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Corrosion of aluminium metal in OPC- and CAC-based cement matrices

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Abstract

Corrosion of aluminium metal in ordinary Portland cement (OPC) based pastes produces hydrogen gas and expansive reaction products causing problems for the encapsulation of aluminium containing nuclear wastes. Although corrosion of aluminium in cements has been long known, the extent of aluminium corrosion in the cement matrices and effects of such reaction on the cement phases are not well established. The present study investigates the corrosion reaction of aluminium in OPC, OPC-blast furnace slag (BFS) and calcium aluminate cement (CAC) based systems. The total amount of aluminium able to corrode in an OPC and 4:1 BFS:OPC system was determined, and the correlation between the amount of calcium hydroxide in the system and the reaction of aluminium obtained. It was also shown that a CAC-based system could offer a potential matrix to incorporate aluminium metal with a further reduction of pH by introduction of phosphate, producing a calcium phosphate cement.
1 Introduction

1.1 Reaction of aluminium in cement

Cement can offer economical options for various applications within the nuclear industry, from the structural members of the power plants to the matrices for nuclear waste encapsulation. Cement based systems, typically containing high replacement levels of blast furnace slag (BFS) or pulverised fly ash (PFA), are used to encapsulate a variety of solid and liquid wastes from the nuclear industry [1]. One of the key features of cement systems based on ordinary Portland cement (OPC) is the high alkaline environment (high internal pH) produced in the hardened materials. This is advantageous for the encapsulation of some wastes, such as heavy metals, promoting precipitation [2,3]. OPC-based systems, however, may not be ideal for the incorporation of reactive metals, in particular aluminium containing wastes, as aluminium corrodes in alkaline solutions [4-6]. The process of corrosion above pH 8.5 is considered to be the oxidation of aluminium metal to aluminate ions Al(OH)$_4^-$, through anodic dissolution of the oxide layer (Al$_2$O$_3$) formed on the surface of the aluminium metal [5,6]. In the corrosion reaction of aluminium with OPC paste, hydrogen gas is generated which can cause problems to the integrity of cemented waste form and increase porosity, which is undesirable for waste encapsulation [7].

It is generally accepted that lowering the pH of the cementing system and/or reducing available free water will reduce the reaction of aluminium in the cement matrix [7,8]. Setiadi et al. [7] reduced aluminium corrosion by using a 9:1 BFS-OPC system which has a lower pH than neat OPC. Other studies have used alternative cement systems
such as calcium sulfoaluminate (CSA) cements [8] or BFS-OPC and PFA-OPC based systems containing excess gypsum (CaSO₄·2H₂O) or anhydrite (CaSO₄) [9].

Reduction in aluminium corrosion was observed with large amounts of ettringite being formed in these cases, due to the availability of excess sulphate. The reduction in corrosion was attributed to the reduced amount of free water available for corrosion reactions, due to incorporation of excess water into ettringite, and the reduction of the internal pH of the cement.

Calcium aluminate cement (CAC) is another alternative cement system. These systems are of interest for aluminium waste encapsulation as they have a lower internal pH (pH=10.5~11.5 [10]) compared with those of OPC-based systems. The reaction between aluminium and CAC has been studied for refractory castables, and some aspects of the reaction e.g. reaction kinetics, effect of temperature and admixture have been reported [11,12]. However, in these studies only small quantities of CAC (2 wt%) were used. With the application of CAC as a matrix for nuclear waste encapsulation in mind, it is of interest to study the corrosion of aluminium in systems with a much higher concentration of CAC. CAC will react with water alone to form a binder of mixed calcium aluminate hydrates. It may also be mixed with a polyphosphate to form a calcium aluminate phosphate cement, through an acid-base reaction [13].

Although some studies have been performed in this area, key information on the corrosion reaction of aluminium in different cement matrices still remains unclear. In particular, to what extent the aluminium corrosion could occur has yet to be quantified, and the effect of corrosion reactions on cement phases formed. These are particularly
important in the OPC-based systems conventionally used in the nuclear industry. Establishing this information will enable the different cementing systems to be ranked and the maximum amount of aluminium-containing waste that may be incorporated estimated. Quantifying these reactions will, therefore, allow a better design of cement matrices for aluminium encapsulation.

### 1.2 Scope of the work

In the present study, a series of experiments were undertaken to investigate the corrosion reaction of aluminium powder in OPC-based systems to establish the maximum extent of aluminium corrosion able to occur. In addition, the reaction between small pieces of aluminium plate and CAC-based systems with/out modification by sodium polyphosphate were assessed to establish the suitability of this matrix for reactive metal encapsulation. The extent of aluminium corrosion between the different cement systems is compared.

### 2 Experimental

#### 2.1 OPC-based systems

Chemical compositions of raw materials used in the present study are shown in Table 1. OPC-based systems containing aluminium powder were produced in the following manner. Between 0 and 7 g of aluminium powder (< 1 mm Φ) was added to the cement matrices, either a neat OPC or a 4:1 BFS-OPC blend as shown in Table 2. The weighed powders were manually mixed in 50 ml plastic containers with water for 5
minutes, sealed and cured at room temperature for 21 days. A second set of grout samples were prepared using the same procedure, and the pH of each grout was measured in air using a pH probe (glass electrode) and meter WTW pH315i. Readings were taken for approximately 10 minutes after mixing with water, up until the grout set and the probe could not be inserted.

2.2 CAC-based system

CAC-based systems, containing small aluminium plates were produced in the following manner. Two cement systems were used as shown in Table 2; a 6:4 PFA-CAC blend and a 6:4 PFA-CAC with polyphosphate system. Firstly CAC (Secar 51 from Kerneos UK) and PFA were slowly added into a mixing bowl containing either distilled water or sodium polyphosphate ((NaPO₃)ₙ, Acros Organics) and boric acid (H₃BO₃, 99.5+ %, Fisher Scientific) dissolved in distilled water. Boric acid was used to counter the accelerated setting of CAC caused by sodium polyphosphate [13], and to improve workability. A Kenwood bench-top planetary mixer was used at speed 1 (ca. 150 rpm) for the initial mixing of 5 minutes, followed by 10 minutes of mixing in a Silverson high shear mixer at 6000 rpm. A portion of mixed cement pastes were cured in a sealed container for 7 days at 20 °C and 95 % R.H. Another portion of cement pastes was poured into a plastic container (50 ml) and an aluminium plate (50 mm x 20 mm x 3 mm) immersed in the grout, as shown in Figure 1. Using this set up, the amount of hydrogen gas generated from the reaction of aluminium with the cement matrix was measured by water displacement in a measuring cylinder. Readings were taken at 7 and 28 days of reaction. The pH of the remaining cement slurries was measured every 30 minutes up to 150 minutes, using the same procedure.
previously outlined. In addition to the CAC-based system samples, a sample of 3:1 BFS-OPC system (W/S = 0.35) was also prepared containing aluminium plate for comparison.

2.3 Analysis

Cured samples were crushed, then immersed into acetone for 7 days to arrest hydration, and subsequently dried under vacuum. Samples were analysed using X-ray diffraction (XRD, Siemens D500 with Cu-Kα radiation (λ = 1.54178 Å)), a differential scanning calorimetry (DSC, Netzsch DSC404C) and scanning electron microscopy (SEM, JEOL JSM 6400) in backscattered electron (BSE) imaging mode. The XRD and DSC samples were ground and sieved to < 63 µm. DSC measurement was run from room temperature to 800 °C at a heating rate of 10 °C/min under N₂ flow. For SEM analysis, samples were prepared by mounting them in epoxy resin, polishing the observation surface to 1/4 µm and carbon coating.

3 Results and discussion

3.1 OPC-based systems

3.1.1 Observations

Visual examination of the cement samples revealed an increase in volume of both OPC and 4:1 BFS-OPC systems when the amount of aluminium powder was increased. A clear increase in porosity was observed, believed to be due to the
generation of hydrogen gas which has been previously reported [8,9]. Backscattered electron images of selected samples obtained during SEM observation are shown in Figure 2. Porosity appeared to become coarser in both in OPC and 4:1 BFS-OPC systems when more aluminium was introduced, indicated in Figure 2b and 2d. The OPC system containing aluminium retained more anhydrous cement particles than the neat OPC system, showing clearly that water was preferentially consumed by the corrosion of aluminium over the hydration of OPC. This is likely to have contributed to the increase in porosity.

3.1.2 Phase analysis

Figure 3 shows the XRD patterns for OPC with different amounts of aluminium powder. The peaks associated with portlandite (Ca(OH)$_2$), one of the main hydration products of OPC, clearly decreased as the amount of the aluminium was increased. Reflections for unhydrated alite (Ca$_3$SiO$_5$) and belite (Ca$_2$SiO$_4$) were identified. Gibbsite (Al(OH)$_3$) was identified in the systems containing aluminium and this appears to be the main crystalline phase formed from the reaction of aluminium in OPC. A weak peak observed around 9-12° (2θ) points to the existence of small amount of sulphate related phases such as monosulphate (Ca$_4$Al$_2$(SO$_4$)(OH)$_{12}$·6H$_2$O). No aluminium was observed in these traces suggesting the majority has been consumed, within the detection limits of the XRD (~5 wt%).

The XRD patterns for samples containing BFS are shown in Figure 4. The phases identified were portlandite, strätlingite (Ca$_3$Al$_2$SiO$_7$·8H$_2$O), alite, belite and gehlenite (Ca$_2$Al$_2$SiO$_7$), a crystalline phase often present in unreacted BFS [7]. Gibbsite was not
observed. The XRD patterns for the 4:1 BFS-OPC system suggest that strätlingite is
the main crystalline corrosion product of aluminium in this system. Bayerite
(Al(OH)₃), reported in a similar system after a much longer curing times (180 days)
[7], was not identified in the present investigation. The most remarkable feature of the
XRD results for the 4:1 BFS-OPC system was clear evidence that aluminium metal
was present in the samples with 4.9 and 7.0 wt% of aluminium loading. This suggests
that aluminium metal is much less reactive in the 4:1 BFS-OPC system and that the
maximum amount of aluminium powder that will corrode in this particular system is
less than 4.9 wt%.

Figure 5 shows the DSC profiles for OPC containing different amounts of aluminium
powder. The endothermic peaks up to 200 °C are considered to indicate the
dehydration of calcium silicate hydrate gel (C-S-H) (95-120 °C), ettringite (125-135
°C) and monosulphate (185-195 °C) [14]. Although ettringite was not identified by
XRD, it is known that its structure can be destroyed rather easily during preparation of
XRD samples [8], and hence may not be observed. In the presence of aluminium, the
amount of C-S-H appears to have decreased slightly whereas ettringite and
monosulphate have increased slightly. In the temperature range of 200-400 °C, there is
a clear endothermic peak around 260 °C for an amorphous alumina gel [15,16] along
with the main dehydroxylation peak of gibbsite at around 280-310 °C [17,18]. Both of
these peaks increase in intensity, with increasing Al content. The amorphous alumina
gel appears to be the main reaction product of aluminium corrosion under the
conditions used in the present study. As it is amorphous, it was not observed in XRD.
The distinctive peak attributed to the dehydroxylation of portlandite at around 450 °C
decreased as the amount of aluminium in the system increased. This is most likely
because hydroxide ion (OH\textsuperscript{-}) was consumed by the corrosion reaction of aluminium which forms Al(OH\textsubscript{4})\textsuperscript{−} and gibbsite, along with amorphous alumina gel. A small peak was also observed at 660 °C, the melting temperature of aluminium metal, suggesting that a small amount of aluminium metal remained unreacted in the system when 7.0 wt\% of aluminium was added. Again this was not observed using XRD suggesting the level was below the detection limit (~5 wt\%) of XRD.

Figure 6 shows the DSC results for 4:1 BFS-OPC system. The profiles are more moderate due to the smaller amount of OPC in the system. As in the OPC system when aluminium was added, the peak area due to C-S-H slightly decreased with increasing aluminium content, whereas those for ettringite and monosulphate increased slightly. The peak for the dehydroxylation of portlandite decreased as the amount of initial aluminium increased, similarly to the OPC system but on a smaller scale. Endothermic peaks around 260 °C suggest that in the 4:1 BFS-OPC system, amorphous alumina gel was again the main reaction product of aluminium corrosion under the conditions of the present study. In contrast, the peak attributed to gibbsite observed in the OPC system at around 280-310 °C was not observed. Instead, the results indicate the existence of strätlingite, with a dehydration peak observed at around 180-220 °C [19,20], which corresponds to the XRD results. These results suggest that corrosion of aluminium tends to form strätlingite rather than gibbsite in the BFS-OPC system, whilst amorphous alumina gel forms in both systems.

Formation of strätlingite in BFS cements with aluminium has been reported in another study [7]. Significantly less Ca(OH)\textsubscript{2} was available in the BFS-OPC system (approximately 1/7 of that available in OPC system) based on the peak area of Ca(OH)\textsubscript{2} in Figures 5 and 6 with 0 wt\% aluminium. It is evident that the extent of the
reaction between the cement system and aluminium metal was much less in the BFS-OPC system. A distinct peak at 660 °C from the melting of aluminium metal was observed and the peaks attributed to reaction products e.g. alumina gel were significantly less intense.

3.1.3 Corrosion of aluminium

Using the DSC results, the corrosion reaction of aluminium in OPC and 4:1 BFS-OPC systems was further analysed. Figure 7 (a) shows the peak area of the endothermic reaction between 640-670 °C for each DSC curve, which is attributed to the fusion (melting) of aluminium metal. Therefore, the peak area simply corresponds to the amount of unreacted aluminium metal left in the system. For the 4:1 BFS-OPC system a linear correlation between the peak area and the initial aluminium content added is clearly observed. Linear fitting of the data suggests that unreacted aluminium metal would be observed in a 4:1 BFS-OPC system when over 2.3 wt% powdered aluminium was added. In other words, the amount of aluminium powder that is able to corrode completely in 4:1 BFS-OPC system under these conditions is approximately 2.3 wt%. The gradient of the linear fit, 1.4 J/g, represents the energy required to melt 1 wt% of aluminium per unit sample. Thus, the same linear gradient can be applied to the OPC system, where only one point for fusion of aluminium was obtained. This estimates the amount of aluminium able to corrode in neat OPC as approximately 6.0 wt% under the conditions of the present study.

Figure 7 (b) shows similar analysis for the endothermic peak between 405-480 °C attributed to the dehydroxylation of Ca(OH)₂. The peak area is proportional to the
The amount of Ca(OH)$_2$ presented in the system. The data indicate that the amount of Ca(OH)$_2$ remaining in both systems decreased with increasing aluminium content, more than would be expected from simple dilution due to aluminium additions alone. This reduction of Ca(OH)$_2$ continued and corresponded to the amount of aluminium corroded in the system. Little Ca(OH)$_2$ was observed in the systems where the maximum corrosion of aluminium took place and excess aluminium metal was left unreacted. This suggests that the corrosion of aluminium consumes OH$^-$ and water in the system, and that the level of OH$^-$ becomes too low to sustain the sufficient formation of Ca(OH)$_2$ and further corrosion of aluminium. A significant effect of pH in alkaline solution on the long-term aluminium corrosion (up to 80 days) has been reported [21], and the results obtained in the present study show that this is also the case for the aluminium corrosion in the cementitious matrices.

The availability of water in the system may also explain the drop in Ca(OH)$_2$ content. A greater amount of unhydrated cement clinker phases remained in the cements with aluminium as observed in the SEM results due to consumption of water in corrosion reactions at the expense of some cement hydration reactions. Consequently less Ca(OH)$_2$ may be expected to have formed. However, this cannot solely be the reason for the suppression of Ca(OH)$_2$ formation, as a significant amount of C-S-H existed in aluminium containing systems as shown in Figures 5 and 6. Therefore, it is reasonable to consider that the consumption of OH$^-$ ions due to the corrosion of aluminium was the main reason for the reduction of Ca(OH)$_2$ in the studied system. The reaction of aluminium with the cement pore solution removes OH$^-$ from solution, reducing the pH. This in turn causes any Ca(OH)$_2$ in the system to dissolve. It is known that Ca(OH)$_2$ releases OH$^-$ at pH < 12.4 whereas C-S-H is able to remain stable as low as pH = 11.0.
~ 10.5 by changing the Ca/Si ratio through incongruent dissolution [3].

The gradient of the liner fit in Figure 7 (b), -15.0 J/g, represents the reduction in the energy needed to dehydroxylate Ca(OH)$_2$ in the system, thus the reduction in the amount of Ca(OH)$_2$ through reaction with 1 wt% of aluminium per unit sample. The data for the OPC system suggests that little Ca(OH)$_2$ should be observed in the system when aluminium content exceeds 5.3 wt%. Since 6.0 wt% of aluminium is estimated to corrode in this systems as discussed previously, there must be a small amount of OH$^-$ provided from other phases. In the BFS-OPC system, little Ca(OH)$_2$ would be produced beyond 0.8 wt% of aluminium content when Ca(OH)$_2$ is assumed to be the only source of OH$^-$ as in the OPC system. However, the amount of aluminium estimated to corrode in this systems is 2.3 wt% (Figure 7 (a)). This gap indicates that the assumption is not correct and that a significant amount of OH$^-$ was provided also from other phases. In the BFS:OPC system this is possibly from dissolution of C-S-H. Further studies are required to understand the role of C-S-H in the corrosion of aluminium. It is important to study the corrosion of aluminium over the longer-term as different hydration products may provide OH$^-$ resulting in different corrosion products at various stages of cement hydration. These results also explain why bayerite (Al(OH)$_3$) formation has been observed in the BFS-OPC system after 180 days [7], which was probably due to the slow formation of Ca(OH)$_2$ in the BFS-OPC system.

3.1.4 Initial pH of cement pastes

Fig. 8 (a) and (b) show the pH of samples at the initial stage of hydration for the OPC
and BFS-OPC systems, respectively, with different aluminium contents. As shown in
the figures, both for the OPC and 4:1 BFS-OPC systems, the pH of the aluminium-
containing samples decreased with time. The decrease occurred more rapidly the more
aluminium was added, indicating the increased consumption of hydroxide ions due to
aluminium corrosion, which is consistent with the DSC results. Because the BFS-
OPC system had a lower pH due to the less OPC and greater effective water volume,
the impact of incorporated aluminium on the pH appeared to be greater than in the
neat OPC system. The BFS:OPC samples lost their fluidity faster, and the pH
decreased more rapidly, however in the longer term the overall amount of corrosion
was less. The drop occurs more rapidly in the BFS:OPC samples, due to the overall
lower amount of OH- ions available compared to the neat OPC samples, where OH- is
more abundant and replenished during OPC hydration.

3.2 CAC-based system

3.2.1 Phase analysis

Figure 9 shows the XRD patterns of the PFA-CAC system after 7 days of curing at 20
°C with and without the addition of sodium polyphosphate and boric acid. For the 6:4
PFA-CAC system, the peaks observed can be attributed to the crystalline phases
usually found in hydrated CAC systems i.e., Gibbsite, CAH_{10} (CaAl_{2}O_{14}H_{10}), C_{2}AH_{8}
(Ca_{2}Al_{2}O_{13}H_{16}) along with the crystalline phases from the original unhydrated CAC
i.e., monocalcium aluminate (CaAl_{2}O_{4}), gehlenite (Ca_{2}Al_{2}SiO_{7}) and perovskite
(CaTiO_{3}) or PFA i.e., quartz (SiO_{2}) and mullite (Al_{6}Si_{2}O_{13}). Some of the peaks at
lower angles may be attributed to a strätlingite-related phase (Ca_{2}Al_{2}SiO_{7}.7.25H_{2}O) or
Formation of such phases related to strätlingite and monosulphate has been reported in a similar system based on PFA-CAC in presence of additional calcium sulphate [22] although this system also formed additional phases ettringite and C₃AH₆ (Ca₃Al₂(OH)₁₂). The difference from the present study is probably due to the presence of calcium sulphate.

When sodium polyphosphate and boric acid were introduced to the 6:4 PFA-CAC system, the XRD results changed significantly. No peaks for the crystalline hydrate phases were observed, with only those from the raw materials were identified. This lack of crystalline CAC hydration products was one of the key features of the sodium polyphosphate modified CAC system in our previous studies [13]. It has been reported that amorphous phases are obtained from CAC with sodium polyphosphate addition [23-25]. Some suggests an amorphous calcium aluminate phosphate hydrate (C-A-P-H) gel [23] while other suggests a mixture of calcium phosphate based gel (NaCaPO₄.xH₂O) and alumina gel (Al₂O₃.xH₂O) [24]. Because of the compositional flexibility, a generic chemical formula of CaₙHₙ(PO₄)₂.nH₂O has been suggested more recently [25].

### 3.2.2 Initial pH of cement pastes

Figure 10 shows the pH of CAC-based cement systems at the initial stages of hydration along with that of the 3:1 BFS-OPC system. The pH of the 3:1 BFS-OPC system (75 wt% BFS) was very similar to that for the 4:1 BFS:OPC (80 wt% BFS) system shown in Figure 8 (b), approximately 13 throughout the measured period. The difference in BFS content appears to have little effect on the pH of BFS-OPC system.
at this early stage of hydration. On the other hand, the PFA-CAC system exhibited a significantly lower pH level, starting from an initial pH 11.7 rising to 12.1 prior to initial set. When sodium polyphosphate and boric acid were introduced into the PFA-CAC system, there was a dramatic decrease in pH, indicating the effect of acid-base reaction between polyphosphate (acid) and CAC (base) [24]. The pH for this system remained lower (pH 10.3) during the measuring period of 150 minutes. This system may have significantly reduced aluminium corrosion.

3.2.3 Corrosion of aluminium

In all systems, the generation of hydrogen gas was observed, although the aluminium plates immersed in the cement matrix did not completely corrode after 28 days of reaction. Table 3 shows the amount of the generated hydrogen gas measured after 7 and 28 days for each system. The 3:1 BFS-OPC system clearly produced a significant amount of hydrogen gas with the majority generated within the first 7 days. The hydrogen gas release rate was 2.07 ml/cm²/day in the initial 7 days, and the rate reduced to 0.02 ml/cm²/day between 7 and 28 days. This reduction is most likely to be caused by the OH⁻ depletion in the local environment surrounding the aluminium plate due to the initial intensive corrosion reaction of aluminium. As discussed in the former sections, the reaction of aluminium in the OPC-based system will cause a reduction of OH⁻ and Ca(OH)₂ in the system, to the level where no further reaction can occur.

The PFA-CAC system produced much smaller amounts of hydrogen gas compared to the 3:1 BFS-OPC system. Since the pH of the paste at initial set was lower in the
PFA-CAC system, it is expected to have a lower level of internal pH (a lower concentration of OH⁻) in the hardened sample compared with the 3:1 BFS-OPC system, which must have contributed to these results. In the PFA-CAC system, however, the generation rate of hydrogen gas did not decrease after 7 days, but slightly increased from 0.14 ml/cm²/day in the initial 7 days to 0.20 ml/cm²/day in the following period. These results suggest that the reaction mechanism of aluminium in the PFA-CAC system is different from that in the OPC-based system. It would appear that the OH⁻ in the PFA-CAC system remained sufficiently high for aluminium corrosion, even after a certain amount of aluminium had reacted. This is most likely due to the conversion reactions of the metastable phases CAH₁₀ and C₂AH₈ which inevitably convert to C₃AH₆ and Al(OH)₃ as shown in Eqs. 1 and 2 [26].

\[
\begin{align*}
2\text{CAH}_{10} & \rightarrow \text{C}_2\text{AH}_8 + 2\text{Al(OH)}_3 + 9\text{H}_2\text{O} \quad (1) \\
3\text{C}_2\text{AH}_8 & \rightarrow 2\text{C}_3\text{AH}_6 + 2\text{Al(OH)}_3 + 9\text{H}_2\text{O} \quad (2)
\end{align*}
\]

Although the pH change during these conversion reactions is considered to be minimal [26], they lead to a release of water, which is then available for further reaction of the remaining anhydrous material. It has been suggested that the amount of aluminium corrosion in a CAC-based system corresponds to the extent of the cement hydration reaction [12].

When sodium polyphosphate and boric acid were introduced into the PFA-CAC system, the generation of hydrogen gas was further reduced, with a release rate as small as 0.02 ml/cm²/day which did not change throughout the measured period. This must be attributed to the obvious fact that the CAH₁₀ and C₂AH₈ phases did not form
in this system so the conversion reactions of these phases could not take place releasing water for further hydration reaction of the system. The results also show that aluminium corrosion in the PFA-CAC system can be effectively reduced by adding polyphosphate and boric acid. Further longer term tests are required to establish the extent of hydrogen generation since the present investigation concerns the initial stage of hydration up to 7 days. As discussed in the previous sections, different hydration products would provide OH\(^-\) for the corrosion of aluminium resulting in different corrosion products at different stages of cement hydration. This is especially important for the PFA-CAC systems as the conversion of metastable phases appeared to have significant effects on the aluminium corrosion.

### 4 Summary

A series of experiments have investigated the reaction of aluminium metal in OPC- and CAC-based systems. The results show that the maximum amount of aluminium powder able to corrode in the neat OPC system investigated in the present study was 6 wt%. The amount of hydroxide ion in the system appeared to determine the extent of aluminium corrosion, mainly through Ca(OH)\(_2\) in the OPC system. It was found that the corrosion of aluminium could cause the severe reduction of Ca(OH)\(_2\) in the system. The corrosion of aluminium was reduced to 2.3 wt% in the 4:1 BFS-OPC system, due to the reduced concentration of OH\(^-\) by dilution of OPC and increased effective water volume.

In the CAC-based system, less initial reaction occurred on the aluminium plate compared with that in the OPC-based system due to the lower matrix pH. However,
aluminium continued to corrode slowly in the PFA-CAC system up to 28 days, the maximum time period tested in the present work. Introducing sodium polyphosphate and boric acid provided an effective way to reduce the reaction of aluminium in the PFA-CAC system. The initial pH of the fluid paste at initial set was reduced, and the formations of metastable calcium aluminate hydrates were avoided by forming an amorphous binding phases. This system generated the lowest hydrogen gas release compared with the CAC-PFA based systems and the 3:1 BFS:OPC system. Further long term tests need to be conducted to establish whether calcium aluminate phosphate cements are suitable for long term aluminium encapsulation.

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Table 1 Chemical composition of raw materials.

<table>
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<td>TiO₂</td>
<td>-</td>
<td>-</td>
<td>2.08</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>P₂O₅</td>
<td>-</td>
<td>-</td>
<td>0.13</td>
<td>-</td>
<td></td>
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<tr>
<td>Chloride</td>
<td>0.05</td>
<td>0.02</td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>Insolubles</td>
<td>0.3</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>LOI</td>
<td>0.7</td>
<td>1.0</td>
<td>-</td>
<td>4.10</td>
<td></td>
</tr>
<tr>
<td>Free lime</td>
<td>0.8</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>Sulphide</td>
<td>-</td>
<td>0.9</td>
<td>-</td>
<td>-</td>
<td></td>
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</tbody>
</table>

a Contains reduced sulphur
b Determined using Leco analysis
Table 2 Formulation of samples, normalised by the weight of base cement (OPC+BFS=100, CAC+PFA=100).

<table>
<thead>
<tr>
<th>OPC based system</th>
<th>OPC (wt%)</th>
<th>BFS (wt%)</th>
<th>Water (wt%)</th>
<th>Al powder (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>100</td>
<td>0</td>
<td>35</td>
<td>0, 2.4, 4.9, 7.0</td>
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<tr>
<td></td>
<td>20</td>
<td>80</td>
<td>35</td>
<td></td>
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</table>

<table>
<thead>
<tr>
<th>CAC based system</th>
<th>CAC (wt%)</th>
<th>PFA (wt%)</th>
<th>Water (wt%)</th>
<th>Phosphate (wt%)</th>
<th>Boric acid (wt%)</th>
<th>Al plate</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>40</td>
<td>60</td>
<td>35</td>
<td>0</td>
<td>0</td>
<td>50x20x3 (mm)</td>
</tr>
<tr>
<td></td>
<td>40</td>
<td>60</td>
<td>35</td>
<td>16</td>
<td>1.2</td>
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</table>
Table 3 Hydrogen gas generated from the reaction of aluminium.

<table>
<thead>
<tr>
<th></th>
<th>H₂ gas generated</th>
<th>Release rate</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>7 days (ml/cm²)</td>
<td>28 days (ml/cm²)</td>
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<tr>
<td>BFS-OPC a</td>
<td>14.5</td>
<td>14.8</td>
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<tr>
<td>PFA-CAC b</td>
<td>1.0</td>
<td>5.2</td>
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<tr>
<td>PFA-CAC +Phosphate +Boric acid b</td>
<td>0.2</td>
<td>0.5</td>
</tr>
</tbody>
</table>

a BFS:OPC=3:1, w/s=0.35, b See Table 2 for details of formulations
Fig. 1 Schematic diagram of experimental setup for hydrogen measurement.
Fig. 2 Backscattered electron images of samples: (a) pure OPC, (b) OPC with 7.0 wt% of Al, (c) 4:1 BFS-OPC, and (d) 4:1 BFS-OPC with 7.0 wt% of Al.
Fig. 3 XRD patterns of OPC system with different amount of aluminium contents after 21 days of curing at room temperature. Reflection peaks are indexed as: A (Alite), B (Belite), C (Calcite), G (Gibbsite), M (Monosulphate), P (Portlandite).
Fig. 4 XRD patterns of 4:1 BFS-OPC system with different amount of aluminium contents after 21 days of curing at room temperature: Reflection peaks are indexed as: A (Alite), Al (Aluminium), B (Belite), C (Calcite), Ge (Gehlenite), M (Monosulphate), P (Portlandite), S (Strätlingite).
Fig. 5 DSC profiles for OPC system with different amount of aluminium powder after 21 days of curing at room temperature.
Fig. 6 DSC profiles for 4:1 BFS-OPC system with different amount of aluminium contents after 21 days of curing at room temperature.
Fig. 7 Peak area in DSC data for OPC and 4:1 BFS-OPC systems with different amount of aluminium content: (a) endothermic peaks of aluminium fusion in 640-670 °C and (b) endothermic peaks of Ca(OH)$_2$ dehydroxylation in 405-480 °C.
Fig. 8 Change in pH of samples at the initial stage of hydration: (a) for OPC system and (b) for 4:1 BFS-OPC system with different amount of aluminium.
Fig. 9 XRD pattern of PFA-CAC system with and without addition of sodium polypophosphate and boric acid after 7 days of curing at 20 °C. Reflection peaks are indexed as: Ca (Monocalcium aluminate), C8 (C$_2$AH$_8$), C10 (CAH$_{10}$), Gi (Gibbsite), Ge (Gehlenite), Mu (Mullite), Mo' (Monosulphate related phase), Pe (Perovskite), Q (Quartz), St' (Strätlingite related phase). Al* is reflection from the Al sample holder.
Fig. 10 Change in pH of cement matrices at the initial stage of hydration: CAC-based systems compared with 3:1 BFS-OPC system.