

SP2 Report on

**Use of Supplementary Cementitious Materials (Pozzolan) in Arresting the Conversion of
CAC and Its Effect on CAC Corrosion-**

Based on Accelerated Corrosion Tests

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Summary

Calcium aluminate cement is used as a protective lining against the corrosive attack of micro-organism and their metabolic products on reinforced concrete sewer pipes. The corrosion behaviour of CAC cement is related to the process of conversion of aluminate hydrates, where full conversion can result in as much as 1-4 times increase in the rate of corrosion. Therefore controlling and understanding the rate and the processes that affects conversion is critical in the effective use of CAC as a mitigation strategy against microbiological attack.

In this study we examined the role of pozzolanic material (fly ash) in arresting the conversion of CAC. CAC cement pastes were prepared with constant ratio of water/binder = 0.4 and with pozzolanic contents of 0 to 25 weight%. To test the effectiveness of the pozzolans, CAC cements were subjected to high temperature treatments (80-100°C) in a water bath to accelerate conversion. Thermal analysis (TGA), X-ray diffraction and electron microscopy with integrated EDS and EBSD system were used to monitor the physical and mineralogical transformation of CAC cement during the conversion and leaching tests. Our study showed that pozzolanic materials are able to arrest conversion by the formation of gehlenite hydrate (C_2ASH_8) or stratlingite and therefore strongly reducing the transformation of hexagonal aluminate hydrates (CAH_{10} , C_2AH_8) into the cubic hydrate (C_3AH_6). The gehlenite hydrates were shown to demonstrate greater resistance to both abiotic and biogenic sulphuric acid attack in comparison to the cubic hydrates, proving the important role of pozzolans in stabilising the properties of CAC. However the introduction of pozzolan also contributes to greater porosity which in turn results in faster rates of corrosion. Thus the merit of using pozzolan must be managed by controlling its addition to achieve the stratlingite formation but also control the formation of porosity and conversion.

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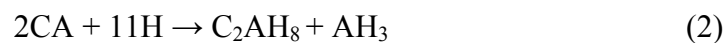
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1.0 INTRODUCTION

Calcium aluminate cements (CAC) is a specialty cement material with a main constituent of calcium aluminate. This material has a wide range of application in both the construction industry and as a sacrificial protective lining against corrosive environment because of its ability to gain early strength and its resistance to aggressive chemical environments and temperatures (Dumas 1990, Midgley 1990, Sand, Dumas et al. 1994, Scrivener, Cabiron et al. 1999, Chotard, Gimet-Breart et al. 2001, Lamberet 2008).

1.1 Hydration Reactions

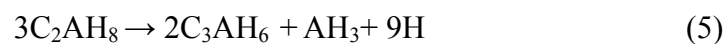
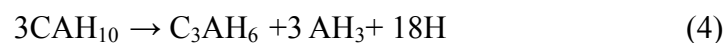
Calcium aluminate once hydrated undergoes a series of chemical reaction that influences both its physical, mechanical and chemical properties. Calcium aluminate cement reacts with water to form metastable (CAH_{10} and C_2AH_8) and stable hydrates (C_3AH_6) through time and temperature dependent reactions (Scrivener, Cabiron et al. 1999, Chotard, Gimet-Breart et al. 2001, Juenger, Winnefeld et al. 2011):



The designations for these chemical formulae are C - CaO, A – Al_2O_3 and H - H_2O .

1.2 Conversion Reactions

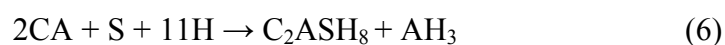
Once hydrated CAC is subjected to further chemical change referred to as conversion that further transform the metastable phases to the stable phase (Bradbury, Callaway et al. 1976):



The key concern with conversion is that it leads to the formation, with time, of less dense precipitates and cement resulting in increased porosity, reduced hydraulic strength and increases susceptibility to corrosive attack (Bradbury, Callaway et al. 1976, Jambor and Skalny 1996, Chotard, Gimet-Breart et al. 2001). This process is thermodynamically driven and is therefore inevitable (Gosselin, Gallucci et al. 2010). The speed of conversion may take years at low temperature but could be accelerated with a high water/cement ratio and at elevated temperatures (Bradbury, Callaway et al. 1976, Barnes and Baxter 1978, Collepardi, Monosi et al. 1995, Pacewska, Wilinska et al. 2011). The continuous conversion of this material will adversely affect the long term durability of CAC.

1.3 Arresting Conversion

There have been various attempts to reduce or overcome conversion. This has included controlling the water/cement ratio to below 0.4, use of phosphate compounds followed by hydrothermal curing to generate hydroxyapatite and AH_3 and with the use of vitreous pozzolanic materials or supplementary cementitious materials (SCMs) including fly ash and granulated blast furnace slag (Singh and Majumdar 1992, Collepardi, Monosi et al. 1995, Ding, Fu et al. 1995, Fu, Ding et al. 1995, Benezet and Benhassaine 1999, Hidalgo, Garcia et al. 2009, Pacewska, Wilinska et al. 2011, Palou, Bagel et al. 2013). The introduction of SCMs provides an alternative reaction to the converted C_3AH_6 phase to an aluminium hydrate with silica C-A-S-H phase, stratlingite (C_2ASH_8) or hydrated gehlenite (C_2AS) (Collepardi, Monosi et al. 1995, Ding, Fu et al. 1995, Bensted 1996, Hidalgo, Garcia et al. 2009):



It appears that although there has been significant work devoted in examining the effect of SCMs addition to CAC strength, work on the effect of stratlingite on the corrosive behaviour of CAC on the other hand is scarce. In this study the aim was to establish the potential of pozzolans (e.g., fly ash) in arresting conversion and its subsequent effect on CAC corrosion.

2.0 EXPERIMENTAL

2.1 Materials

The materials used in this study included a commercially available calcium aluminate cement (Sewpercoat) sourced from Kerneos, Australia and fly ash from a power station. The chemical compositions of these materials were determined by X-ray fluorescence spectroscopy and are shown in Table 1.

Table 1. Composition of calcium aluminate cement and pozzolanic materials

Oxides (wt%)	Calcium Aluminate Cement	Fly Ash
Al_2O_3	41.3	6.86
CaO	37.4	9.53
Cr_2O_3	0.13	0.06
Fe_2O_3	9.54	2.03
K_2O	0.3	0.18
MnO	0.12	0.05
MgO	0.3	1.8
NiO	0.137	0.114
SiO_2	6.97	79.1
TiO_2	1.93	0.36
V_2O_5	0.05	--
ZrO_2	0.14	--

2.2 Preparation of the calcium aluminate cement specimens

The cement specimens were prepared by replacing the calcium aluminate cement with 5% and 25% of the pozzolan material by weight. To obtain a homogeneous mixture, the raw materials were ground and mixed together in a Retsch planetary ball mill PM 100 CM for 3 minutes at 500 rpm. The water to cement ratio used for the plain CAC was 0.4. This ratio was maintained for the CAC and pozzolan mixes and as such for higher pozzolan replacement lower amount of water was added. The cement mixture and water were mixed mechanically for 3 minutes and poured into 2 x 4 inch stainless steel molds, compacted and the surface smoothed manually. The molded specimens were cured for 24 hours at 21°C in 98% relative humidity environmental chamber, demolded and cured further in a water bath with a controlled temperature of 30°C at various periods of time up to 28 days.

2.3 Characterisation of cement specimen

The phase transformations during the curing and conversion of CAC were monitored with X-ray diffraction analysis using XRD Siemens D5000 and by thermal gravimetric analysis using Perkin Elmer TGA 4000. Thermal analysis was carried out by heating the samples from 30 to 1000°C with a heating rate of 10°C/min in nitrogen metered at 20 ml/min. The microstructure and mineralogy of selected specimens were examined by scanning electron microscopy using Zeiss ULTRA *plus* with Oxford Instruments Aztec integrated EDS and EBSD system.

2.4 Accelerated and field corrosion tests

To simulate the corrosion of CAC in sewers, the cured specimens were immersed in 5 wt% sulphuric and citric acids maintained at 26-27°C. The pH and temperature of the solutions were monitored with pH-temperature probes coupled with a HNH19143 meter. Additional acids were added to adjust and maintain the pH. To measure the thickness loss, loose or soft corrosion products were scraped off. The specimen diameters were then measured using a vernier caliper. Field testing involved the installation of coupon specimens of CAC in the Southern and Western Suburbs Ocean Outfall Sewers (SWSOOS), South Barrel in Sydney for 364 days.

3.0 RESULTS

3.1 Effect of pozzolan on mineralogical transformation during conversion of CAC

The conversion of CAC during curing was examined by Xray diffraction, SEM with EBSD and thermally by thermal gravimetric method. The CAC hydrates were identified according to Table 2.

Table 2. Thermal decomposition of calcium aluminate hydrates.

Calcium Aluminate Hydrates						Heating Rate	Method	References
CAH ₁₀	C ₂ AH ₈	C ₃ AH ₆	AH ₃ gel	Al(OH) ₃	C ₂ ASH ₈			
	110, 175, 295					10°C/min	DTG	(Ukrainczyk, Matusinovic et al. 2007)
96				266		20°C/min	DTG	(Barnes and Baxter 1978)
110				267		5°C/min	DTG	(Guirado, Gali et al. 1998)
	170, 230, 275	320				10°C/min	DTG	(Das, Mitra et al. 1996)
110-120		320-350		295-310		25°C/min	DTA	(Bradbury, Callaway et al. 1976)
120		310		290		10°C/min	DTA	(Nilforoushan and Talebian 2007)
			90			10°C/min	DTA	(Calvo, Alonso et al. 2013)
137	137				280-350	10°C/min	DTA	(Hidalgo, Garcia et al. 2009)
					100, 138 and 240	10°C/min	DTG	(Kuzel 1976)
					120, 165 and 220	10°C/min	DTG	(Matschei, Lothenbach et al. 2007)

The X-ray diffraction pattern of CAC at day 28 in Figure 1 confirms the conversion with the presence of both metastable and stable phases. It is also apparent that particular CAC stratlingite (C_2ASH_8) also formed by day 28 of curing such composition of this CAC include pozzolanic material. Table 1, shows the raw data of this study contained 6.97% SiO_2 . The CAC was converted by heating at $100^\circ C$ for comparison of the effect of conversion on the corrosion rates in citric and sulphuric acid shown in Figure 3.

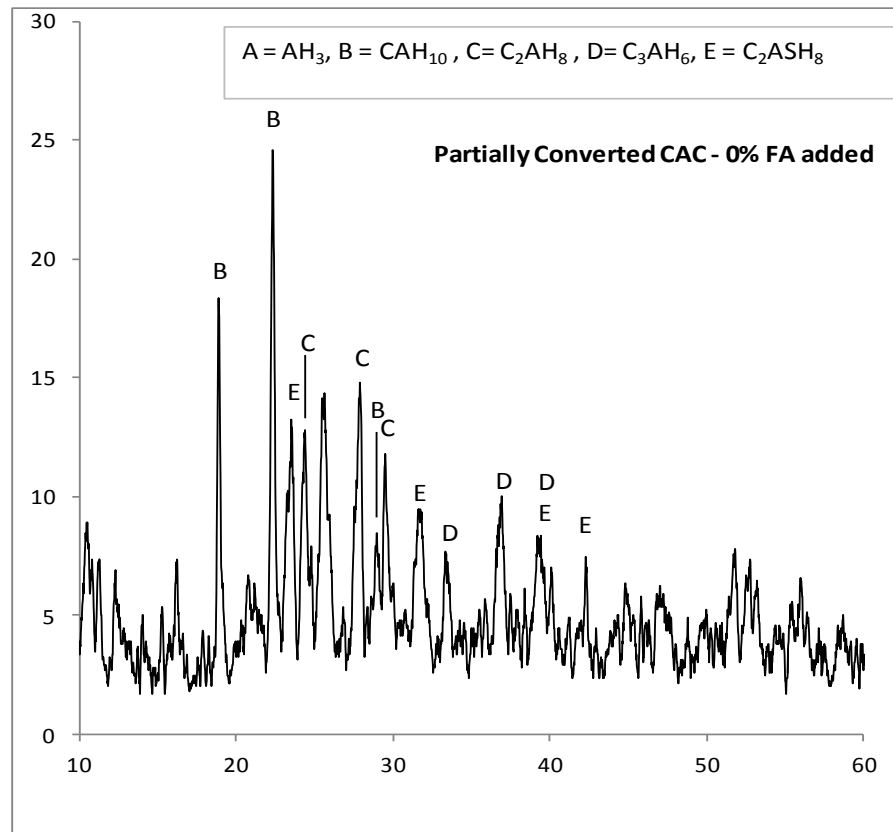


Figure 1. X-ray diffraction pattern for partially converted CAC ($30^\circ C$ in water for 28 days)

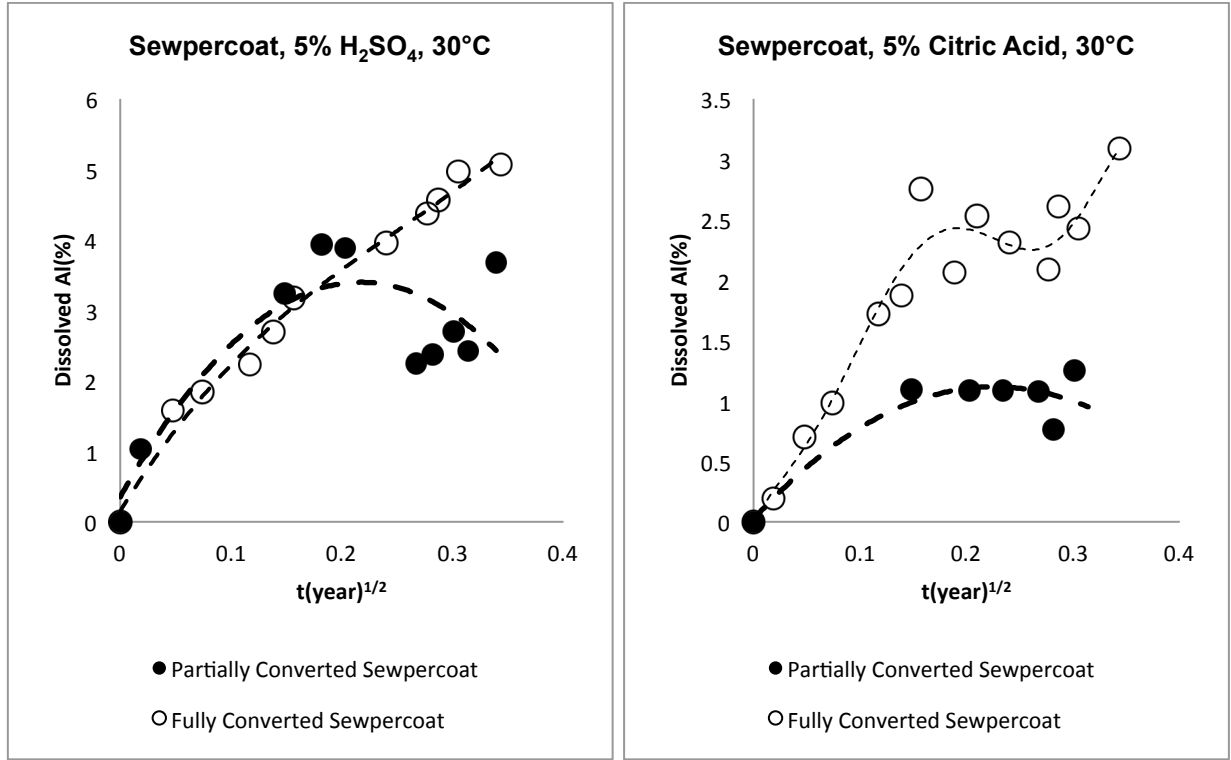


Figure 2. Effect of conversion on the rates of corrosion in 5% citric and sulphuric acid.

Addition of supplementary cementitious materials (SCMs) such as fly ash has previously been found to arrest the formation of the hydrogarnet by providing an alternative reaction to an aluminium hydrate with silica to C-A-S-H phase or stratlingite (C₂ASH₈) (Collepari, Monosi et al. 1995, Ding, Fu et al. 1995, Bensted 1996, Hidalgo, Garcia et al. 2009). Various studies of stratlingite have demonstrated its corrosion resistance to sulphuric acid (Torii and Kawamura 1994, Min, Song et al. 2011). Figure 1.0 has demonstrated that CAC used in this study contain SCMs that result in the generation of stratlingite. However, the amount of SCMs present in this CAC material appears insufficient to control the effects of conversion. This is evident in the faster rate of corrosion of converted CAC in Figure 2.

This aspect of the study examined the effect of increasing the amount of pozzolan (fly ash) in arresting the conversion of CAC to calcium aluminium hydrate (C₃AH₆). About 5 and 25 wt% of fly ash was added to CAC using an inter-grinding method of mixing the two components in a ball mill. The effect of adding greater quantities of fly ash on the DTG of converted CAC is shown in Figure 3. To examine the mineral transformation more carefully, the unresolved multi-component bands associated with the individual converted component peaks were separated by using a curve resolving algorithm, based on the Levenberg-Marquardt method (Marquardt 1963). The peak function was a mixed Gauss-Lorentz line shape of the form:

$$f(x) = (1 - L)He^{-\left[\left(\frac{x-x_0}{w}\right)^2 4 \ln 2\right]} + \frac{LH}{4\left(\frac{x-x_0}{w}\right)^2 + 1} \quad (6)$$

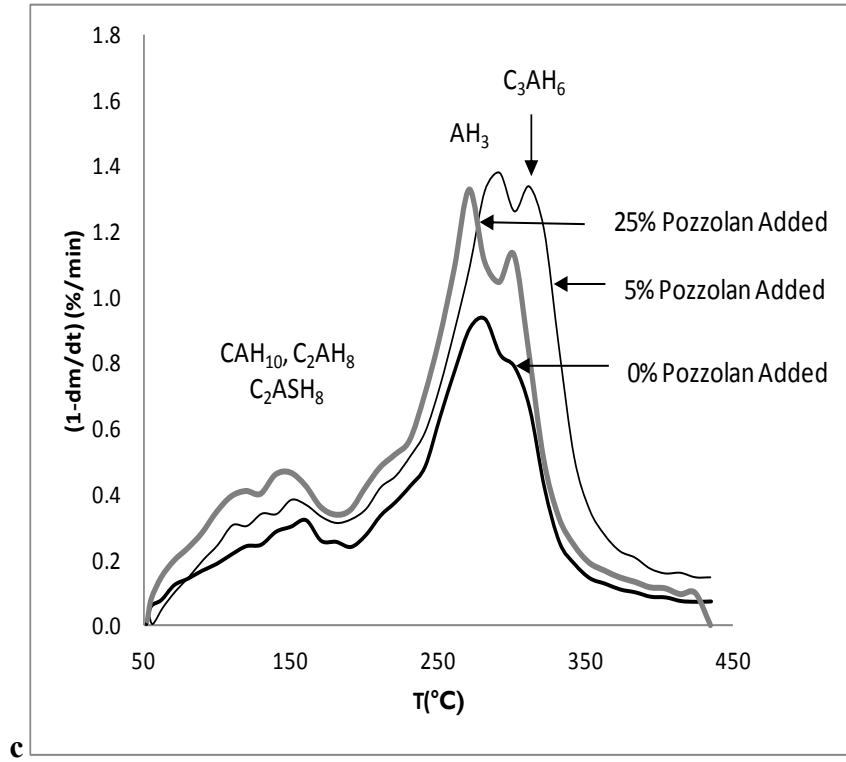


Figure 3. DTG of converted CAC with fly ash pozzolan.

where x_0) peak position; H) peak height; w) peak width; L) fraction of Lorentz character. The corresponding resolved peaks associated with the DTG of the CAC hydrates from Figure 3 are shown in Figure 4. Comparing the C_3AH_6 peak directly, it would appear the addition of fly ash promoted the faster conversion to hydrogarnet C_3AH_6 in comparison to if no additional fly ash was added. This is particularly more prevalent with 5% additional fly ash. As fly ash addition increased to 25%, the C_3AH_6 peak was reduced in comparison to CAC with 5% fly ash. Although this may suggest the extent of conversion was reduced, the susceptibility of C_3AH_6 to carbonation should be taken into account. A more accurate consideration is to examine the formation of AH_3 (Blenkinsop, Currell et al. 1985) relative to the metastable phases. The degree of conversion (D_c) can be measured thermally by DTG according to the following equation(Barnes and Baxter 1978):

$$D_c = \frac{AH_3}{AH_3 + CAH_{10}} \times 100. \quad (7)$$

Because the degree of conversion is unlikely to be always complete, a conversion equation that also takes into account the presence of other metastable phases into account is:

$$D_c = \frac{AH_3}{AH_3 + CAH_{10} + C_2AH_8 + C_2ASH_8} \times 100. \quad (8)$$

Based on equation (8), the degree of conversion for 0%, 5% and 25% additional fly were estimated to be 66%, 42.6% and 48% respectively. This confirms the role of the additional fly

ash in arresting the conversion and this is consistent with the observed effects of supplementary cement materials in CAC conversion (Hidalgo, Garcia et al. 2009, Gosselin, Gallucci et al. 2010, Mostafa, Zaki et al. 2012). The optimum was achieved with 5% of fly ash. It is also apparent that a greater quantity of the stratlingite is generated with the addition of fly ash. The stratlingite/AH₃ ratio based on the areas of the peaks for 0%, 5% and 25% additional fly are 0.3, 1.16 and 1.02.

The X-ray diffraction patterns in Figure 5 showed the presence of both metastable (CA₁₀, C₂AH₈ and brownmillerite), stable (C₃AH₆) CAC hydrates and stratlingite. The hydrated brownmillerite mineral has a similar structure to the metastable hexagonal C₂AH₈ phase where components of Al is substituted with Fe in Al/(Al+Fe) ratio of 0.4. It undergoes a similar conversion as the metastable C₂AH₈ forming a stable hydrogarnet structure of Ca₃(Al,Fe)(OH)₁₂ (Meller, Hall et al. 2004). For all the converted CAC examined, the AH₃ appeared as minor structure suggesting it is present mostly as an amorphous phase. Figure 5 shows C₃AH₆ peaks are still relatively strong in CAC even with additional 5% and 25% fly ash in comparison to the control sample. It appears that even in the presence of fly ash the conversion process still proceeded to a significant extent and this partially appears to be related to the temperature of curing. Hidalgo et al. (Hidalgo, Garcia et al. 2009) have shown that SCMs significantly reduced the formation of both AH₃ and C₃AH₆ when CAC is cured at 20°C, whilst work by Heikal et al. (Heikal, Radwan et al. 2004) show that curing at higher temperatures, 40°C and 60°C will allow conversion to C₃AH₆ to proceed strongly even in the presence of SCMs. Curing at 30°C, as conducted in this study does not fully prevent conversion but in fact allowed both the strong formation of both stable phase C₃AH₆ and stratlingite in CAC containing additional fly ash. However as shown by the thermal analysis, the conversion is partially suppressed.

Figure 6 shows the scanning electron image of converted CAC with 5% additional fly ash and the EBSD analysis of a component (white boxed area in Figure 6 a) in the same sample. There is a considerable amount of voids that have been formed in this sample and is consistent with the formation of denser precipitates with conversion (Bradbury, Callaway et al. 1976, Chotard, Gimet-Breart et al. 2001). The EBSD analysis of a small section of this sample shows the formation of key four phases, gehlenite, CA, brownmillerite (Ca₂(Al,F)₂O₅ or C₂(A,F)H₈) and an iron spinel and is consistent with the XRD analysis in Figure 4. The corresponding phase fraction analysis of Figure 6b is reported in Table 3. This particular section of converted CAC shows 37.32% of the fraction consist of metastable phases (CA₁₀, C₂(A,F)H₈) and 25.3% is gehlenite or un-hydrated stratlingite. The high proportion of metastable phase further confirms the effect of fly ash in partially suppressing conversion and in diverting the stable phase to the C-A-S-H structure.

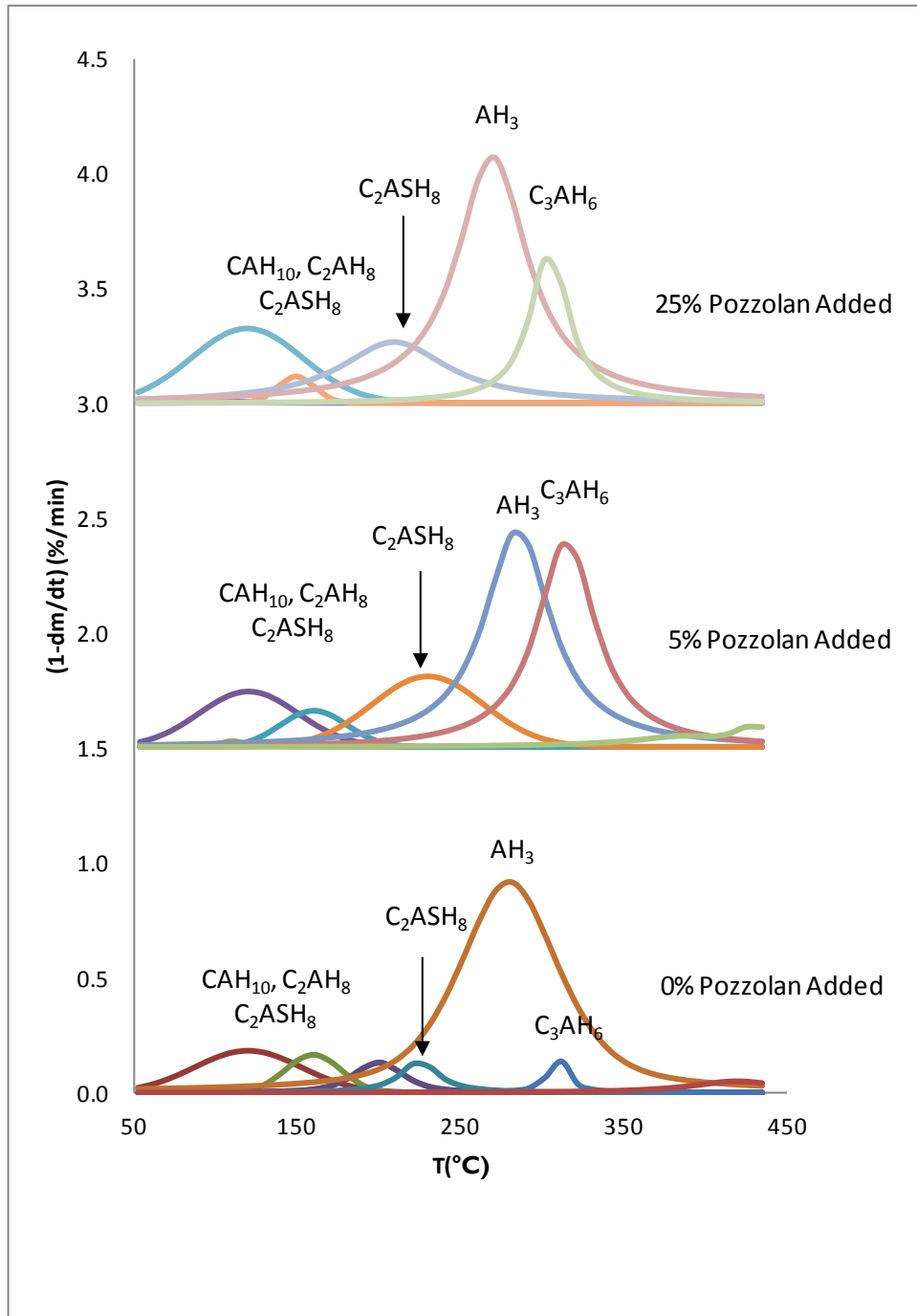


Figure 4. Curve fitting analysis of converted component phases from DTG of converted CAC with fly ash pozzolan.

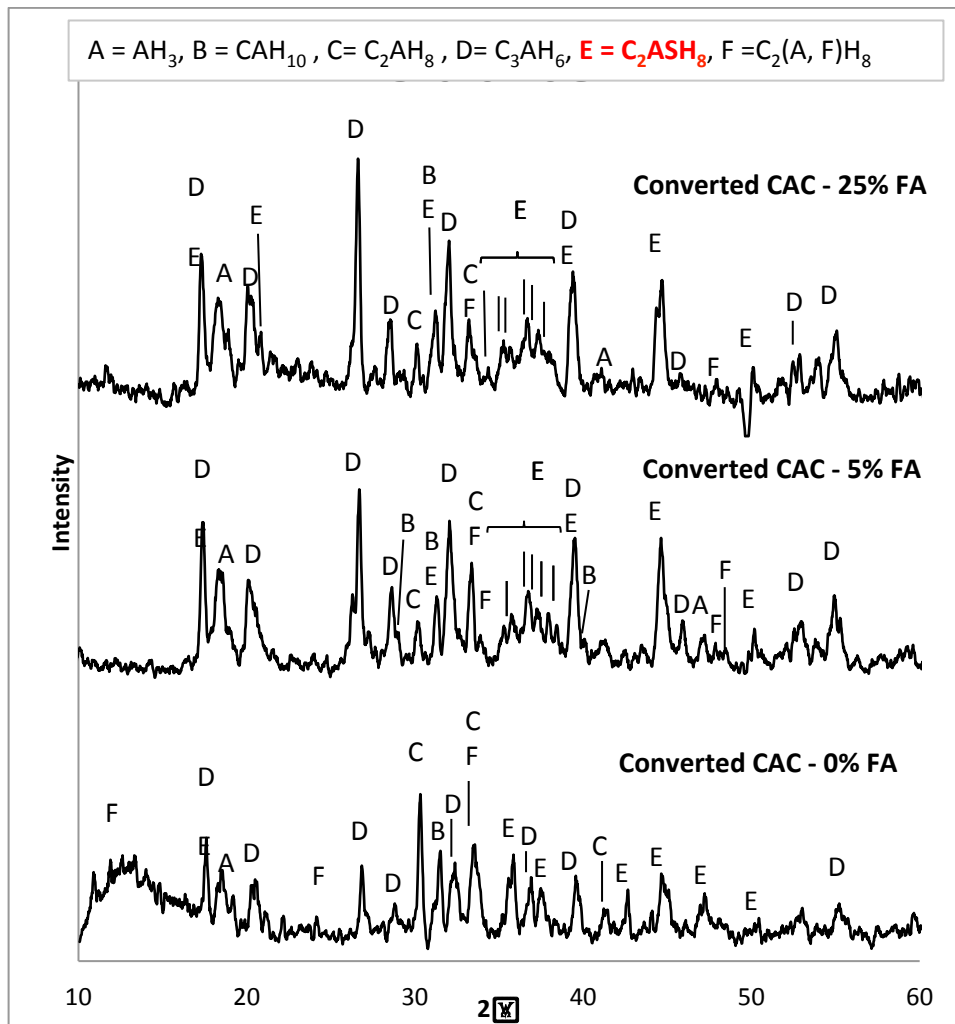


Figure 5. X-ray diffraction pattern of converted CAC with fly ash pozzolan.

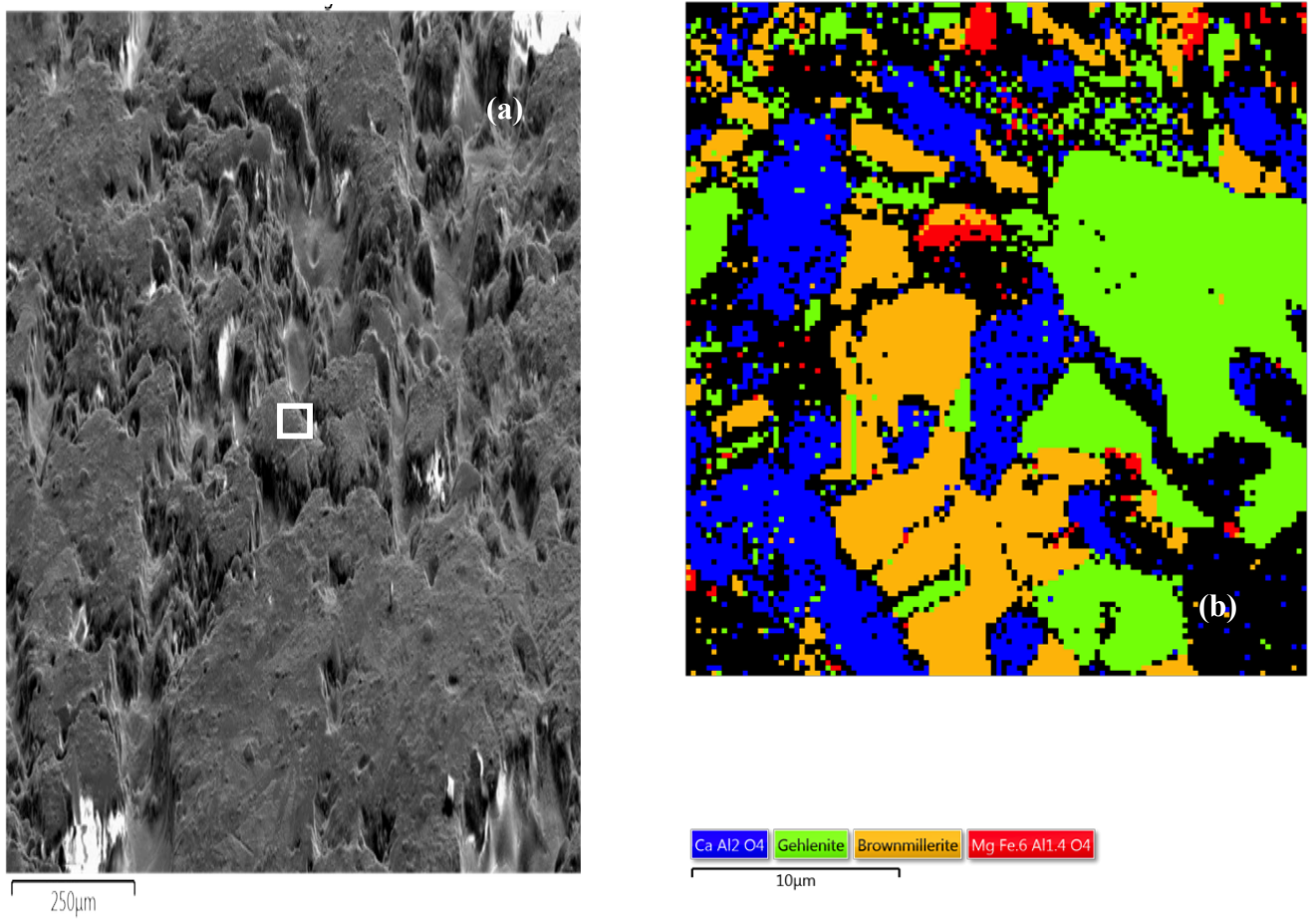


Figure 6. Scanning electron microscope: a) image of CAC + 5% flyash converted and b) EBSD analysis of white boxed area in a.

Table 3. Phase fraction analysis of converted CAC + 5% fly.

Phase Name	Phase Fraction (%)
CA	18.53
Gehlenite	25.28
Brownmillerite	18.79
Mg Fe ₆ Al ₁₄ O ₄	1.58
Unaccounted fractions	35.81

3.2 Effect of Pozzolan on Corrosion of CAC

The effect of the additional fly ash on the corrosion of converted CAC in 10g/L sulphuric and citric acids are shown in Figures 7 and 8. It is apparent that additional fly ash appear to control the rate of corrosion based on the thickness loss. It appear to maintain similar rates of corrosion as the partially converted CAC.

However the corresponding analysis of the rate of corrosion based on dissolved Al in Figure 9 and 10 in 10g/L sulphuric and citric acids demonstrate that conversion and the addition of pozzolan results in faster rate of corrosion. It should be note however that the core specimen used for CAC pozzolan tests were 1/3 of the size of the CAC without pozzolan. This may contribute to the slightly faster rate of corrosion.

As shown in Table 4, both conversion and the addition of fly ash contributes to greater porosity. It appears that the greater porosity led to faster rate of corrosion. The expansion of CAC in the presence of flyash appears mask the true effect of corrosion appearing to result in lower rates of corrosion.

Figure 11 demonstrate the product from CAC and fly ash results in the formation of more corrosion resistant phase. The results shows the phase profile of C_3AH_6 and stratlingite in field CAC; 0-1 cm representing the top layer closer to the sewer front and 2-3 cm layer from the sewer front. These CAC samples were obtained from the roof in Hayden Pl SWSOOS 2 after 6 years of service. It is evident that most of the C_3AH_6 has been removed from the first 0-1 cm layer, whilst the stratlingite remains demonstrating its greater corrosion resistance.

The product of the pozzolan and CAC does results in more corrosion resistant stratlingite phase. However its use must be managed to control the conversion reaction and the formation of porosity that results from its incorporation in the CAC.

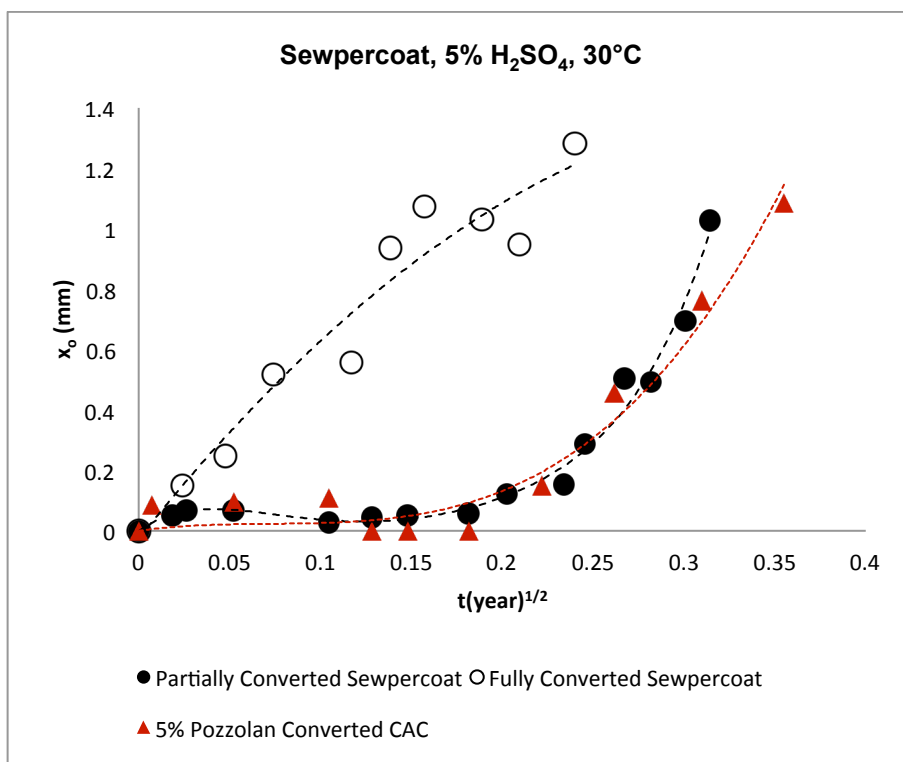


Figure 7. Rate of corrosion (based on thickness loss) of converted CAC with and without additional pozzolan in 10g/L H₂SO₄.

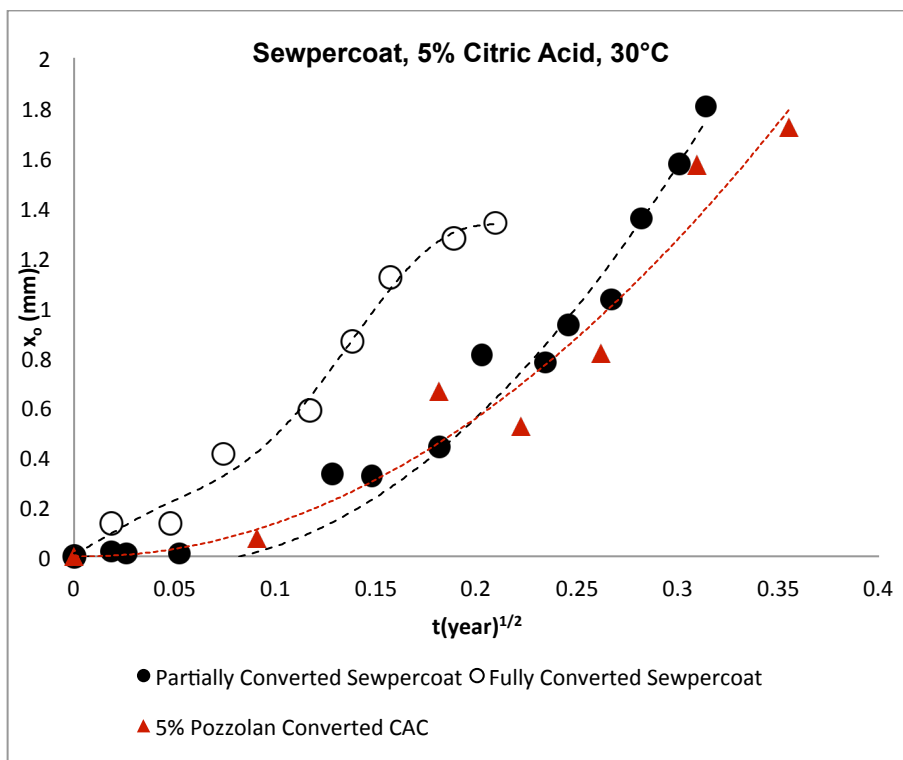


Figure 8. Rate of corrosion (based on thickness loss) of converted CAC with and without additional pozzolan in 5% citric acid.

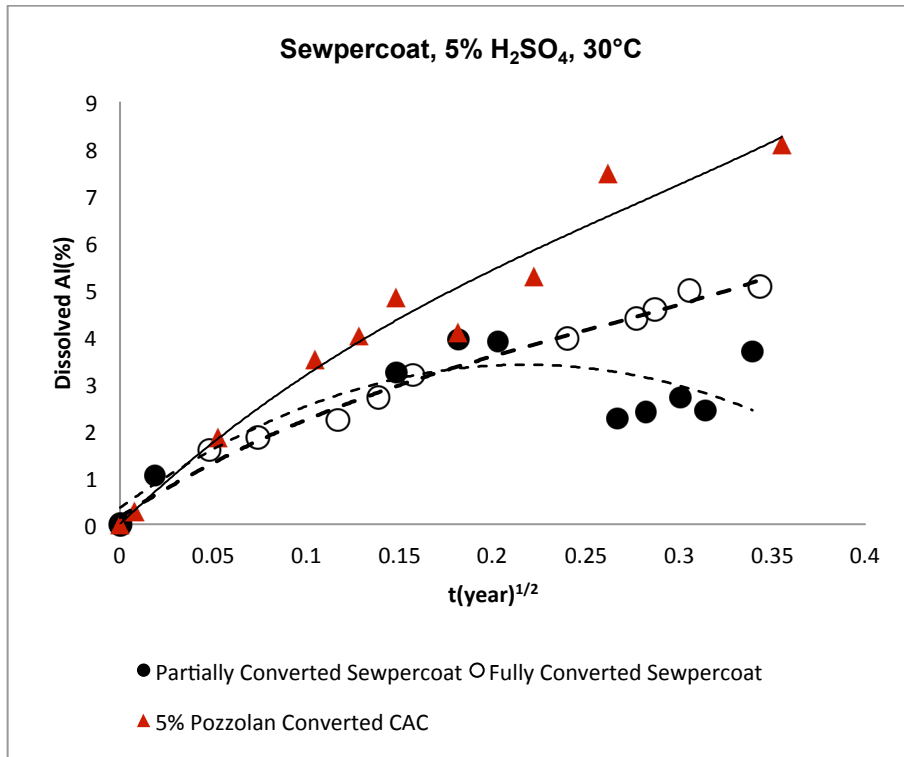


Figure 9. Rate of corrosion (based on dissolved Al) of converted CAC with and without additional pozzolan in 10g/L H₂SO₄.

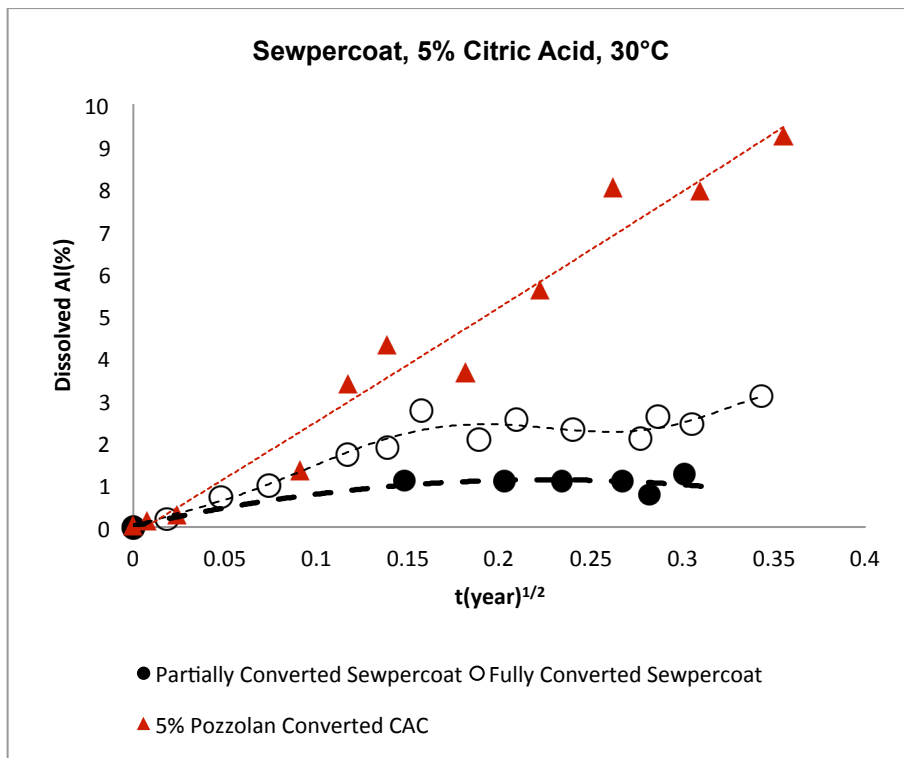
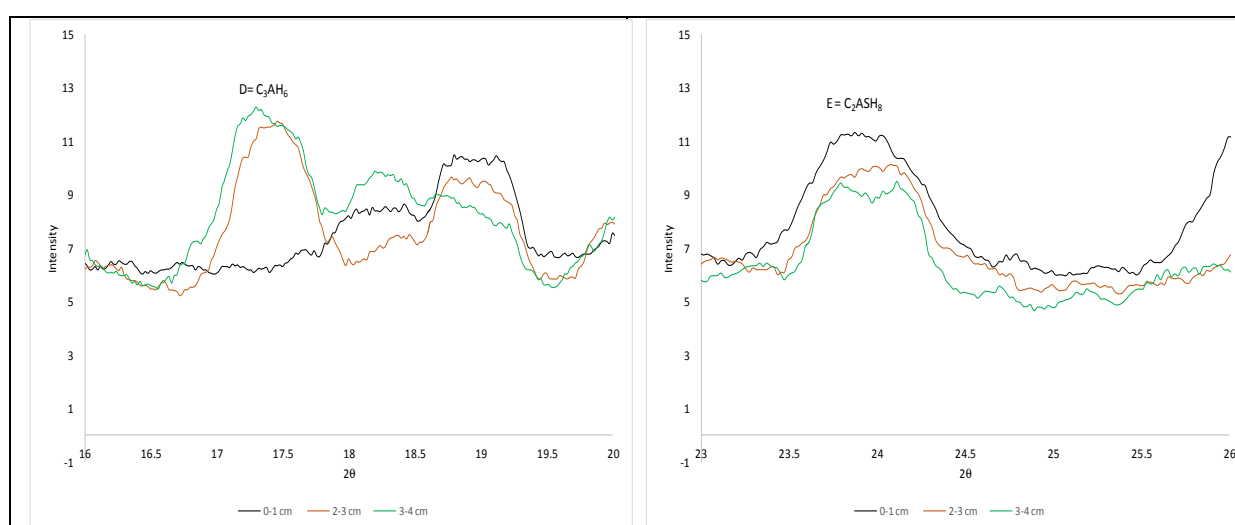


Figure 10. Rate of corrosion (based on thickness loss) of converted CAC with and without additional pozzolan in 5% citric acid.

Table 4. Density and Porosity of CAC with conversion and addition of fly ash.

	CAC + 0% FA Partially converted at 28 days, 30°C	CAC + 0% FA Cured at 100°C, 2 hours	CAC + 5% FA Cured at 100°C, 2 hours	CAC + 55% FA Cured at 100°C, 2 hours
Bulk density (g/cm ³)	2.22	2.14	2.01	2.02
True density (g/cm ³)	2.25	2.29	2.78	3.11
Porosity %	1.33	8.25	15.72	19.1

**Figure 11.** Relative corrosion resistance of C_3AH_6 and stratlingite in 6 year field corrosion tests (Hayden Pl. Banksmeadow, SWSOOS 2).

4.0 CONCLUSIONS

This study has shown the metastable phases of CAC has a higher corrosion resistance to both biotic and biogenic acids generated in sewers. The stable phase (C_3AH_6) and AH_3 are preferentially corroded in both abiotic and biogenic acids. The conversion of CAC with time increased its susceptibility to corrosion with biogenic acid and CO_2 . It is however possible to reduce or arrest conversion with the addition of fly ash. The addition of fly, and in this study this was achieved with an optimal value of 5%, was found to reduce the conversion process through the formation of stratlingite, however in the process greater porosity also developed. Although the corrosion resistance of stratlingite was demonstrated from the analysis of corrosion residues. Its incorporation in CAC results in greater porosity resulting in faster rate of corrosion.

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