples. Sufficient polyphosphate content can inhibit the precipitation of conventional crystalline CAC hydration phases for at least 180 days, and also reduces the extent of hydration of the CAC. It is proposed that the mechanism of inhibition of conventional hydration is via the complexation of calcium and aluminium ions in the C-A-P-H gel formed as a direct result of the polyphosphate modification of the CAC. The monophosphate is thought to be retarding the hydration via the formation of a diffusion barrier and hence only affects the dissolution and precipitation rates of conventional CAC hydration phases. The low pH chemistry of the CAC system in addition to the enhanced phase stability up to 180 days indicates suitability for the encapsulation of aluminium containing intermediate level waste.

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