Modification of Calcium Aluminate Cement with Phosphate for Incorporation of Strontium Chloride

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Abstract

Large quantities of aqueous secondary waste are generated from the processing of contaminated water after the nuclear accident in Japan. Cementation of these wastes is challenging because their significant radioactivity may cause the radiolysis of water contents in cement, posing a risk of hydrogen gas generation. The application of calcium aluminate cement modified with phosphates (CAP), as an alternative cementing system, is interesting because this system is based on acid-base reaction, and its water content can be reduced by mild heating once the system is mixed. The present study focused in the use of Secar 71, a calcium aluminate cement with a high alumina and low silica compositions, and its effects of on the production of CAP system at elevated temperatures. The modification of Secar 71 with phosphates was successful, and the reduction of water content by about 35% was achieved in the CAP system containing SrCl₂ after curing the system at 80°C for 7 days. The micro cracks, typically observed in the CAP system cured at lower temperature, was significantly reduced by curing at 80°C. The obtained results show a potential of Secar 71 to prepare CAP for cementation of aqueous secondary wastes.

1. Introduction

1.1 Background

The contaminated water generated from the nuclear accident is currently being processed in Japan. Radionuclides have been removed from the water utilising e.g., caesium adsorption apparatus (KURION), secondary caesium adsorption apparatus (SARRY), a mobile Sr removal system, and an advanced liquid processing system (ALPS) (Igarashi et al. 2021). The processing of contaminated water, however, results in a large amount of aqueous secondary wastes (AESJ 2013): the evaporation facility initially used for the processing of contaminated water produced a concentrated effluent (concentrated sea water supernatant, 8891 m³); ALPS have been generating two types of aqueous wastes i.e., “iron co-precipitation slurry” (iron hydroxide with organic polymer, diluted sea water supernatant, 610 m³) and “carbonate salt slurry” (calcium carbonate and magnesium hydroxide, diluted sea water and sodium carbonate supernatant, ≈3000 m³). The most notable characteristics of these secondary wastes are that they are highly contaminated with ⁹⁰Sr, and that they contain sea salt (mainly sodium chloride) due to the initial use of sea water to cool down the reactor core at the accident site (TEPCO 2015; AESJ 2013).

Such aqueous wastes can usually be cemented, using grouts based on Portland cement (PC). However, cementation by the conventional PC-based matrices is challenging for this particular secondary waste, because its significant radioactivity could cause the generation of hydrogen gas through the radiolysis of the water intrinsically exists in the conventional cementing system as the pore solution and the hydrated phases. The chloride ion from the sea salt also need to be immobilised to assure the long-term integrity of the material. Therefore, there is a clear need to develop a technology that is capable of restricting the generation of hydrogen gas in the wasteform, stabilising ⁹⁰Sr, and retaining sodium chloride to enable the safe long-term storage.

To address this issue, we have been developing an alternative cementing technique with reduced water content for the safe storage of these secondary wastes (Garcia-Lodeiro et al. 2018). The cementation technique proposed is based on calcium aluminate cement (CAC) modified with phosphates (CAP) (Irisawa et al. 2020; Chavda et al. 2015; Swift et al. 2013; Sugama et al. 1992). While the conventional cementing systems based on PC relies on the hydration of clinker phase for their solidification, the solidification of CAP systems is based on the acid-base reaction between the CAC serving as a base and the phosphate solution serving as an acid (Sugama et al. 1992). Because the solidification does not rely solely on a hydration process, the water content in CAP can be reduced through a direct water removal by mild heating, once the water in the system has served its purpose in providing sufficient fluidity to be cast. This technique was used in our previous study to successfully reduce the water content of the system (capillary water and gel water) and reduction of pore size, by about 60%
Table 1 Oxide composition of calcium aluminates cements (Kerneos 2016a, 2016b).

| Type      | Al₂O₃  | CaO   | SiO₂  | Fe₂O₃ | TiO₂ | MgO   | SO₃   | K₂O+Na₂O |
|-----------|--------|-------|-------|-------|------|-------|-------|----------|
| Secar 51 (wt.%) | ≥50.0  | ≤40.0 | ≤6.0  | ≤3.0  | <4.0 | <1.0  | <0.4  | <0.5     |
| Secar 71 (wt.%) | ≥68.5  | ≤31.0 | ≤0.8  | ≤0.4  | <0.4 | <0.5  | <0.3  | <0.5     |

Table 2 Formulation and curing temperature of samples.

|       | Solution          | Curing temperature (°C) |
|-------|------------------|-------------------------|
|       | SrCl₂ (g) | Distilled water (g)     |
| CAC   | 120.0       | -                       | 35, 80               |
| CAP   | 120.0       | 42.0                    | 35, 80               |

The present study explored the utilisation of a different type of CAC, to further extend our understanding of CAP system. In our previous study, Secar 51 was used as a precursor CAC as a precursor material to produce CAP (Garcia-Lodeiro et al. 2018) while Secar 71 was used in the present investigation. The main clinker phases of Secar 51 are monocalcium aluminate (CA) and gehlenite (Ca₂As), whereas CA and grossite (CA₂) are the main clinkers in Secar 71 (Kerneos 2016a, 2016b). Secar 71 accordingly has an increased Al₂O₃ composition with a significantly less CaO and SiO₂ contents compared with Secar 51 as shown in Table 1, which is considered to be more suitable for high temperature applications (Kerneos 2016b).

1.2 Focus of the study

The use of Secar 71 and its effects of on the production of CAP at elevated temperature were examined focusing on: the water content in the products; and integrity of the microstructures. Studies on similar systems have been reported, but they were focused on either the initial reaction up to 30 hours at 25°C (Ma and Brown 1992) or the strength development at ambient condition (Ma and Brown 1994b). For the nuclear waste encapsulation, usually water to cement ratio (w/c) of 0.35-0.4 is required (IAEA 2013). Higher w/c ratio is advantageous for better workability, but w/c of above 0.3-0.35 usually leaves unconsumed water and increases the porosity and permeability of the system, leading to the reduced long-term chemical durability of the wasteform. The present investigation used w/c of 0.35 as a starting formulation, and reduction of evaporable water content was attempted by curing the samples at elevated temperatures.

The effect of strontium chloride incorporation was also investigated. Strontium chloride was selected because the contaminated water being processed in Japan typically contains chloride ions originated from sea water (TEPCO 2015). The investigation was conducted generally in comparison with CAC system without phosphate modification as a reference.

The reduced SiO₂ content in Secar 71 can be advantageous when examining the distribution of strontium in the samples using energy dispersive X-ray spectroscopy (EDX). Because the energies of their characteristic X-ray are similar (La of strontium is 1.806 keV while Kα of silicane is 1.739 keV (JEOL 2019), analysis of strontium in the silicate rich systems could become challenging, due to the significant overlap of their peaks in the EDX spectrum. This was recognised in our preliminary study using Secar 51 (Kamaluddin et al. 2019), and is expected to be minimal in the present investigation.

2. Experimental

2.1 Materials

In the present investigation, Secar 71 used as a precursor CAC was sourced from Kerneos. Its oxide composition and the main clinker phases are provided in the previous section. Sodium metaphosphate, (NaPO₃)₉ (97%, Acros Organics) was used as the primary phosphate modifier, and sodium dihydrogen phosphate dihydrate, NaH₂PO₄·2H₂O (99%, Acros Organics) was introduced as a setting retarder (Chavda et al. 2014). These phosphates are referred to as polyphosphate and monophosphate, respectively, throughout the present study for simplicity. Reagent grade of strontium chloride, SrCl₂ (99.99% Sigma-Aldrich) was also used, together with distilled water prepared in the laboratory.

2.2 Preparation of pastes

Table 2 summarises the formulations used for the samples together with the curing temperatures. Based on our previous study (Garcia-Lodeiro et al. 2018), water to cement ratio (w/c) of 0.35 by mass was used for CAC system. The CAP system used the same w/c ratio, but contained additional polyphosphate at 40 wt.% and monophosphate at 5 wt.% of Secar 71. When SrCl₂ was
introduced, for both systems, the quantity of water was adjusted to make the SrCl₂ solution to cement ratio (SrCl₂ sol./c) of 0.35. The concentration of the SrCl₂ solution was 0.5 M (0.5 mol/L).

For each formulation, desired amount of the solid components, either Secar 71 powder or a mixture of Secar 71 with polyphosphate and monophosphate powders were placed into a beaker and mixed manually for 30 seconds. Liquid components, either distilled water or SrCl₂ solution was then introduced, and mixed manually until a viscous paste had formed. The paste was then mixed using a Silverson L4RT high shear mixer at 2500 rpm for 2 minutes. The mixed paste was poured into 2 plastic centrifuge tubes (diameter of 2.5 mm and length of 10 cm), and both tubes were vibrated using a vortex mixer for approximately 30 seconds to remove obvious bubbles. Approximately half of the container was filled with the paste.

2.3 Curing and water evaporation
The prepared samples, 2 tubes for each formulation, were placed in an oven, one to be cured at 35°C and the other to be cured at 80°C. All samples were kept in the chambers for 7 days without sealing in direct contact with air to allow water evaporation from the top of the container. During this period, the sample weights were recorded periodically to estimate the weight change due to the loss of water content.

After curing, samples were removed from the plastic centrifuge tubes and immersed in acetone for 4-6 hours to prevent further hydration and/or reaction with water. The samples were then air dried, cut into 5 of 5 mm disks and a cone (due to the shape of centrifuge tube) using a slow saw and washed in an ultrasonic bath with isopropanol to remove oil from the saw lubricant.

2.4 Characterisation
The bottom part of the sample (cut into a cone) were broken with a hammer, and ground to a fine powder using a pestle and mortar with a 63 μm sieve. The powdered samples were used for the characterisation by X-ray diffraction (XRD) to identify crystalline phases. The XRD measurements were performed using Siemens D5000 diffractometer with a copper radiation source, in the range of 5-60° (2θ) with a step size of 0.02° at a rate of 1°/min.

Fourier Transfer Infrared spectroscopy (FT-IR) was also used to characterise the powered samples. The measurements were conducted using Perkin Elmer FTIR Model 1600. For each FT-IR measurement, 3 mg of sample was mixed with 300 mg of potassium bromide, pressed into a thin disk, and used as a specimen. Anhydrous Secar 71 was also analysed using FT-IR as a reference.

The middle discs (10-15 mm depth from the exposure surface) were broken into small pieces and mounted into epoxy resin to examine the microstructural features using scanning electron microscopy (SEM). The observation surface was polished using diamond paste to 1/4 μm of fineness. The SEM analysis was performed using Hitachi TM3030 on backscattering electron (BSE) mode with a 15 kV accelerating voltage at a working distance of 8.5 to 10 mm. Energy dispersive X-ray (EDX) was also utilised with a Bruker Quantax 70 detector for 3-10 min to examine the elemental distribution in the samples.

3. Results and discussion
3.1 Mixing behaviour
It was easy to mix for CAC system with distilled water. The paste of a creamy consistency with moderate viscosity was produced. When SrCl₂ was included, the CAC system became stiff and was difficult to mix initially, and took longer to form a creamy consistency with moderate viscosity similar to the CAC system without SrCl₂.

The CAP system with distilled water was also easy to mix. The paste formed a creamy consistency with viscosity much lower than that of CAC pastes. The CAP paste also generated a significant amount of heat, suggesting the fast progress of the acid-base reaction. Formation of bubbles were observed in the paste. When SrCl₂ was included, the behaviour of the CAP system was similar to that of the CAC system, and was difficult to mix initially. Once mixed, however, this paste exhibited a lower viscosity and generated more heat compared with the CAC systems. Formation of bubbles were observed also in this paste.

The prepared materials did not indicate any signs of bleeding or salt precipitation at the top of the samples.

3.2 Reduction of water content
Based on the weight loss of the samples during the curing period, the amount of water content remaining in each system was estimated, and the estimations are shown in Fig. 1 in percentages relative to the corresponding original water contents. It should be noted that, for each formulation and temperature, one sample was examined, and the values shown in Fig. 1 are the direct estimation from them. For the CAC system shown in Fig. 1(a), the inclusion of SrCl₂ appears to be little influence on the reduction of water when the system was cured in 80°C. The system indicated a rapid water loss in the initial few hours, and little reduction in the water content was observed after this period, which is consistent with our previous study using Secar 51 (Garcia-Lodeiro et al. 2018).

On the other hand, the CAC system cured at 35°C, both with or without SrCl₂ inclusion, indicated a gradual initial water loss. A possible explanation is a slower conversion reaction of hydrate phases. It is known that CAC initially forms hexagonal metastable phases CAH₁₀ and C₂AH₈ at ambient temperature which convert into thermodynamically more stable C₃AH₆ and AH₃ with more time and/or temperature (Scrivener et al. 2018).
Since the conversion reactions involve release of water, slower conversion reactions at lower temperature could cause a slower water release compared with the high temperature. Since this slower water loss was not observed in our previous study using Secar 51 (Garcia-Lodeiro et al. 2018), this may be caused by the different type of CAC used in the present work. It should also be noted that the CAC sample containing SrCl$_2$ lost more water, suggesting that the interaction of SrCl$_2$ resulted in either the increased conversion reactions or the formation of stable hydration phases that are different from the conventional stable phases (C$_3$AH$_6$ and AH$_3$) with less water content. It is also possible that this system had less hydration, and thus, more free water to evaporate. This effect must be also related to the interaction of SrCl$_2$ and Secar 71 since it was not observed in our preliminary study using Secar 51 (Kamaluddin et al. 2019).

The amount of remaining water content estimated for the CAP samples are shown in Fig. 1(b). The CAP samples exhibited a gradual water loss for the entire curing period of 168 hours. A similar trend was observed in our previous study using Secar 51 (Garcia-Lodeiro et al. 2018). The CAP samples cured at 35°C with and without SrCl$_2$ inclusion indicated almost identical water loss across the curing period, suggesting little impact of SrCl$_2$. The water loss in these samples were also minimal among the samples tested in the present work.

The samples cured at 80°C, on the other hand, experienced greater water loss compared with those cured at 35°C, and a clear effect of SrCl$_2$ is observable. The CAP system with inclusion of SrCl$_2$ had less water loss compared with the CAP system without SrCl$_2$. This may be related to the inclusion of hygroscopic chloride salt. This trend was not observed in our previous study using Secar 51 with 1.0 M (1.0 mol/L) of SrCl$_2$ concentration (Kamaluddin et al. 2019), and thus, this could be attributed to the type of CAC. Further investigation is required to fully understand this.

Figure 2 compares the water loss of the samples ex-
examined in the present study after 168 hours (7 days) of curing period with those reported in the literature. A significant deviation from the literature data can be clearly seen in the CAC sample with SrCl₂ at 35°C and the CAP sample with SrCl₂ at 80°C. As previously discussed, the interaction of CAC system with SrCl₂ at 35°C may have resulted in either the increased conversion reactions of metastable hydration phases or formation of phases with less bound water, leading to the increased release of evaporable water. It is also possible that this system had less hydration, and thus, more free water to evaporate. The deviation of the CAP sample with SrCl₂ at 80°C is due to the less evaporable water, and this may be related to the hygroscopic nature of chloride salt or attributed to the type of CAC, as discussed previously. The CAP system with Secar 71 appears to retain water slightly more than those with Secar 51 at 35°C with or without inclusion of SrCl₂.

3.3 Phase analysis by XRD
The XRD patterns of the CAC samples are shown in Fig. 3. The CAC systems hydrated with distilled water indicated very similar XRD profiles, both in the 35 and 80°C curing. The reflection peaks corresponding to unreacted clinker phases, monocalcium aluminate (CA) and grossite (CA₂) were observed in these samples. They also indicated the presence of stable hydration products of CAC i.e., hydrogarnet (H) and gibbsite (G), but the peaks associated with the metastable hydration products i.e., CAH₁₀ and C₂AH₈ were not observed. The curing temperature of >35°C was sufficiently high to convert them into the stable phases, consistent with our previous study using Secar 51 (Garcia-Lodeiro et al. 2018). The reflection peaks of gibbsite at 18.5° and 20.5° (2θ) show broadening, suggesting the less crystalline nature of this product.

The CAC systems hydrated with SrCl₂ solution show the presence of CAC clinker phases, monocalcium aluminate (CA) and grossite (CA₂), as in those without SrCl₂. However, they indicated a significantly different features in hydration products. When SrCl₂ is included, hydrogarnet and gibbsite appear to form much less in the sample cured at 80°C compared with the CAC cured without SrCl₂, suggesting reduced hydration of CAC.

On the other hand, these stable hydration products of the conventional CAC hydration reaction were not identified in the sample cured at 35°C. Also, the intensity of the reflection peaks for CA and CA₂ appears to be more significant in this particular sample, again suggesting reduced hydration of CAC. Since the conventional hydration products were not identified in this sample, these results suggest that the CAC forms other hydration products through the interaction of SrCl₂, most likely with the metastable hydration products i.e., CAH₁₀ and C₂AH₈. When the curing temperature is lower (e.g., 35°C), this interaction can take place to consume CAH₁₀ and C₂AH₈, but the metastable phases would be quickly converted to the stable phases at higher temperature (e.g., 80°C), and thus less interaction with SrCl₂ is available. Since other crystalline phases were not found in the XRD data, the hydration products formed through the interaction of SrCl₂ is expected to be

![Fig. 3 XRD patterns of CAC systems after curing for 168 hours (7 days). The major reflection peaks are labelled as: monocalcium aluminate (CA); grossite (CA₂); hydrogarnet (H); gibbsite (G); Friedel's salt (F). Clinker phases of CAC are labelled in black, and the other phases in red. Unlabelled small peaks are attributed to clinker phases, either CA or CA₂.](image-url)
amorphous in nature.

In the previous section, the increased water loss was identified for the CAC system with SrCl₂ when cured at 35°C. The XRD data suggests that this was likely not because of the increased conversion reactions in the samples but the reduced hydration of CAC and the formation of stable hydration phases that are different from the conventional stable phases and less water content.

The XRD data also show the formation of Friedel’s salt \( \text{Ca}_2\text{Al(OH)}_6(\text{Cl,OH})\cdot2\text{H}_2\text{O} \), also known as hydrocalumite, in the CAC system with SrCl₂ both at 35 and 80°C. Friedel’s salt \( \text{Ca}_2\text{Al(OH)}_6(\text{Cl,OH})\cdot2\text{H}_2\text{O} \) is related to an AFm phase observed in Portland cement, and can form when the sulphate ions are replaced by chloride ions (Matschei et al. 2007; Birnin-Yauri and Glasser 1998). This is consistent with the CAC system formed with Secar 51 (Kamaluddin et al. 2019).

The XRD patterns of the CAP samples are shown in Fig. 4. All CAP systems, both with and without SrCl₂ and cured at 35 and 80°C indicated similar XRD profile. The reflection peaks attributed to unreacted clinker phases, monocalcium aluminate (CA) and grossite (CA₂) were clearly observed. However, in contrast to the CAC systems, neither hydrogarnet nor gibbsite were detected, suggesting that the conventional hydration reactions of CAC did not occur in the CAP system. Friedel’s salt observed in the CAC system was not identified in the CAP system.

The obtained results confirm that the phosphate modification was successful on Secar 71 and inhibited conventional hydration process of CAC, similar to the systems using Secar 51 (Irisawa et al. 2020; Kamaluddin et al. 2019; Garcia-Lodeiro et al. 2018; Chavda et al. 2015; Swift et al. 2013). The broad hump in the range of 25°-35° 2θ suggests the presence of an amorphous phase as previously observed in the Secar 51 systems modified with phosphates. However, the reflection peaks associated with hydroxyapatite, as previously reported in the Secar 51 system (Garcia-Lodeiro et al. 2018), was not observed in the present study. Since the XRD patterns did not indicate other compounds, strontium and chloride ions may have been bound to the amorphous phase formed in the CAP system. It has been reported that strontium (Raičević et al. 1995) and chloride (Nzihou and Sharrock 2002) can be bound to such an amorphous phase formed in similar calcium phosphate systems.

3.4 Phase analysis by FT-IR

Figure 5 shows FT-IR spectra of CAC samples after 168 hours (7 days) of curing. The spectrum of anhydrous Secar 71 is also shown for comparison. All CAC samples indicated a broad absorption peak in the range of 3700-3200 cm⁻¹, due to the overlapping νas O-H bands in AH₃ (3620, 3530, 3450 cm⁻¹) consistent with our previous study using Secar 51. The absorption attributed to C₃AΗ₆ at 3660 cm⁻¹ (Fernandez-Carrasco et al. 2001; Hidalgo et al. 2009) is clearly observed in the CAC samples hydrated with distilled water, but this band is not observed in the CAC with inclusion of SrCl₂ cured at 35°C, suggesting the lack of this conventional hydration product of CAC in this particular system, consistent with the XRD data.

A small absorption band at ≈1640 cm⁻¹ is attributed to...
δ H-O-H, suggesting the presence of H$_2$O, while a small signal at ≈1430 cm$^{-1}$ for $\nu_{as}$ C-O in CO$_3^{2-}$ groups (Fernández-Carrasco et al. 2001; Hidalgo et al. 2009) indicates the presence of carbonates. The absorption peaks located in the range of 1100-800 cm$^{-1}$ are associated with $\delta$ O-H in AH$_3$. A group of peaks partly overlapped in this range, from 950 to 410 cm$^{-1}$ are for the $\nu$ Al-O vibrations of both the AlO$_4$ and AlO$_6$ groups. These bands with a strong peak at ≈810 cm$^{-1}$ and ≈420 m$^{-1}$ represent clinker phases of Secar 71, CA and CA$_2$ (Fernández-Carrasco et al. 2012). The strong absorption band located at ≈520 cm$^{-1}$ is attributed to the $\nu$ Al-O in C$_3$AH$_6$ (Hidalgo et al. 2009), which appears to be missing in the CAC sample with inclusion of SrCl$_2$ cured at 35°C, further confirming the lack of this conventional hydration product in this sample. Since the absorption by the clinker phases (CA and CA$_2$) for this sample is in a similar level to that cured at 80°C, a similar level of hydration reaction must have occurred in these samples. Therefore, the increase water loss observed in the CAC sample with SrCl$_2$ cured at 35°C [Fig. 1(a)] is not likely because of the less hydration in the system.

FT-IR spectra of CAP samples after 168 hours (7 days) of curing are shown in Fig. 6. A broad absorption band located in the range of 3700-3000 cm$^{-1}$ suggests the presence of $\nu_{as}$ O-H, but it does not clearly show the overlapping feature observed in the CAC systems associated with AH$_3$ (Fig. 5). On the other hand, the absorption at ≈1640 cm$^{-1}$ associated with δ H-O-H in H$_2$O can be seen more clearly in the CAP system compared with CAC system.

All CAP samples had their main absorption peak at ≈1100 cm$^{-1}$, with shoulders at ≈1160 cm$^{-1}$ and ≈1040 cm$^{-1}$. These peaks were previously attributed to orthophosphate groups (PO$_4$) in the CAP system with Secar 51 as orthophosphates usually have strong and broad absorptions in the range of 1150-1000 cm$^{-1}$ (Garcia-Lodeiro et al. 2018). The orthophosphates suggested to be present in amorphous state for the CAP with Secar 51 are summarised in Table 3. They may be present also in the CAP system produced with Secar 71. The amorphous NaCaPO$_4\cdot$xH$_2$O and Ca(HPO$_4$)\cdot$xH$_2$O type products could co-exist with a poorly crystallised hydroxypatite. The evolution of these two phases to hydroxypatite has been observed (Sugama et al. 1992, 1995) under hydrothermal conditions. As previously men-

### Table 3 Orthophosphate phases discussed in the authors’ previous study (Garcia-Lodeiro et al. 2018).

| Phases          | Absorption band (cm$^{-1}$) | References               |
|-----------------|-----------------------------|---------------------------|
| NaCaPO$_4\cdot$xH$_2$O | SCOP salt          | 1110                      | Sugama and Carciello 1995 |
| Ca$_6$(PO$_4$)$_4$(OH)$_2$ | Hydroxyapatite | 1070, 1040, 960          | Sugama et al. 1992        |
| Ca(HPO$_4$)$_2$\cdot$xH$_2$O | Dibasic calcium phosphate | 1060                      | Sugama et al. 2002        |
tioned, the apatite family of calcium phosphates is a good host material for Sr, and can also retain halogens. A group of peaks partly overlapped in this range, from 950 to 410 cm\(^{-1}\) are for the \(\nu\) Al-O vibrations of both the AlO\(_4\) and AlO\(_6\) groups, and mostly associated with the clinker phases of Secar 71, CA and CA\(_2\) as observed in the CAC systems. The significant absorption in the range of 700-500 cm\(^{-1}\) represents AlO\(_6\) group, indicating the AH\(_3\)-like environment of aluminium ions. This may suggest either the presence of a separate AH\(_3\) phase or AH\(_3\)-like environment in the amorphous phosphate phases identified above. A potential incorporation of aluminium has been reported in a similar phosphate system (Chavda et al. 2015).

3.5 Microstructure

Figure 7 shows the BSE images of the CAC samples after curing for 168 hours (7 days). The angular CAC clinkers are surrounded by the porous binding phase in all samples. The clinker particles indicate two different shades of grey, representing different phases, likely CA (lighter grey, 2.84 g/cm\(^3\)) and CA\(_2\) (darker grey, 2.80 g/cm\(^3\)). The CAC hydrated without SrCl\(_2\), when cured at 80°C [Fig. 7(b)], appears to have a heterogeneous matrix composed of dense hydration product with significantly porous sections. On the other hand, the inclusion of SrCl\(_2\) seem to result in a slightly denser structure at 35°C [Fig. 7(e)], and less heterogeneity at 80°C [Fig. 7(d)]. More CAC clinker particles are observable in the samples containing SrCl\(_2\), especially in the sample cured at 35°C.

The CAP samples have a microstructure significantly different from the CAC samples, as shown in Fig. 8. The CAC clinkers are surrounded by a dense matrix with less obvious porosity. However, the samples cured at 35°C [Figs. 8(a) and 8(c)] indicate significant cracks. Similar microstructural feature was observed in the CAP systems cured at lower temperatures (Irisawa et al. 2020; Garcia-Lodeiro et al. 2018; Swift et al. 2013). Since the SEM observation was conducted using the environmental SEM that does not require high vacuum condition for the measurement, a significant dry shrinkage is not expected during SEM measurement, and these cracks are likely formed during the curing period. However, a minor dry shrinkage could occur during the SEM observation, and this aspect requires further investigation. On the other hand, only a limited amount of cracks was observed in those cured at 80°C [Figs. 8(b) and 8(d)]. Such an improvement in microstructure was previously recognised in the CAP system using Secar 51 (Garcia-Lodeiro et al. 2018), and the obtained results confirms the same effect in the Secar 71 CAP system with and without inclusion of SrCl\(_2\).

As discussed in the former section (Section 3.1), the CAP systems generate when the starting materials are mixed because of the rapid nature of acid-base reaction. The CAP systems would initially start setting and form amorphous binding phase in this hot state. When they are cured at lower temperatures, thermal contraction would occur. The small loss of gel water would also have contributed to the shrinkage of amorphous binding phase during the period. The contraction (attributed to the combination of these effects) appears to be much greater in the amorphous gel phase than that of the unreacted CAC particles when the amorphous phase has sufficient water content.

Fig. 6 FT-IR spectra of CAP systems after curing for 168 hours (7 days).
Fig. 7 BSE images (magnification: 500) of CAC systems after curing for 168 hours (7 days): (a) CAC cured at 35°C; (b) CAC cured at 80°C; (c) CAC with SrCl₂ cured at 35°C; (d) CAC with SrCl₂ cured at 80°C. The specimen was taken from the depth of 10-15 mm from the exposure surface.

Fig. 8 BSE images (magnification: 500) of CAP systems after curing for 168 hours (7 days): (a) CAP cured at 35°C; (b) CAP cured at 80°C; (c) CAP with SrCl₂ cured at 35°C; (d) CAP with SrCl₂ cured at 80°C. The specimen was taken from the depth of 10-15 mm from the exposure surface.
On the other hand, when cured in a higher temperature, the system is expected to experience less thermal contraction during the curing period. By the time the sample is taken out from the oven to cool down at the end of the curing period, significant amount of evaporable water has already been removed from the system. In such a case, the thermal contraction of the amorphous binding phase seems smaller and not too different from that of the unreacted CAC particles. It has been known that thermal expansion coefficient of Portland cement paste has a nonlinear function of the internal relative humidity (IRH) of the system, having the maximum at IRH of approximately 70% (Wang et al. 2018). Thus, the CAP system appears to have a similar behaviour, with much smaller thermal expansion (and contraction) coefficient when a significant amount of evaporable water is removed.

### 3.6 Elemental distribution

Distribution of elements was investigated for selected samples of interest. Figure 9 shows the EDX mapping of the CAC sample with inclusion of SrCl₂ after curing at 35°C for 168 hours (7 days). Clinker particles show regions with higher concentrations of Al, matching with the darker grey regions in the BSE image, which confirms that they are CA₂ while the lighter grey regions are CA. Ca-rich and Al-rich regions can be observed in the porous matrix formed through the hydration of CAC (e.g., the region between two clinker particles), suggesting a possibility of two different hydration products. Sr and Cl generally distribute in the matrix quite evenly. The data is not clear enough to make further distinctions, but the Cl data may show some concentration (top, middle and bottom on the right hand side of the image), potentially indicating the locations of Friedel’s salt.
identified in the XRD data (Fig. 3). Distribution of elements in the CAP sample with SrCl$_2$ after curing at 80°C for 168 hours (7 days) is shown in Fig. 10. The distribution of elements seems to

Fig. 10 EDX mapping (magnification: 1000) of CAP sample with inclusion of SrCl$_2$ after curing at 80°C for 168 hours (7 days). The specimen was taken from the depth of 10-15 mm from the exposure surface.
be quite even throughout the matrix. The distribution of P may be showing a slight concentration of this element around the clinker particles (e.g., bottom on the right hand side of the image). Interestingly, the distribution of Al appears to be limited in the corresponding area. This may suggest the presence of different product phases. The data is not clear enough to understand the distribution of Sr and Cl, except their presence in the matrix. Compared with the shown in Fig. 9 for the CAC system, the EDX signals in general look weaker for all elements in Fig. 10. The measurement condition was likely not sufficiently optimised for the EDX, resulting in less clear mapping.

4. CAP as cementing matrix

The mild heating of the CAP system at 80°C during the curing period of 7 days removed some of evaporable water (capillary and gel water), allowing for the reduction of total water content of the system by approximately 34% with inclusion of SrCl2 and 53% without SrCl2. Since w/c of the original formulation was 0.35, these correspond to w/c of 0.23 and 0.16, respectively. As previously mentioned, the rate of hydrogen gas generation by irradiation decreases with the decrease in the evaporable water (Rosseel et al. 2016). Therefore, this is considered to be a significant improvement against the risk of hydrogen gas generation. The reduction of water content also resulted in the improvement in the microstructure by reducing the thermal contraction. Since this eliminates the micro cracks which are often observed in the materials produced at the lower temperature, the long-term chemical durability of the CAP system must be improved when cured at a higher temperature, although this aspect should be carefully examined to assure its long-term durability.

Although the incorporation mechanism of the Sr and Cl ions in the CAP system was not directly identified, they are likely incorporated in the amorphous binding phase. The amorphous orthophosphate e.g., NaCaPO4·xH2O and Ca(HPO4)·xH2O type products could co-exist with a poorly crystallised hydroxyapatite in the system. These orthophosphates can evolve to hydroxyapatite under the suitable conditions (Sugama et al. 1992, 1995). As previously mentioned, the apatite family of calcium phosphates can incorporate Sr and Cl ions.

5. Conclusions

The use of Secar 71 and its effects of on the production of CAP system at elevated temperature were examined. It was possible to modify the CAC of Secar 71 with phosphates, similar to the Secar 51 previously reported in the literature. Thus, the increased composition of Al and the reduced amount of Si in Secar 71 did not appear to cause issues for the production of CAP system.

Reduction of water content was possible for the Secar 71 CAC system by about 30%, but the water could be reduced by about 40% when cured at 35°C with SrCl2 inclusion. The obtained results suggest that the interaction between the SrCl2 and metastable CAC hydration products resulted in products with less water retention compared with the stable CAC hydration products (CAHx and AHx). Inclusion of SrCl2 also resulted in the formation of Friedel’s salt.

The effects of SrCl2 was not clear in the CAP system cured at 35°C, but it had a significant impact on the retention of water at 80°C. The water content was reduced by about 35% with SrCl2 inclusion, while greater than 50% reduction of water content was achieved in the CAP without inclusion of SrCl2. Both Sr and Cl appeared to be retained in the amorphous matrix of CAP system. The improvement of microstructure previously reported only for Secar 51 CAP system was achieved with Secar 71 by curing at 80°C.

For the application of Secar 71 for the encapsulation of secondary radioactive wastes, both CAC and CAP systems are possible to achieve about 35% of water reduction. The advantage of CAC system is the lower temperature required (35°C), but the CAP system can offer a dense matrix with limited porosity. Establishing long-term stability and chemical durability would be highly beneficial, as a next step of the research, for the actual application of these materials.

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