

promoting access to White Rose research papers



Universities of Leeds, Sheffield and York
<http://eprints.whiterose.ac.uk/>

This is an author produced version of a paper published in **Advances in Applied Ceramics**.

White Rose Research Online URL for this paper:
<http://eprints.whiterose.ac.uk/76060>

Published paper

Swift, P., Kinoshita, H., Collier, N. and Utton, C. (2013) *Phosphate-modified calcium aluminate cement for radioactive waste encapsulation*. *Advances in Applied Ceramics*, 112 (1). pp. 1-8. ISSN 1743-6753
<http://dx.doi.org/10.1179/1743676112Y.0000000033>

Phosphate-modified calcium aluminate cement for radioactive waste encapsulation

P. Swift*¹ (p.swift@sheffield.ac.uk), H. Kinoshita¹ (h.kinoshita@sheffield.ac.uk), N. C. Collier² (nick.collier@nnl.co.uk), C. A. Utton¹ (c.utton@sheffield.ac.uk),

¹Immobilisation Science Laboratory, Department of Materials Science and Engineering, The University of Sheffield, Sir Robert Hadfield Building, Portobello Street, S1 3JD

²Immobilisation Science and Technology Team, National Nuclear Laboratory, Chadwick House, Warrington Road, Birchwood Park, Warrington, WA3 6AE

* Corresponding author, email p.swift@sheffield.ac.uk

Abstract

The present study is part of a wider investigation to develop an alternative cementing system for the encapsulation of problematic low and intermediate level radioactive waste. It has been suggested that alternative cementing systems, with lower internal pH than conventional Portland cement-based composite cements may reduce the corrosion of some reactive metals and may be beneficial for the long-term durability of wasteforms. A potential alternative is an acid-base cementing system, based on mixing calcium aluminate cement with acidic phosphate solutions. Although these systems have been studied previously, there has been no systematic investigation to identify phosphates for producing suitable matrices for application in radioactive waste encapsulation.

In the current study monophosphate-modified calcium aluminate cement formulations did not set or develop significant strength, whereas polyphosphate-modified calcium aluminate cement formulations exhibited rapid setting and strength development. It is proposed that polyphosphate-modified systems form amorphous reaction products, which act as binders between the partially- and un-reacted calcium aluminate cement particles, and were responsible for high strength development. Thermogravimetric analysis and scanning electron microscopy results suggest that this binding matrix consists of amorphous calcium phosphate and alumina gel. The results presented in this investigation suggest that polyphosphate-modified calcium aluminate cement has potential as an alternative cementing system for radioactive waste encapsulation.

Keywords: Calcium Aluminate Cement; Calcium Phosphate Cement; Encapsulation; Immobilisation; Aluminium; Corrosion

1. Introduction

Cementation has become the accepted method for the immobilisation of low and intermediate level radioactive waste (LLW and ILW respectively) in the UK^{1, 2}. Current systems, known as composite cements, are based on Portland cement with high replacement levels of blast furnace slag (BFS) or pulverised fuel ash (PFA). However, there are compatibility issues between these composite systems and some wastes. The high internal pH ($> 12.8^3$) and availability of free water in Portland cement-based composite cementing systems cause corrosion of reactive metals such as aluminium⁴. Aluminium, along with magnesium and uranium arise from the Magnox waste stream, and represent a significant proportion of the UK's LLW and ILW⁵. The corrosion of these reactive metals results in expansive reaction products and the generation of considerable amounts of hydrogen gas, both of which compromise the integrity of the solid wasteforms^{4, 6}. Therefore, it has been deemed necessary to develop alternative cementing systems which are compatible with these reactive metals^{6, 7}. The present investigation is part of a wider project to formulate an alternative cementing system to incorporate certain problematic reactive metals from the UK nuclear industry without detrimentally affecting the resultant wasteform.

Acid-base cements (ABCs), such as magnesium phosphate cement and calcium phosphate cement, have been identified as potential alternative cementing systems⁶. ABC are formed by the reaction of a base, usually a cation-leachable powder, with an acidic solution. They have unique properties, such as rapid setting and strength development, and good durability in harsh conditions⁸. ABCs have primarily been used in small quantities in biomedical applications; as bone replacement materials and for dental repairs⁹. Due to the acid-base nature of these systems, the resulting hardened cement pastes should exhibit a lower internal pH than the conventional Portland cement-based composite cement systems¹⁰. Therefore, they may have the potential to encapsulate problematic LLW and ILW without causing significant corrosion.

Various researchers have studied the modification of calcium aluminate cements (CAC) by different phosphates for industrial applications. Most of the available literature has been published by Sugama *et al.*¹⁰⁻¹⁹. They developed phosphate-modified CAC for geothermal well applications. Acid-base reactions between CAC and acidic phosphate-based solutions produced cementitious matrices, which were then hydrothermally treated. It should be noted that most of the work reported by Sugama *et al.* involved elevated temperatures (*e.g.* 100-300°C) to simulate the conditions of a geothermal well. In early studies, Sugama and Carciello^{13, 15, 16} mixed Poly-N

(an ammonium phosphate-based fertiliser) with commercially available CAC. The resulting cements exhibited rapid setting and strength development of > 20 MPa after 1 h at 25°C. Fourier-transform infra red spectroscopy (FTIR) suggested that amorphous ammonium calcium pyrophosphate ((NH₄)₂Ca(P₂O₇)·xH₂O) was the principle reaction product, and was responsible for strength development. Although, in a later study¹² this was revised to amorphous ammonium calcium orthophosphate (NH₄CaPO₄·xH₂O). However, subsequent hydrothermal treatment resulted in the liberation of ammonia, which was deemed environmentally questionable. As a result, Sugama and Carciello¹⁷ investigated sodium phosphate compounds (sodium monophosphate (NaH₂PO₄) and sodium polyphosphate ((NaPO₃)_n)) as alternative precursor powders. It was reported that sodium polyphosphate reacted more favourably than sodium monophosphate with CAC, resulting in compressive strength > 6.85 MPa after 24 h at 25°C. FTIR results suggested that sodium calcium orthophosphate hydrate (NaCaPO₄·xH₂O) and alumina gel were responsible for strength development in these systems. Although, in a later study Sugama *et al.*¹⁸ revised this, instead proposing that the binding matrix responsible for strength development was calcium hydrogen phosphate hydrate (Ca(HPO₄)·xH₂O) and alumina gel. Ma and Brown²⁰ studied the effect of various sodium phosphates and a calcium phosphate modifications on the mechanical properties of CAC. They concluded that high flexural strengths can be achieved by the modification of CAC by various phosphates, and the strength is dependent on the type of phosphate as well as the phosphate concentration. In a later study²¹, Ma and Brown studied CAC modified by various sodium phosphates using isothermal calorimetry, powder X-ray diffraction (XRD) and environmental scanning electron microscopy (ESEM). They proposed that hydration of CAC was accelerated by phosphate-based modifications. Their XRD results showed that crystalline hydration products do not form. It was suggested that amorphous calcium aluminate phosphate hydrate (C-A-P-H) was responsible for strength development. Walter and Odler²² investigated the setting and mechanical properties of cement resulting from mixing CAC with various sodium polyphosphates, having varying chain lengths. They concluded that phosphate-modified CAC resulted in amorphous reaction products, and setting and mechanical properties could be controlled by the chain length of sodium polyphosphate used.

Several characteristics, such as setting time, slurry fluidity, heat of hydration, generation of bleed water, and compressive strength should be considered when developing cementing systems

in terms of practical application. For example, the initial setting time should be such that the cement does not set before it has been cast, *e.g.* Initial set > 4 h^{23, 24}. The final setting time should be such that the resulting wastepackage can be moved and transported after 24 h.

In the present investigation, modification of CAC by various monophosphate- and polyphosphate-based solutions was studied in order to identify a suitable phosphate powder for use in producing an appropriate cement matrix for the encapsulation of LLW and ILW. Until now, there has been no systematic study to identify a suitable phosphate precursor for the synthesis of a cementing system for radioactive waste encapsulation. As candidate phosphates, some phosphate powders reported in the literature^{17, 20, 21} were selected in addition to NaH₂PO₄·2H₂O, NH₄H₂PO₄ and KH₂PO₄. Setting times and strength development, which are important properties for practical application, were investigated using Vicat measurements and compressive strength tests. Phase analysis of each system was also conducted using XRD and thermogravimetric analysis (TG). The use of TG to assess phosphate-modified CAC has not been reported previously in the literature. Selected systems were further investigated using scanning electron microscopy (SEM) incorporating energy dispersive X-ray spectroscopy (EDX)

2. Experimental

Table 1 shows the constituents of the formulations investigated, with the relative proportions normalised to 100g of CAC. A commercially available CAC (Secar 51, supplied by Kerneos UK) was used as the basic-solid reactant. The composition of the CAC is shown in Table 2, determined by X-ray fluorescence (XRF). XRD confirmed the major crystalline phase to be monocalcium aluminate (CAⁱ, ICDD file no. 23-1036), with gehlenite (C₂AS, ICDD file no. 79-1726) and perovskite (CT, ICDD file no. 42-423) also present as secondary phases. Three monophosphates, NaH₂PO₄·2H₂O (Alfa Aesar, 99%), KH₂PO₄ (Acros Organics, 99+%), NH₄H₂PO₄ (Alfa Aesar, 98%) and two polyphosphates, (NaPO₃)_n (Acros Organics, pure) and (NaPO₃)₆ (Fisher Scientific, general purpose grade) were investigated in the present study. Each phosphate was mixed with distilled water to make up a variety of acidic phosphate-based solutions prior to adding CAC. The water/cement ratio (w/c) and phosphate/cement ratio (p/c) of

ⁱ Cement chemistry nomenclature: C = CaO, A = Al₂O₃, S = SiO₂, T = TiO₂, H = H₂O

the formulations were 0.37 and 0.2, respectively. Samples of unmodified Secar 51 were hydrated at the same w/c (0.37) to allow direct comparison with the phosphate-modified systems.

Table 1 also shows the analyses undertaken after specific curing periods. Samples for setting time measurements were prepared by adding CAC to the prepared phosphate solutions over a period of *ca.* 1 min and hand mixing for *ca.* 2 min. Setting times were measured using automatic Vicat measuring apparatus, based on BS EN 196-3:2005+A1:2008²⁵. The samples for compressive strength measurements were prepared by adding the CAC to prepared phosphate solutions in a Kenwood bench-top planetary mixer over a period of *ca.* 1 min, and mixing at speed setting 1 (*ca.* 150 rpm) for *ca.* 5 min. The resulting cement slurry was then poured into triplicate stainless steel moulds (50 x 50 x 50 mm), and cured in an environmental chamber at 20°C and > 95 % RH. The compressive strengths of selected formulations were measured at 1, 3, 7, 14 and 28 days of curing using a Controls Automax5 automatic compressive strength testing machine, taking the average compressive strength of three specimens for each formulation and age.

Samples were also prepared to analyse the phase composition and microstructure of the resulting cement pastes using XRD, TG, and SEM/EDX. For these samples, CAC was added to the prepared phosphate solution and mixed by hand for *ca.* 2 min. The cement slurry was then cured in sealed 50 ml centrifuge tubes at room temperature (20 ± 3 °C) for 7 days. After curing, the samples were crushed and immersed in acetone for 3 days and dried in a vacuum desiccator for 7 days to arrest hydration and remove free water. XRD was performed with a Siemens D500 diffractometer using Cu K_{α} radiation ($\lambda = 1.54178 \text{ \AA}$) over the range 5-65° 2 θ , with a step size of 0.02° and scanning speed of 2° 2 θ /min. TG was performed using a Perkin Elmer Pyris 1 Thermogravimetric analyser, under a nitrogen atmosphere with a heating profile of 10°C/min over the temperature range 40-1000°C. Analysis by SEM was undertaken on a polished and carbon coated sample mounted in epoxy resin using a Jeol JSM 6400 scanning electron microscope with integrated Link ISIS EDX analyser.

3. Results and discussion

3.1. Setting and strength development

Table 3 shows the results from Vicat setting time measurements for phosphate-modified CAC and unmodified CAC. The unmodified CAC system exhibited initial and final setting times of

330 and 390 min, respectively. The results show that phosphate modifications decreased the initial setting time of CAC. Although monophosphate-modified systems exhibited an initial setting time ranging from 5-180 min, they did not exhibit a final set. In other words, the monophosphate-modified CAC showed some degree of thickening, but did not fully harden. As such the compressive strengths of these systems were not determined.

The $(\text{NaPO}_3)_n$ - and $(\text{NaPO}_3)_6$ -modified formulations exhibited rapid setting, with initial and final set of *ca.* 5-6 min and *ca.* 11-12 min respectively. On setting, these polyphosphate-modified CAC systems produced a significant exotherm, though no quantitative data was obtained. This exotherm was attributed to the acid-base setting reactions. Both polyphosphate-modified systems attained compressive strengths of *ca.* 75 MPa after 24 h, compared to *ca.* 40 MPa for conventionally hydrated CAC (Figure 1). The strength of $(\text{NaPO}_3)_n$ - and $(\text{NaPO}_3)_6$ -modified systems increased over the first 3 days of curing, then exhibited further strength development to 95 MPa after 28 days of curing, which was more than four times the compressive strength of the conventionally hydrated CAC system at the same age. Sugama and Carciello¹⁷ studied compressive strength of sodium monophosphate- and sodium polyphosphate-modified CAC after 24 h curing at room temperature, with varying concentration of phosphate solutions. Similarly, they reported that monophosphate systems did not set and as such compressive strength could not be measured. Their sodium polyphosphate systems attained compressive strengths between 6.85-28.42 MPa (data points shown in Figure 1) which are significantly lower than the strength obtained in the present study.

The unmodified CAC system exhibited rapid strength gain in the first 24 h of curing, which was followed by a strength regression up to 14 days, after which the strength appeared to plateau. This strength regression up to 14 days is attributable to the thermodynamically driven metastable to stable phase conversion reactions, which are widely discussed in the literature²⁶⁻²⁹.

3.2. Phase analysis

Figure 2 shows the XRD results for the systems investigated in the present study. In anhydrous CAC, CA was the principle crystalline phase present, and C_2AS and CT are present as secondary phases. When hydrated for 7 days, calcium aluminate hydrate phase, tricalcium aluminate hexahydrate (C_3AH_6 , ICDD file no. 76-557), and gibbsite ($\gamma\text{-AH}_3$, ICDD file no. 70-2038) were identified. The CA-related reflections, the principal of which was observed at *ca.* 30° 2θ ,

decreased in intensity due to CA being consumed in the hydration reactions. The reflections relating to C_2AS and CT also remained present with little or no loss in intensity, suggesting they took little part in the hydration reactions.

The XRD results of the phosphate-modified formulations were very similar to that of anhydrous CAC. The crystalline phases identified were identical to those in the anhydrous CAC powder, with CA present as the principle crystalline phase, and C_2AS and CT present as secondary phases. The $(NaPO_3)_n$ -based system also exhibited very weak reflections associated with the stable crystalline hydrate phase, C_3AH_6 . In some formulations, the intensities of CA-related reflections (*e.g.* the principle reflection at *ca.* $30^\circ 2\theta$) had significantly decreased compared to that of anhydrous CAC powder, suggesting that CA had been consumed in reactions. Polyphosphate modifications caused a larger reduction in the intensity of the CA-related reflections, which was symptomatic of more CA having been consumed in these systems. However, as no significant crystalline hydrate phases were identified, except the minor formation of C_3AH_6 in $(NaPO_3)_n$ -based system, introduction of phosphate must have modified the normal hydration mechanism of CAC, and produced amorphous reaction products. Ma and Brown^{20, 21} and Walter and Odler²² reported similar results. As with the present study, they observed that the usual crystalline calcium aluminate hydration products were not developed, despite improved mechanical properties compared to unmodified CAC.

The TG results are shown in Figure 3. The total weight loss of the various systems up to $1000^\circ C$ vary significantly but can be categorised into three groups; the conventionally hydrated Secar 51 (24.1 wt%), the polyphosphate-modified CAC systems (15.4-16.7 wt%), and the monophosphate-modified CAC systems (7.9-10.1 wt%). These results show that phosphate modified systems exhibit distinct dehydration behaviour to that of unmodified CAC, assuming most of the weight loss is due to dehydration of reaction products.

The differential thermogravimetric (DTG) curves for monophosphate- and polyphosphate-modified systems are shown in Figure 4 and Figure 5, respectively, along with the result from unmodified CAC. Conventionally hydrated Secar 51 experienced principal weight losses over the range *ca.* $200-360^\circ C$, which encompasses the temperature range during which $\gamma-AH_3$, and C_3AH_6 dehydroxylate and dehydrate, respectively²⁶. This supports the XRD results, asserting that C_3AH_6 is the primary crystalline phase present after 7 days of hydration, with $\gamma-AH_3$ present as a secondary crystalline phase. Phosphate-modified systems exhibited

distinct weight loss behaviours to those of conventionally hydrated Secar 51, with the majority of weight loss occurring over the temperature range *ca.* 50-200°C and additional weight losses at *ca.* 230-340°C. In conventionally hydrated CAC, weight losses in the temperature range *ca.* 50-200°C could be attributable to the dehydration of alumina gel (AH₃-gel) or the calcium aluminate hydrate amorphous phase (C-A-H) described by Bushnell-Watson and Sharp²⁶, as well as the crystalline CA-hydrate phases, CAH₁₀ and C₂AH₈. For the phosphate-modified systems investigated here, the initial weight loss events were more likely to be the result of the dehydration of an amorphous phase because, as previously discussed in the XRD results, significant crystalline phases were not observed. The small weight loss *ca.* 230-270°C may be due to the dehydroxylation of AH₃-gel or aluminium hydroxide; either gibbsite (γ -AH₃) or bayerite (α -AH₃). The (NaPO₃)_n-derived systems also exhibited an additional small weight loss at *ca.* 300°C, which was attributed to the dehydration of C₃AH₆. This latter weight loss would correspond to only a small amount of C₃AH₆, and indeed weak reflections corresponding to C₃AH₆ were detected by XRD as discussed previously. These results suggest that the principal weight losses experienced by phosphate-modified systems were due to the dehydration of an amorphous phase, as well as a small amount of aluminium hydroxide. This amorphous phase may be AH₃-gel or C-A-H gel, but it may also be a distinct amorphous hydrate phase that incorporates some phosphate, e.g a calcium phosphate-based amorphous phase.

3.3. Microstructure

Backscattered electron imaging (BSE) micrographs obtained from SEM analysis of a (NaPO₃)_n-modified CAC (Figure 6) revealed a microstructure of partially- and un-reacted CAC particles surrounded by a dense binding matrix. Micro-cracks were observed within the dense matrix, which may have been the result of thermally induced stresses caused by the exothermic acid-base setting reactions or may have occurred during sample preparation. A similar microstructure, observed by Walter and Odler²², was described as a homogeneous, compact matrix without crystallinity in which residual CAC particles were embedded. They also observed cracks within the cement matrix, attributing them to chemical shrinkage which occurred during hardening. The microstructural development of various sodium phosphate-modified CAC systems has also been studied by Ma and Brown²¹ using Environmental Scanning Electron Microscopy (ESEM). They also observed the formation of an amorphous phase, which bound the CAC particles, resulting in

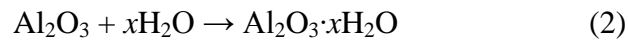
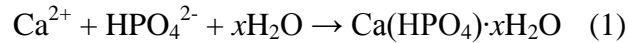
superior mechanical properties compared to conventionally hydrated CAC. It is suggested that a similar binding mechanism was responsible for the high compressive strength exhibited by the polyphosphate-modified CAC systems in the present investigation. As previously discussed, monophosphate-based systems did not fully harden or develop significant strength. Therefore, although the TG results suggested the existence of a similar amorphous phase to that in the polyphosphate systems, the nature of the amorphous phase in the monophosphate-based system must be different to that in polyphosphate-based systems.

EDX elemental mapping (Figure 6) showed that the amorphous binding matrix observed in $(\text{NaPO}_3)_n$ -modified CAC consisted of calcium, aluminium, phosphorus and oxygen, with trace amounts of silicon and sodium. Table 4 shows the results from EDX point spectra of the amorphous binding phase, calculated as the average of 12 individual point spectra - confirmed the major elements present in the amorphous binding matrix, were calcium, aluminium, phosphorous and oxygen, with a small quantity of sodium and silicon.

4. Further discussion

The exact composition and mechanism of formation of the amorphous binding matrix is not well understood in the literature. Ma and Brown²¹ used EDX to determine the chemical composition of cement pastes resulting from mixing CAC with various sodium phosphates, observing that the amorphous binding phase consisted of calcium, aluminium, and phosphorus. They inferred that the binding phase was an amorphous calcium aluminate phosphate hydrate (C-A-P-H) gel, the microstructure and composition of which was variable and phosphate dependant. On the other hand, Sugama *et al.* suggested a combination of a calcium phosphate-based amorphous phase and alumina gel. Using X-ray photoelectron spectroscopy (XPS), Sugama and Allen¹² reported that on mixing with calcium aluminate compounds with an ammonium phosphate-based fertiliser (Poly-N), the phosphate material reacted preferentially with Ca rather than Al to form ammonium calcium phosphate hydrate ($\text{NH}_4\text{CaPO}_4 \cdot x\text{H}_2\text{O}$) and alumina gel. Sugama and Carciello¹⁷ investigated sodium monophosphate- and sodium polyphosphate-modified CAC cement systems using Fourier transform infrared spectroscopy (FTIR). They suggested that on mixing a $(\text{NaPO}_3)_n$ -based solution with CAC, amorphous sodium calcium orthophosphate hydrate ($\text{NaCaPO}_4 \cdot x\text{H}_2\text{O}$) was formed as the principle reaction product, and was responsible for setting and strength development. In a later study, Sugama *et al.*¹⁸ proposed an alternative

composition and formation mechanism of the paste binding phase. Having investigated a $(\text{NaPO}_3)_n$ -modified CAC/pulverised fuel ash (PFA) system, they suggested that hydrogen phosphate anions produced by the dissolution of sodium polyphosphate reacted favourably with calcium cations released from CAC, to form calcium hydrogen phosphate hydrate $(\text{Ca}(\text{HPO}_4) \cdot x\text{H}_2\text{O})$ according to equation 1 below. Concurrently, the decalcification of CAC particles liberated reactive alumina, which hydrated to form alumina gel $(\text{Al}_2\text{O}_3 \cdot x\text{H}_2\text{O})$ as shown below in equation 2.



The TG results obtained in the present study support the assertion that alumina gel was present as a reaction product, and EDX confirmed the binding matrix contained Ca, P and Al. Therefore, the amorphous binding matrix obtained in a $(\text{NaPO}_3)_n$ -modified CAC appears to be composed of a combination of a calcium phosphate-based phase and alumina gel. However, this does not account for the presence of sodium, which is derived from the sodium phosphates used. Therefore an alternative composition is proposed for this amorphous binding matrix, albeit via a similar formation mechanism as that suggested by Sugama *et al.*¹⁸. It is proposed that, on dissolution, $(\text{NaPO}_3)_n$ forms hydrogen phosphate anions which react favourably with calcium cations liberated from CAC, to form amorphous calcium phosphate (ACP, $\text{Ca}_x\text{H}_y(\text{PO}_4)_z \cdot n\text{H}_2\text{O}$)^{30, 31}. ACP has variable composition with Ca/P ratio = 1.0-2.2, as well as a flexible structure which can incorporate sodium. The results from the EDX point spectra obtained in this study suggested a Ca/P ratio *ca.* 2, which exists within the range for ACP. In addition, a significant amount of sodium may be incorporated into the ACP by substitution for calcium as the ionic radius of Na^+ (0.102 nm) is similar to that of Ca^{2+} (0.100 nm)³². As described by Sugama *et al.*¹⁸, hydrated alumina gel would also be formed due to the decalcification of CAC particles.

5. Conclusions

The results from this study confirmed previous studies and provide additional information on how phosphate modifications significantly affect the setting, mechanical properties and phase composition of CAC-based cement systems. The setting and compressive strength development

in these systems is phosphate dependent; and in the work reported here monophosphate-modified formulations did not fully set or develop significant compressive strength, whereas polyphosphate-modified formulations exhibited rapid setting and high strength development. Although the phosphate-modified systems exhibited similar XRD results, monophosphate-modified systems showed little reduction in the intensity of CA-related reflections, suggesting that very little reaction had occurred and that monophosphate modifications restricted the normal mechanism of CAC hydration. In contrast, the polyphosphate-modified CAC formulations exhibited considerable reduction in the intensity of CA-related reflections, suggesting that significant amounts of CA had been consumed during the acid-base reactions. Furthermore, these reactions were distinct from the usual hydration mechanism of CAC, as the normal calcium aluminate hydrate phases were not formed. Instead, polyphosphate-modified CAC resulted in the formation of amorphous reaction products, which acted as binding phases between the partially- and un-reacted CAC particles, and were responsible for the high strength development. The results presented here suggest that hydration was modified rather than accelerated, as described by other researchers^{20, 21}. Together with the TG results, it is proposed that the binding matrix consisted of ACP and hydrated alumina gel.

The present study has shown that monophosphate-based modifications are not suitable for producing cementitious matrices for radioactive waste encapsulation, based on the lack of setting or significant strength development. On the other hand, sodium polyphosphate-modified CAC set and developed significant strength. As such, these systems have potential as an alternative matrix for the encapsulation of LLW and ILW, and in particular for problematic reactive metals. However, the rapid setting and significant heat output generated by these systems mean that further development is required before use in industrial applications. Future work will assess the use of additives, such as supplementary materials and setting retarders to improve these characteristics.

Acknowledgements

Thanks are given to the Immobilisation Science Laboratory (ISL) at The University of Sheffield. Special thanks are given to Bev Lane of the Department of Materials Science and Engineering, Dr. Martin Hayes of the National Nuclear Laboratory (NNL), and Dr. Neil Milestone of Milestone and Associates Ltd., New Zealand, for helpful discussions and support. The authors

gratefully acknowledge the Engineering and Physical Sciences Research Council (EPSRC) and NNL for funding.

References

1. F. P. Glasser: 'Progress in the Immobilization of Radioactive Wastes in Cement', *Cement and Concrete Research*, 1992, **22**, 201-216.
2. F. P. Glasser: 'Fundamental aspects of cement solidification and stabilisation', *Journal of Hazardous Materials*, 1997, **52**(2-3), 151-170.
3. M. Atkins and F. P. Glasser: 'Application of Portland cement-based materials to radioactive waste immobilization', *Waste Management*, 1992, **12**(2-3), 105-131.
4. A. Setiadi, N. B. Milestone, J. Hill, and M. Hayes: 'Corrosion of aluminium and magnesium in BFS composite cements', *Advances in Applied Ceramics*, 2006, **105**, 191-196.
5. 'The 2007 UK Radioactive Waste Inventory', Department for Environment, Food and Rural Affairs and Nuclear Decommissioning Authority, 2007.
6. N. B. Milestone: 'Reactions in cement encapsulated nuclear wastes: need for toolbox of different cement types', *Advances in Applied Ceramics*, 2006, **105**(1), 13-20.
7. 'Proposed Research and Development Strategy', Nuclear Decommissioning Authority Radioactive Waste Management Directorate, 2008.
8. A. D. Wilson and J. W. Nicholson: 'Theory of acid-base cements', in 'Acid-base cements: their biomedical and industrial applications', 5-29; 1993, Cambridge, Press Syndicate of the University of Cambridge.
9. A. S. Wagh: 'Introduction to Chemically Bonded Ceramics', in 'Chemically Bonded Phosphate Ceramics: 21st Century Materials with Diverse Applications', 1-13; 2004, Oxford, Elsevier Ltd.
10. T. Sugama and M. Taylor: 'Interfacial and mechanical behavior of fiber-reinforced calcium phosphate cement composites', *Cement and Concrete Composites*, 1994, **16**(2), 93-106.
11. T. Sugama: 'Hot Alkali Carbonation of Sodium Metaphosphate Modified Fly Ash/Calcium Aluminate Blend Hydrothermal Cements', *Cement and Concrete Research*, 1996, **26**(11), 1661-1672.
12. T. Sugama, M. Allan, and J. M. Hill: 'Calcium Phosphate Cements Prepared by Acid-Base Reaction', *Journal of the American Ceramic Society*, 1992, **75**(8), 2076-2087.
13. T. Sugama and N. R. Carciello: 'Strength Development in Phosphate-Bonded Calcium Aluminate Cements', *Journal of the American Ceramic Society*, 1991, **74**(5), 1023-1030.
14. T. Sugama, L. Weber, and L. E. Brothers: 'Sodium-polyphosphate-modified fly ash/calcium aluminate blend cement: durability in wet, harsh geothermal environments', *Materials Letters*, 2000, **44**(1), 45-53.
15. T. Sugama and N. R. Carciello: 'Carbonation of Hydrothermally Treated Phosphate-Bonded Calcium Aluminate Cements', *Cement and Concrete Research*, 1992, **22**(5), 783-792.
16. T. Sugama and N. R. Carciello: 'Carbonation of Calcium Phosphate Cements After Long-term Exposure to Na₂CO₃-laden Water at 250°C', *Cement and Concrete Research*, 1993, **23**(6), 1409-1417.

17. T. Sugama and N. R. Carciello: 'Sodium phosphate-derived calcium phosphate cements', *Cement and Concrete Research*, 1995, **25**(1), 91-101.
18. T. Sugama, L. Weber, and L. E. Brothers: 'Resistance of sodium polyphosphate-modified fly ash/calcium aluminate blend cements to hot H₂SO₄ solution', *Cement and Concrete Research*, 1999, **29**(12), 1969-1976.
19. T. Sugama and E. Wetzel: 'Microsphere-filled lightweight calcium phosphate cements', *Journal of Materials Science*, 1994, **29**(19), 5165-5176.
20. W. Ma and P. W. Brown: 'Mechanical behavior and microstructural development in phosphate modified high alumina cement', *Cement and Concrete Research*, 1992, **22**(6), 1192-1200.
21. W. Ma and P. W. Brown: 'Hydration of sodium phosphate-modified high alumina cement', *Journal of Materials Research*, 1994, **9**(5).
22. D. Walter and I. Odler: 'Investigation of MgO and CaO/Al₂O₃ polyphosphate cements', *Advances in Cement Research*, 1996, **8**(29), 41-46.
23. N. C. Collier: National Nuclear Laboratory, Personal communication, 2010.
24. M. Hayes: National Nuclear Laboratory, Personal communication, 2010.
25. *Methods of testing cement. Determination of setting times and soundness*, in *BS EN 196-3:2005+A1:2008*. 2005.
26. S. M. Bushnell-Watson and J. H. Sharp: 'The application of thermal analysis to the hydration and conversion reactions of calcium aluminate cements', *Materiales de Construcción*, 1992, **42**(228), 13-32.
27. J. Bensted: 'Calcium aluminate cements', in 'Structure and Performance of Cements', (eds. J. Bensted, et al.), 2002, London, Spon Press.
28. C. Bradbury, P. M. Callaway, and D. D. Double: 'The conversion of high alumina cement/concrete', *Materials Science and Engineering*, 1976, **23**(1), 43-53.
29. K. L. Scrivener and A. Campas: 'Calcium Aluminate Cements', in 'Lea's Chemistry of Cement and Concrete', (ed. P. C. Hewlett), Fourth Edition edn, 711-782; 2006, Oxford, Butterworth-Heinemann.
30. S. V. Dorozhkin: 'Amorphous calcium (ortho)phosphates', *Acta Biomaterialia*, 2010, **6**(12), 4457-4475.
31. S. Dorozhkin: 'Calcium Orthophosphates in Nature, Biology and Medicine', *Materials*, 2009, **2**(2), 399-498.
32. R. Shannon: 'Revised effective ionic radii and systematic studies of interatomic distances in halides and chalcogenides', *Acta Crystallographica Section A*, 1976, **32**(5), 751-767.

Table 1 Details of formulations investigated and analyses undertaken

Formulation			Analysis (days curing)						
CAC	Solution		H ₂ O	0	1	3	7	14	28
(g)	Type	Mass (g)	(g)						
Secar 51	Unmodified	-	37	V	σ	σ	σ, X, T	σ	σ
100	NaH ₂ PO ₄ ·2H ₂ O	20	37	V	-	-	X, T	-	-
100	KH ₂ PO ₄	20	37	V	-	-	X, T	-	-
100	NH ₄ H ₂ PO ₄	20	37	V	-	-	X, T	-	-
100	(NaPO ₃) _n	20	37	V	σ	σ	σ, X, T, S	σ	σ
100	(NaPO ₃) ₆	20	37	V	σ	σ	σ, X, T	σ	σ

(Note: V = Vicat, σ = compressive strength, X = XRD, T = TG, S = SEM)

Table 2 Composition of CAC determined by XRF

Element/Oxide	Quantity (wt%)	Error (wt%)
CaO	36.84	±0.24
Al ₂ O ₃	51.10	±0.29
SiO ₂	5.04	±0.09
Fe ₂ O ₃	1.98	±0.06
TiO ₂	2.08	±0.06
Na ₂ O	0.11	±0.01
MgO	0.48	±0.03
K ₂ O	0.42	±0.03
P ₂ O ₅	0.13	±0.01
S*	0.018	±0.005

(Note: * determined using Leco analysis)

Table 3 Vicat setting time measurements for various phosphate-modified CAC systems

Formulation (phosphate modification)	Initial setting time (min)	Final setting time (min)
Unmodified	330 (± 15)	390 (± 15)
$\text{NaH}_2\text{PO}_4 \cdot 2\text{H}_2\text{O}$	30 (± 5)	*
KH_2PO_4	180 (± 7.5)	*
$\text{NH}_4\text{H}_2\text{PO}_4$	6 (± 0.5)	*
$(\text{NaPO}_3)_n$	6 (± 0.5)	11 (± 0.5)
$(\text{NaPO}_3)_6$	5 (± 0.5)	12 (± 0.5)

Note: * = Did not exhibit final set

Table 4 EDX point spectra data for amorphous binding phase in $(\text{NaPO}_3)_n$ -modified CAC

Element	Atomic % (%)	S.D. (%)
Ca	13.9	2.3
Al	16.9	1.9
P	6.6	1.2
Na	2.4	0.6
Si	1.1	0.3
O	59.1	0.5

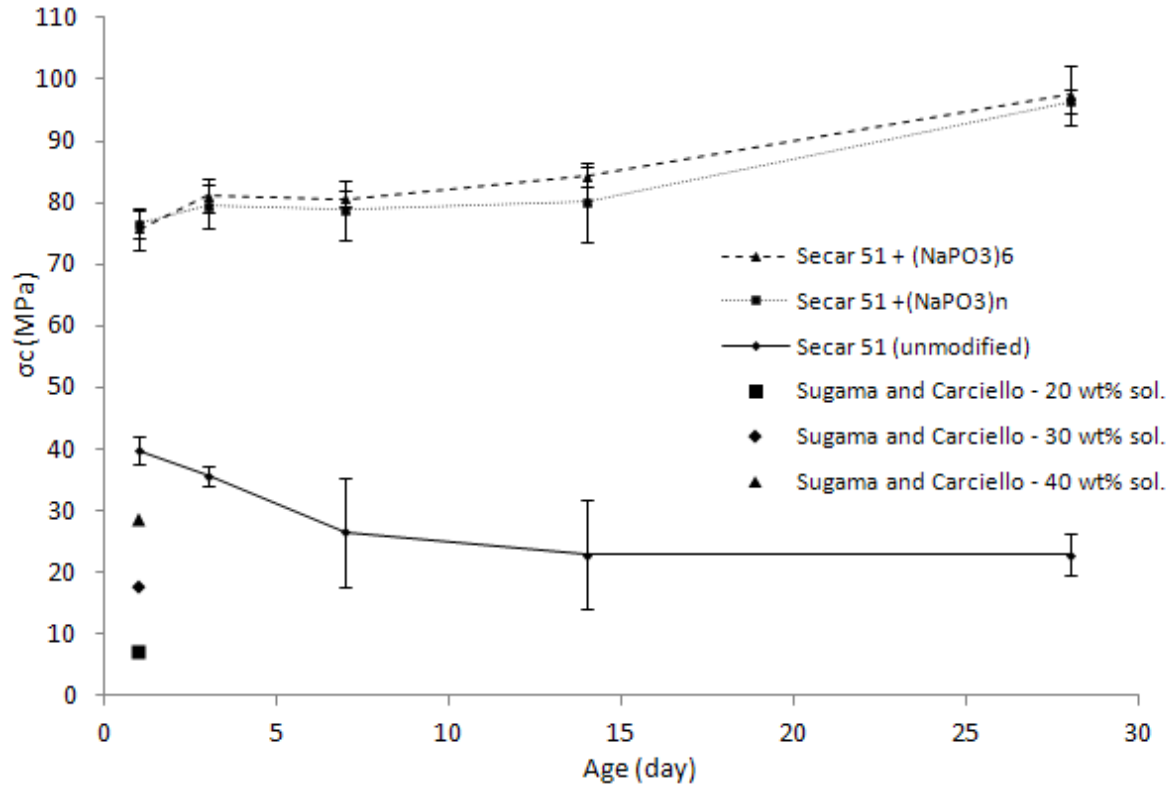


Fig. 1 Compressive strength of selected formulations up to 28 days

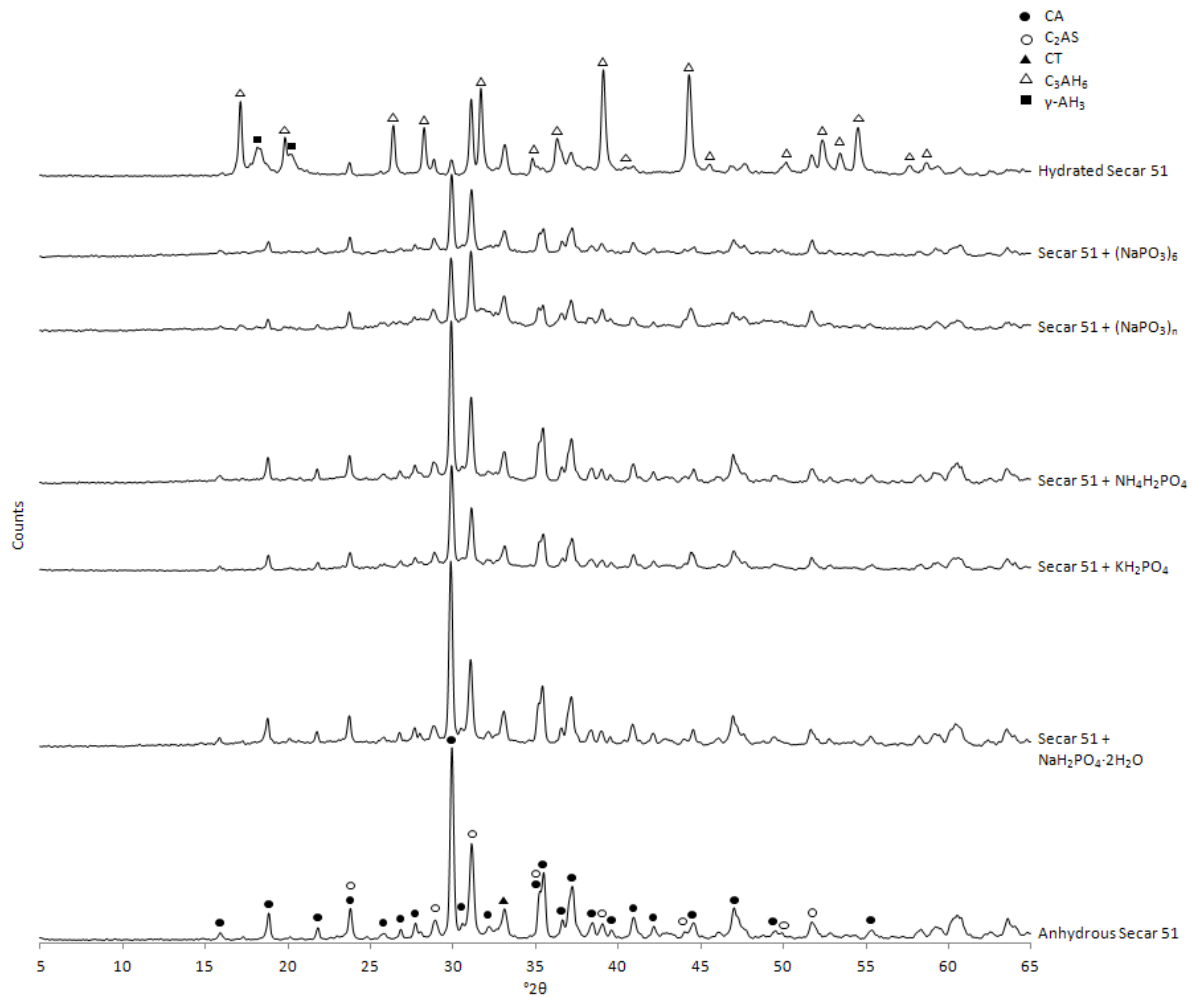


Fig. 2 XRD traces of anhydrous and hydrated CAC, and various phosphate-modified CAC formulations after 7 days

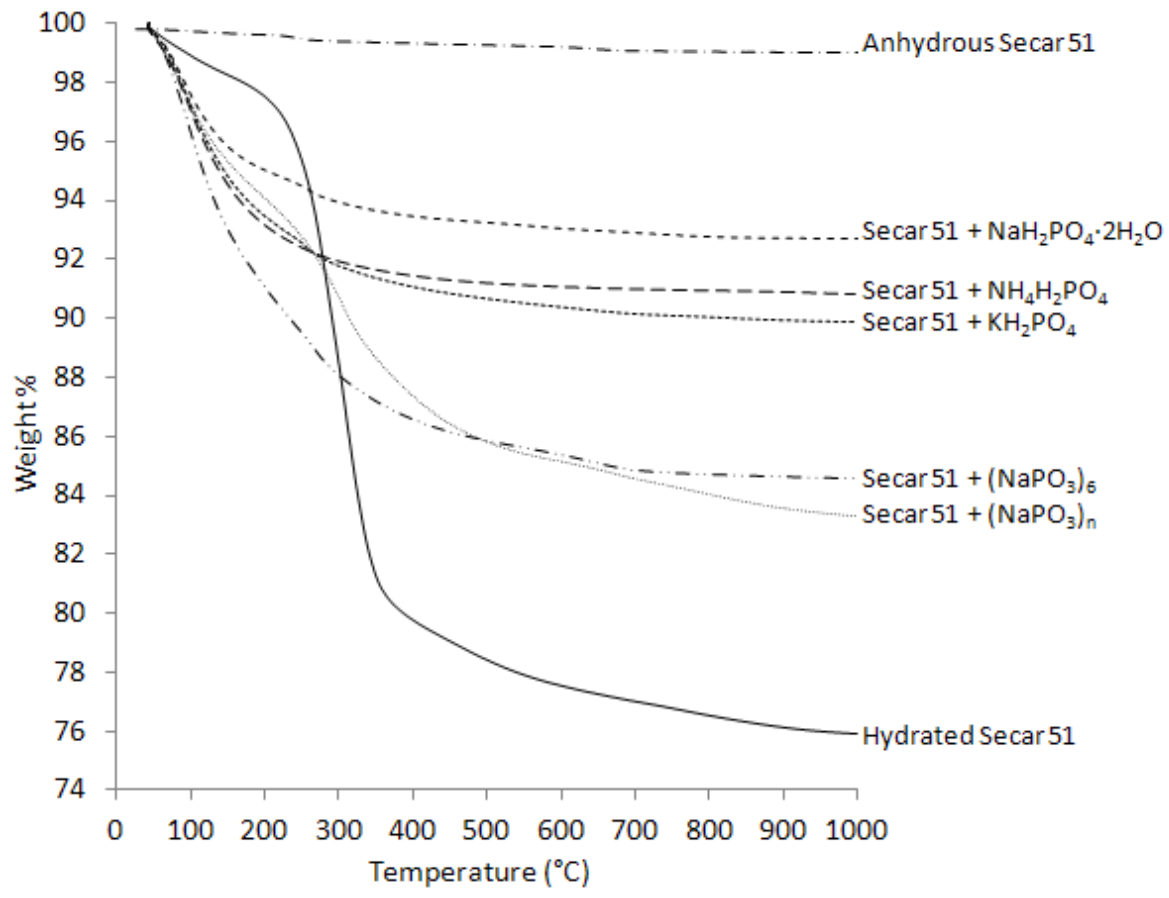


Fig. 3 TG of anhydrous and hydrated CAC, and various phosphate-modified CAC formulations after 7 days

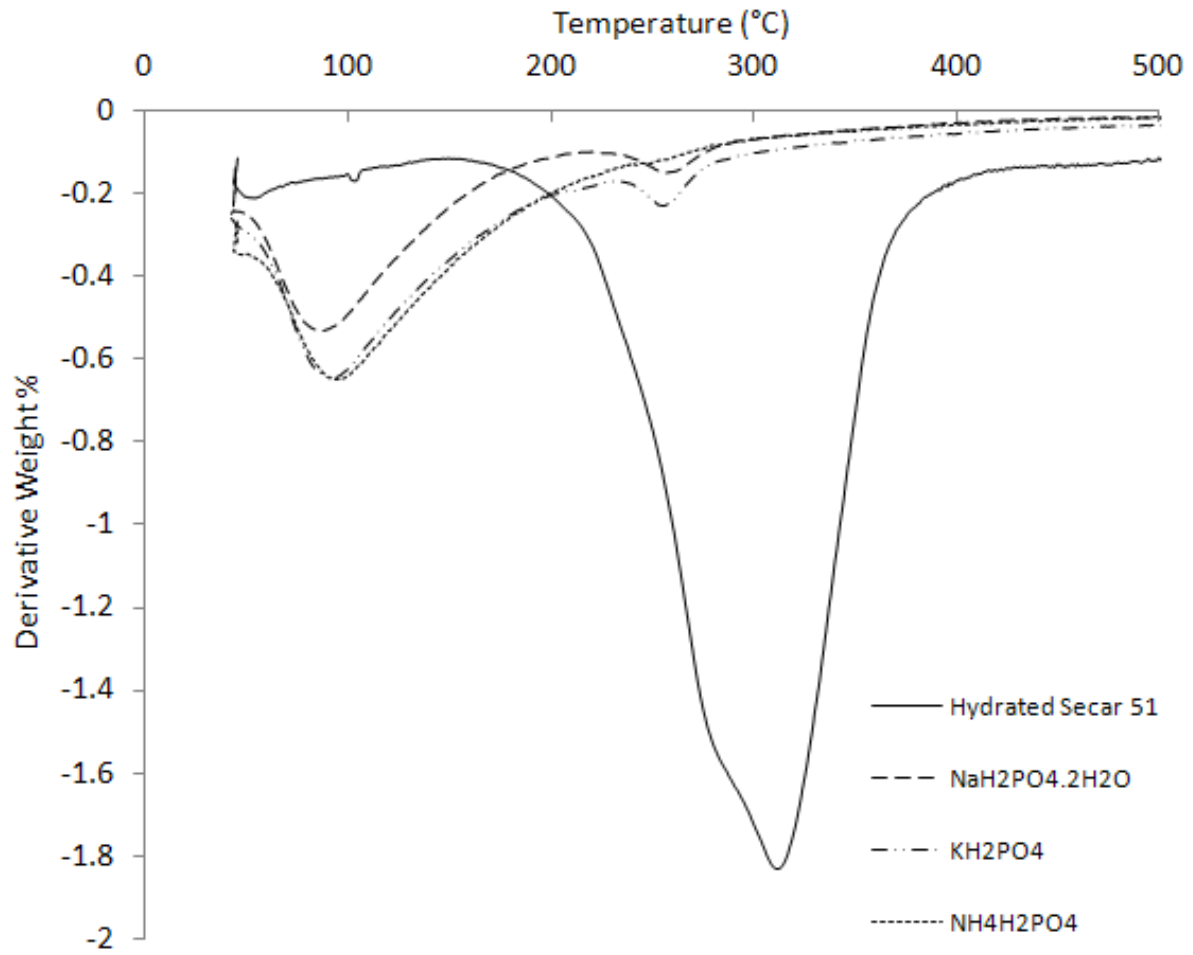


Fig. 4 DTG of monophosphate-modified CAC and unmodified CAC formulations after 7 days

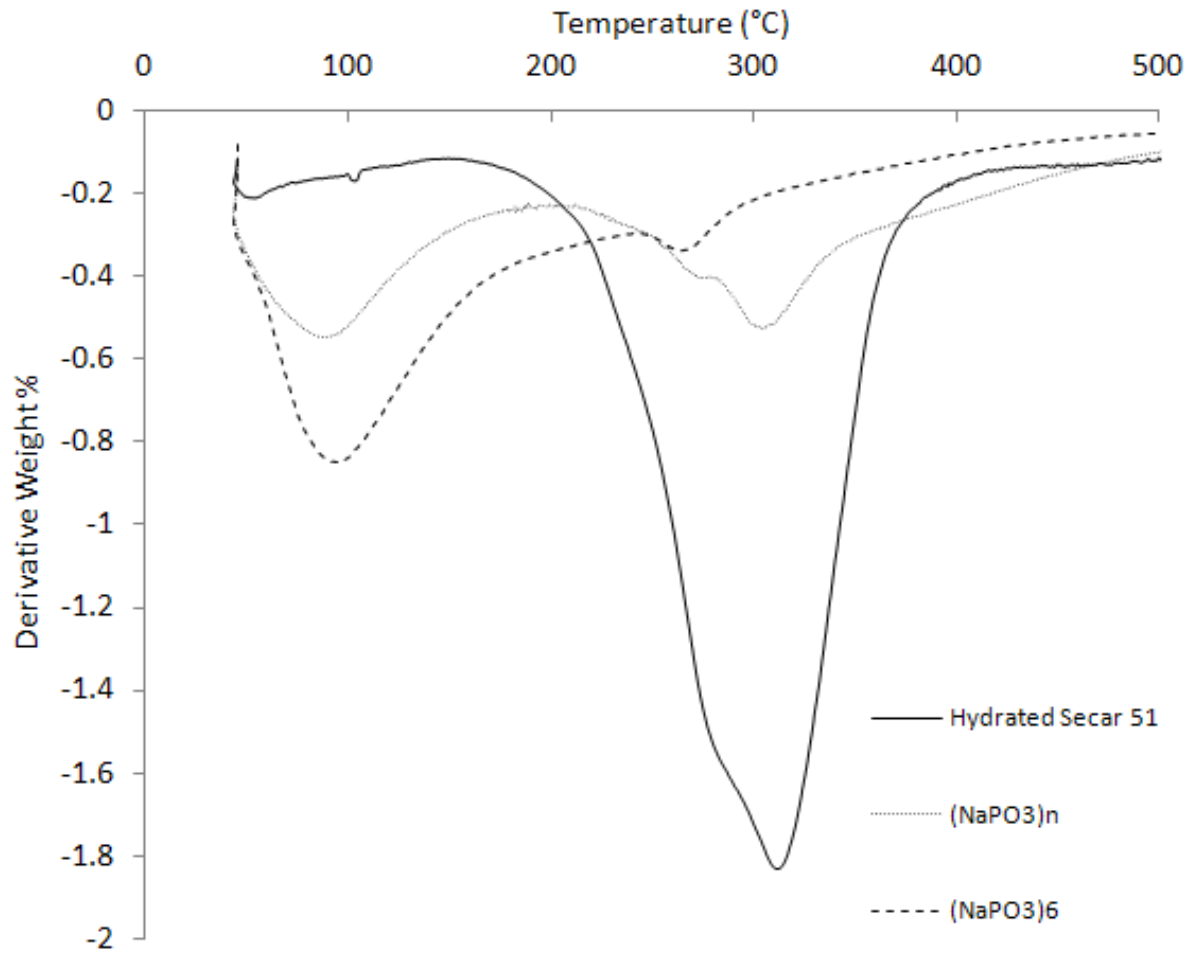


Fig. 5 DTG of polyphosphate-modified CAC and unmodified CAC formulations after 7 days

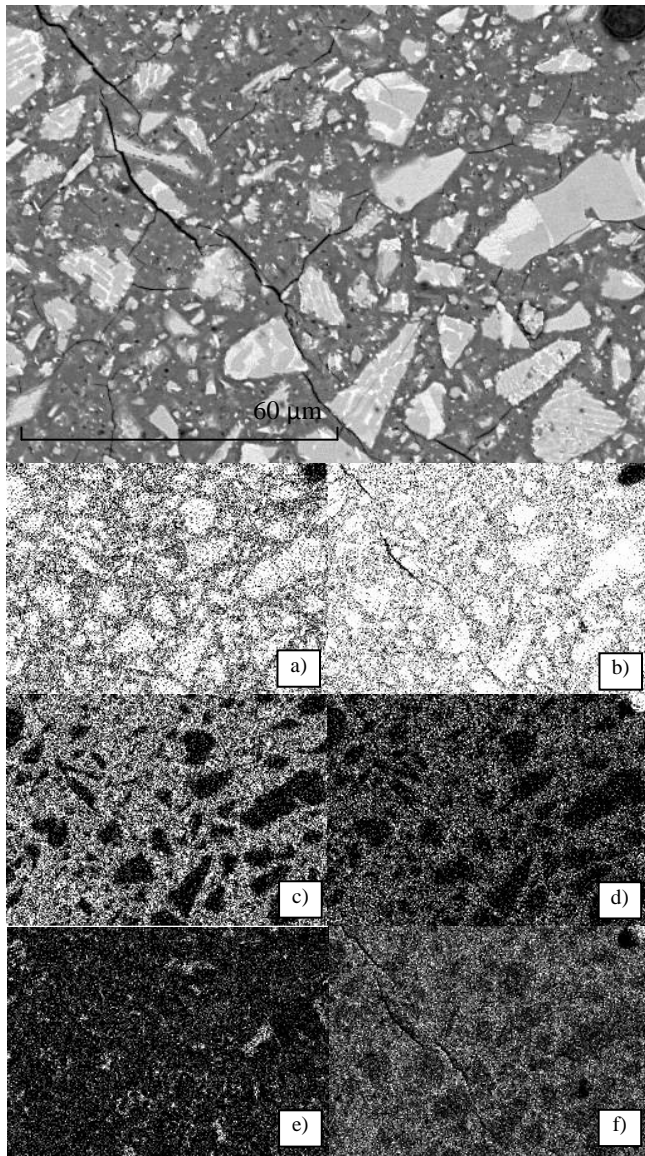


Fig. 6 SEM-BSE micrograph of polished $(\text{NaPO}_3)_n$ -modified CAC formulations after 7 days (top) with EDX-elemental maps of a) calcium, b) aluminium, c) phosphorus, d) sodium, e) silicon, f) oxygen