

## 1 Calcium Aluminate Cement

### 1.1 What is Calcium Aluminate Cement?

- Calcium aluminate cement (CAC) is mainly made up of lime (C or CaO) and alumina (A or Al<sub>2</sub>O<sub>3</sub>).
- The lime-alumina (Al<sub>2</sub>O<sub>3</sub> to CaO) ratio ranges from 0.6 to 1.0 (Neville 1975).
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- CAC is used widely to combat the effect of corrosion, particularly those associated with microbiologically induced corrosion of concrete (MICC). It is suggested that CAC's key protective features include high early strength, low porosity, high acid neutralisation capacity, the toxicity of Al<sup>3+</sup> and its alkalinity that assist in controlling microbial growth and that its curing is enhanced in high humidity or high moisture environments, which is an advantage in sewers.

#### **Aggregates**

- Various types of aggregates including silica sand and dolomite may be used in conjunction with CAC in making concrete. There is a type of CAC that contains calcium aluminate aggregate. This type of CAC is showing a better resistance to MIC.

#### **Reactive Fillers**

- Reactive filler such as silica fumes and reactive alumina, with admixtures allowed lower amount of water for flow of CAC.

#### **Admixtures**

- Admixtures are added to the CA mix to control the setting time and the flow properties of CAC. These include:
  - **Accelerator:** The most effective accelerator is lithium carbonate (Li<sub>2</sub>CO<sub>3</sub>). Adding 0.005 wt. % can reduce the setting time from 30 to 25 min and 0.01% down to 15 min.
  - **Retarder:** A common retarded is tri-sodium citrate and its effect is to reduce the setting time allowing control of the workability of the concrete. Both accelerator and retarded could be used together to control the hardening and setting time of CAC.
  - **Plasticiser:** The plasticiser as it suggest imparts a plasticising property (or fluid like behavior) to CAC. The various types of plasticisers used include tri-sodium citrate, trisodium polyphosphate, sodium polymethacrylate (Darvan 7S) and sulfonated polycondensation product of melamine (Melment F10).

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- Table 1 provides the approximate composition of standard CAC grades, and a comparison with the typical composition of Portland cement.
- CAC was previously known as high-alumina cement (HAC) and was developed as a solution to the problem of decomposition of Portland cement under sulfate attack.
- CAC is used widely to combat the effect of corrosion, particularly those associated with microbiologically induced corrosion of concrete (MICC). It is suggested that CAC's key protective features include high early strength, low porosity, high acid neutralisation capacity, the toxicity of  $\text{Al}^{3+}$  and its alkalinity that assist in controlling microbial growth and that its curing is enhanced in high humidity or high moisture environments, which is an advantage in sewers.

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Table 1: Composition of calcium aluminate and Portland cements

Chemical Constituents	Cement Type		
	High alumina CAC	Low alumina, CAC	Portland cement
Al <sub>2</sub> O <sub>3</sub>	39-44	16-18	5.6
CaO	34-38	10-12	65.5
SiO <sub>2</sub>	6-8	65-70	21.1
Fe <sub>2</sub> O <sub>3</sub> +FeO	12-20	0.8-2	3
TiO <sub>2</sub>	<2	<1	<1
MgO	~1	~0.1	<2
Na <sub>2</sub> O	~0.1	~0.1	<2
K <sub>2</sub> O	~0.15	~0.05	<1

### 1.1.1 Calcium Aluminate Chemistry

CAC undergoes three forms of reaction which affects its performance. These include:

#### Hydration Reactions

- When calcium aluminate (CA) reacts with water it hardens as it undergoes a series of hydration reactions.
- These hydration reactions are:



(C: CaO, A: Al<sub>2</sub>O<sub>3</sub>, H: H<sub>2</sub>O)

- Three types of CAC hydrate products (CAH<sub>10</sub>, C<sub>2</sub>AH<sub>8</sub> and C<sub>3</sub>AH<sub>6</sub>) are generated as a result of the hydration reaction. The first two (CAH<sub>10</sub>, C<sub>2</sub>AH<sub>8</sub>) are referred to as metastable phases. The C<sub>3</sub>AH<sub>6</sub> is referred to as the stable phase.
- The types of CAC hydrates formed are influenced by various factors including CAC composition, CAC particle size, water: cement ratio and temperature of curing.

- The type of CAC hydrates formed will dictate the rate of CAC corrosion. The metastable phases shows greater resistance to acid attack, whilst  $C_3AH_6$  is more susceptible to corrosion (see Figure 1).

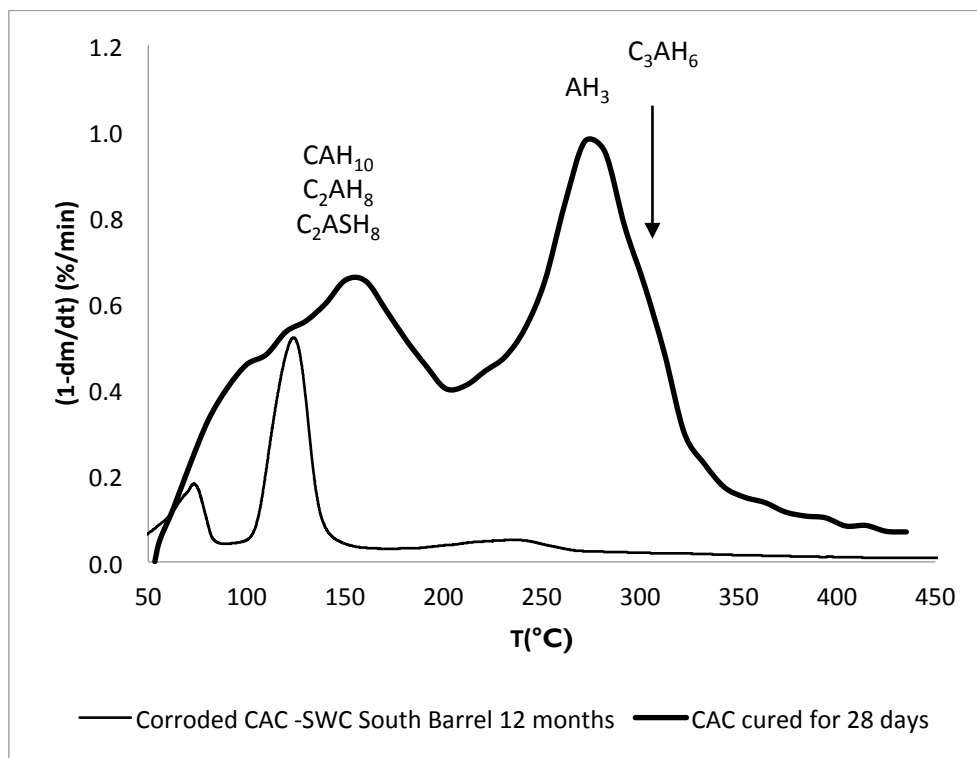


Figure 1. DTG of cured CAC and CAC corroded in the Sydney Water's SWSOOS 2 South Barrel sewer for 364 days.

- The hydration reaction is exothermic and could generate temperature up to 70°C, although higher temperatures have been reported. This high temperature drives the formation of the stable hydrate ( $C_3AH_6$ ).
- The extent of CA hydration can be controlled by limiting the water: cement ratio. The CA hydration can continue to occur for many years in the field depending on the availability of moisture (see Figure 2). That is it can continue to replace metastable phases that have been converted. This process can therefore control the CAC hydrate composition with time and thus the general CAC rate of corrosion.

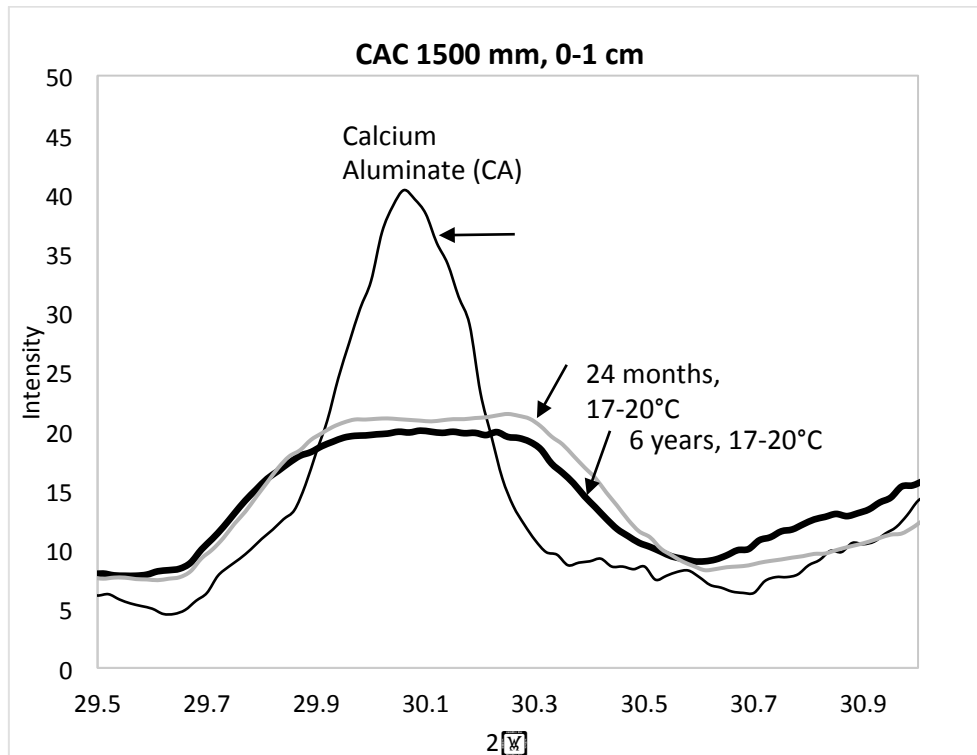
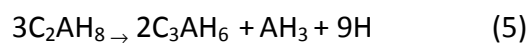
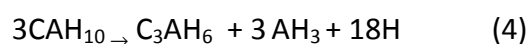


Figure 1. XRD of the calcium aluminate (CA) phase in CAC corroded in the wall (1500 mm above the sewage floor) of Sydney Water's SWSOOS 2 South Barrel and Hayden Place with time.

### Conversion

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



- The formation of  $\text{C}_3\text{AH}_6$  can increase the rate of corrosion of CAC because  $\text{C}_3\text{AH}_6$  is more susceptible to corrosion,  $\text{C}_3\text{AH}_6$  has higher density relative to the metastable phase and its formation leads to greater porosity, greater porosity makes CAC more susceptible to corrosion attack and from the carbonation reaction.
- 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 by elevated temperatures and humidity (Bradbury, Callaway et al. 1976, Barnes and Baxter 1978, Collepardi, Monosi et al. 1995, Pacewska, Wilinska et al. 2011).

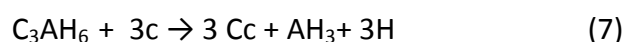
- The conversion reaction can be minimised by :
  - Controlling the water: cement ratio to 0.4 or lower
  - Use of phosphate compounds followed by hydrothermal curing to generate hydroxyapatite and  $AH_3$
  - Use of vitreous pozzolanic materials or supplementary cementitious materials (SCMs) including fly ash and granulated blast furnace slag
  - In the presence of pozzolanic vitreous silica or supplementary cementitious materials, it has been suggested that the silica would react with the CA phase to form stratlingite ( $C_2ASH_8$ ) avoiding the formation of  $C_2AH_8$  and thus the conversion to  $C_3AH_6$  (Hidalgo, Garcia et al. 2009):



Stratlingite has a greater corrosion resistance than  $C_3AH_6$ .

### **Carbonation**

- The stable phase  $C_3AH_6$  can also react with  $CO_2$  in the atmosphere to form  $CaCO_3$  (Cc) (Blenkinsop, Currell et al. 1985):

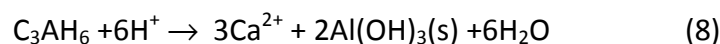


- Carbonation lowers the pH of CAC thereby reducing its corrosion resistance.

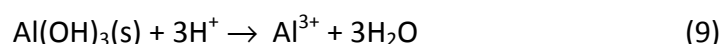
### **Corrosion**

#### **Corrosion in $H_2SO_4$**

- The dissolution of the calcium cement hydrate in mineral acids (e.g.,  $H_2SO_4$  that are generated by sulphur oxidising bacteria) leads to a combination of the dissolution of the calcium component of CAC and of aluminium precipitation to alumina hydrate of  $Al(OH)_3$  (Scrivener, Cabiron et al. 1999):



- Alumina hydrate is usually stable at pH from 3.5-4.0. Below pH 4.0, the hydrate will dissolve to form monomeric  $Al^{3+}$  (Scrivener, Cabiron et al. 1999):

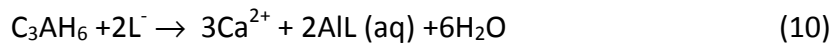


- As shown 12 moles of  $H^+$  will be required to neutralise 1 mole of  $C_3AH_6$ .

#### **Corrosion in Organic Acids**

- Wide range of organic acids (acetic, gluconic, glucuronic, citric, oxalic, oxalacetic, succinic, malic and glyoxylic acids) are generated by fungi, and they take part in corroding the cementitious materials in sewer.

- The corrosion in organic acid (e.g., citric acid ( $\text{H}_3\text{L}$ ), L = citrate ligand) proceeds by a complexation reaction:



- The stability of [AIL] complex will prevent the precipitation of  $\text{Al(OH)}_3$ . In the presence of organic acids the passivation observed with the formation of  $\text{Al(OH)}_3$  is avoided.

## 1.2 Actions

- When CAC is applied in the rehabilitation of corroded concrete, it behaves as a 'sacrificial coating'. That is it is preferentially corroded extending the life of the concrete infrastructure.
- CAC protection may be provided in the following ways:
  - CAC acid neutralisation capacity is higher than Portland cement (40 millimoles of acid ( $\text{H}^+$ ) is required to completely dissolve 1 gram of 100% CAC, whereas 22.5 millimoles of  $\text{H}^+$  is required to dissolve the same mass of Portland cement).
  - CAC shows acid resistance at two regions, pH 10 and pH 4.0. Maintaining its surface pH to 4.0 will prevent the growth of acidophilic bacteria that contributes to significant corrosion. Neutrophilic bacteria and fungi, however will continue to grow above pH 4.0.
  - CAC generates toxic  $\text{Al}^{3+}$  ions that may initially control the growth of micro-organisms. However most microbes in the sewer eventually develop tolerance to  $\text{Al}^{3+}$  toxicity.
  - Under micro-organism inhibition, CAC corrosion will proceed from the corrosive effects of hydrolysis gases ( $\text{CO}_2$ ,  $\text{NO}_2$ ,  $\text{SO}_2$ ) and  $\text{H}_2\text{S}$ .
  - CAC has lower porosity than Portland cement. This can hamper the diffusion of acid and its corrosion rate.

## 1.3 Application

The technical information or criteria that could be used as decision support in selection and/or assessment of new coating, designing and condition assessment of CAC as protective coating are listed below:

### 1.3.1

### Specifications

- There are currently two known specifications in Australia for qualifying cement based coatings:
  - i) Sydney Water's Standard Specification SS208 – "Rehabilitation and Corrosion Protection of Sewers using Calcium Aluminate Cement Mortar" (Standard-Specification-208 2011)
  - ii) SA Water TS 137 – "Rehabilitation of Concrete Wastewater Manholes" 1(TS3C 2007). This has been updated in 2011.
- Current specifications are based on the strength of CAC and acid neutralisation capacity imparted by the composition of CAC.
- Specifying material composition that averts the effect of CAC conversion should be considered.

### 1.3.2 Design

- The actual service life of CAC has been difficult to assess and predict because the corrosion of CAC is complex. The corrosion process is accompanied by shrinkage, expansion, the formation of precipitates on the surface of CAC, hydration, conversion and carbonation reactions.
- Current basic design principle appears to be based on specified coating thickness. The coating thickness specified under SS208 is that CAC must have a minimum thickness of 25 mm for a 50 years design life. This was based on Pomeroy's equation for calculating sacrificial protective lining thickness made of cementitious material (Concrete Pipe Handbook, 1998) and supported by some field trial data.
- Service life models were developed under SP2 based on corrosion kinetics predicting thickness loss for periods from 30 months up to 15 years based on field tests results. The following diffusion models apply to corrosion in the sewer crown.

$$dX = kt^{0.5} \quad (10)$$

where



$dX$  = thickness loss (mm)

$t$  = time (days)

$k$  = rate constants. Models of the rate constants for the various cities are given below:

$$k_{\text{Sydney}} = 43.05[H_2S]^{-0.39}[T]^{3.47}[RH]^{-2.17}[Al_2O_3]^{-2.39} \quad (11)$$

$$k_{\text{Melbourne}} = 13.86[H_2S]^{-0.60}[T]^{-0.49}[RH]^{2.34}[Al_2O_3]^{-4.27} \quad (12)$$

$$k_{\text{Perth}} = 7.23[H_2S]^{-0.68}[T]^{22.8}[RH]^{-10.6}[Al_2O_3]^{-8.11} \quad (13)$$

where

$H_2S$  = hydrogen sulphide concentration (ppm)

$T$  = temperature ( $^{\circ}C$ )

$RH$  = relative humidity (%)

$Al_2O_3$  = alumina content (wt%)

- Predicted and raw corrosion data are compared in Figures 3 and 4 for Sydney and Melbourne sites.

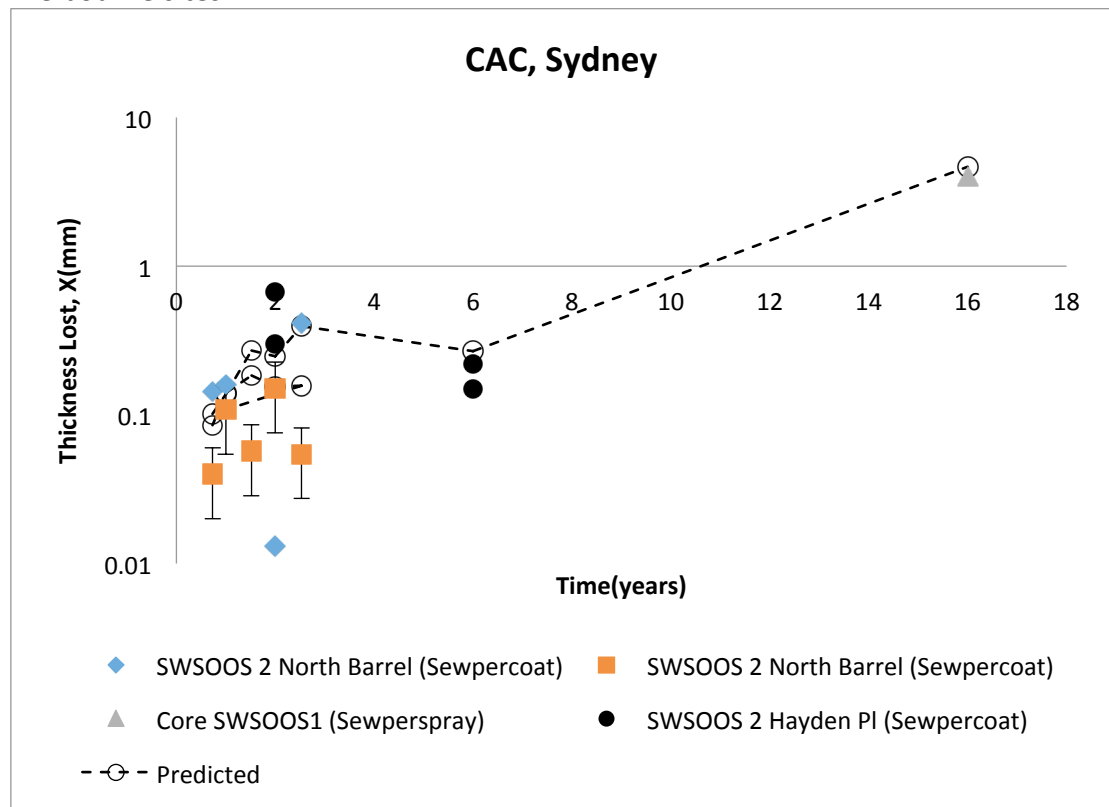


Figure 3. Predicted and raw corrosion data for CAC installed in Sydney Water sewers.

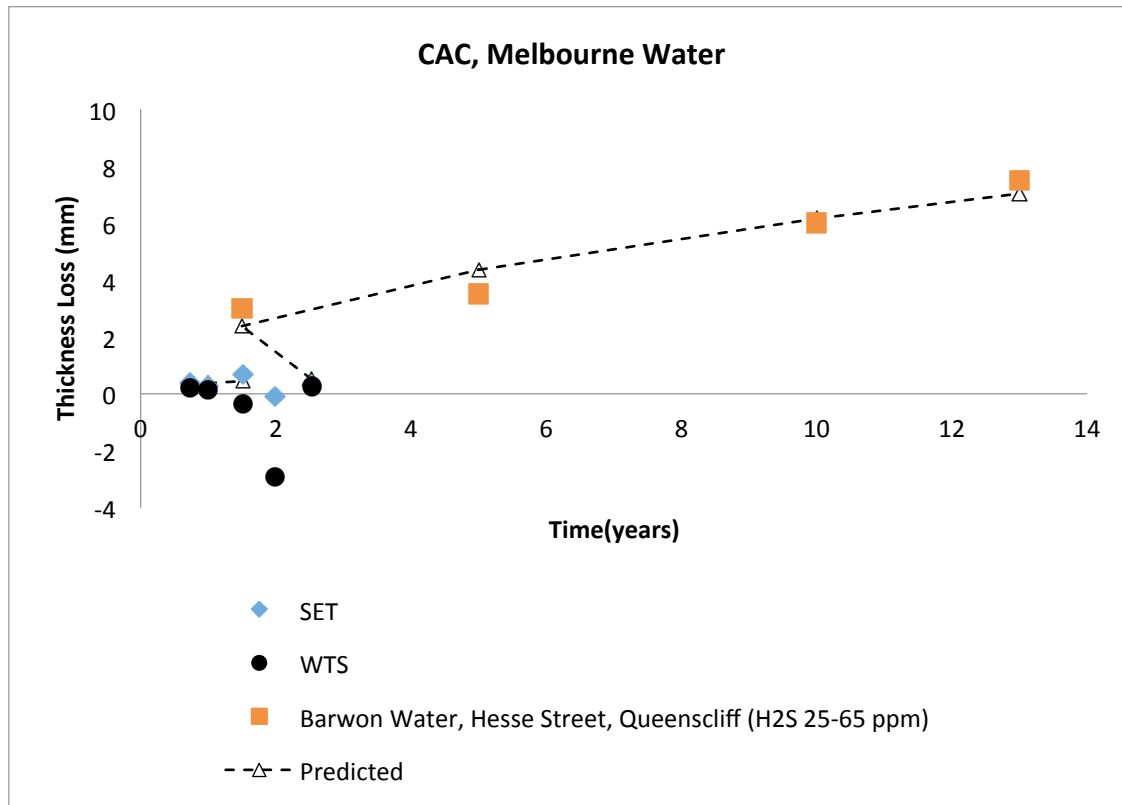


Figure 4. Predicted and raw corrosion data for CAC installed in Melbourne Water sewers.

### 1.3.3 Condition Assessment of CAC

Monitoring the performance of calcium aluminate cement could involve the following characterisations:

- **Corrosion**
  - i) Thickness loss
- **Physical Changes**
  - i) Bonding Strength
  - ii) Shrinkage, Expansion, Porosity Profile
- **Chemical and Mineralogical Transformation**
  - i) Extent of Conversion
  - ii) Acid Neutralisation Capacity
  - iii) Un-hydrated Calcium Aluminate

### 1.3.4 Accelerated and Field –Short and Long Term Test

- Accelerated laboratory test involves immersing a CAC cylinder in specific acid bath or corroding environment to monitor its rate of corrosion. The rates of corrosion could be measured from the thickness loss, weight loss and amount of dissolved  $\text{Al}^{3+}$ . The

acids used are typical of the biogenic acids obtained in the sewer ( $\text{H}_2\text{SO}_4$ , organic acids,  $\text{H}_2\text{CO}_3$ ).

- Short term (1-3 years) and medium to long term (3-15 years) tests are performed by applying the coating directly on sewer walls and periodically examining its corrosion and corresponding physical and chemical changes.
- Short term field test with controlled  $\text{H}_2\text{S}$  conditions can also be obtained by installing coupons in the SA Water's Bolivar Chamber in South Australia.

## 1.4 Cost

Typically CAC used for sewer protection is roughly 3 to 5 times more expensive than Portland cement. The price will vary according to the  $\text{Al}_2\text{O}_3$  content of CAC.

## 1.5 Impact on WWTP

- Application of CAC in Australia has been demonstrated to provide suitable protection of concrete within 10- 16 years in Sydney Water, Melbourne Water and Barwon Water trials. Data beyond this is currently not available. A summary of these results are shown in Figure 5.

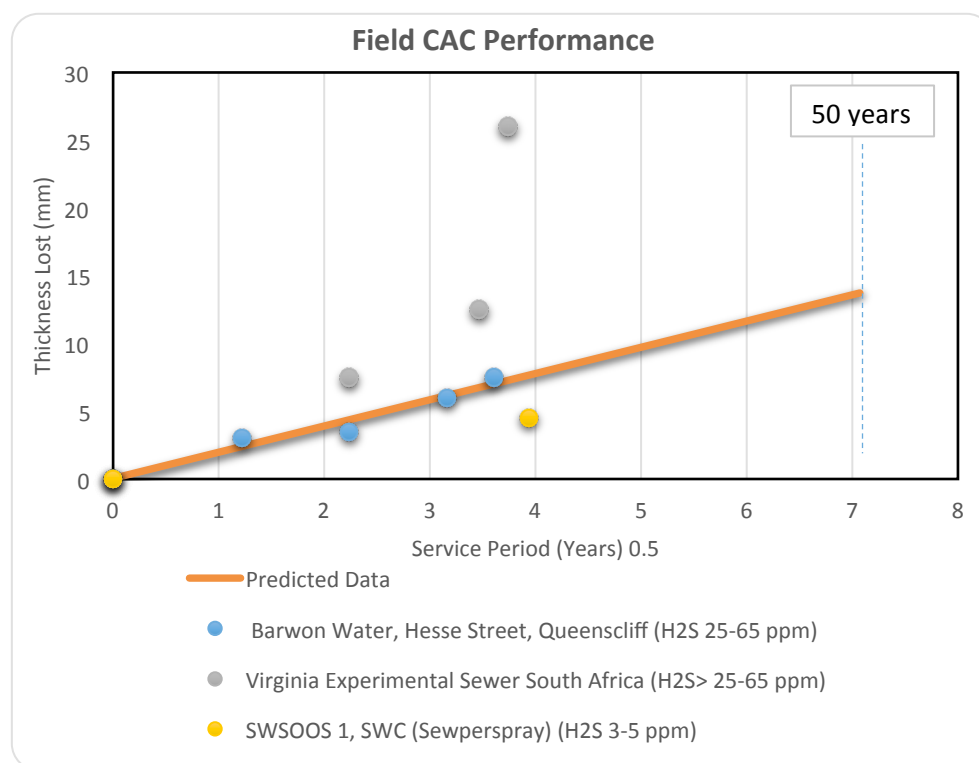


Figure 5. CAC current and predicted performance in Barwon Water (Hesse St, Queenscliff) (Wubben. 2008), Virginia Experimental Sewer, South Africa and SWSOOS 1, SWC. (Note thickness measurements in Barwon Waters were corrected for expansion of CAC e.g. actual thickness loss of 20-40 mm is equivalent to 4-8 mm. Measurements were confirmed by actual remaining thickness left).

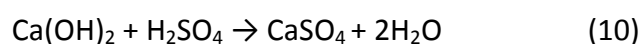
- Trial results of the Virginia experimental sewer in South Africa was also included. The later performance of CAC in this trial demonstrated the rapid corrosion of CAC might have been attributed to CAC conversion. The conversion of CAC, which is inevitable, converts its mineralogy to the more reactive phase.
- The rates of corrosion increases with time. For example in Sydney sewers, the observed rate in 30 months is about 0.1 mm/yr and this increases to about an average of 0.3 mm/yr for a 16 years period. The increase in rate might have been attributed to increased porosity as a result of conversion and expansion of CAC from the formation of ettringite.

## 1.6 Major Limitations

These are not major limitations to CAC performance, but they do affect the ability of CAC to resist corrosion.

### Shrinkage/Expansion, Cracking and Cracking

- The shrinkage and expansion resulting in changes in porosity, cracking and crazing of CAC results from the differences in the density of the CAC hydrates. These are listed in Table 2.
- The observed expansion in the field is between 0.4 to 30 (mm/mm)% based on SP2 field tests.
- The shrinkage of CAC results from the conversion of the metastable phases to  $C_3AH_6$  and the substitution of Fe into for Al in the CAC hydrate to form brownmillerite ( $C_4AF$ ).
- The expansion of CAC results from the formation of ettringite from the sulfate attack of CAC hydrates (Evju and Hansen 2001, Tixier and Mobasher 2003, Nocun-Wczelik, Konik et al. 2011, Zuo, Sun et al. 2012). This reaction begins with the sulfate attack of  $Ca(OH)_2$  (O'Connell, McNally et al. 2010):



- The hydrated  $CaSO_4$  form gypsum, which attacks the stable phase  $C_3A$ :

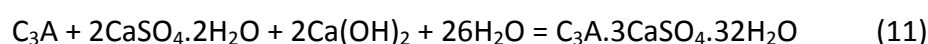


Table 2: Density of CAC Hydrates

CAC Phases	Density (kg/m <sup>3</sup> )	References
CAH <sub>10</sub>	1720	(Parr 2004)
α-C <sub>2</sub> AH <sub>8</sub>	1950	(Scheller 1974)
β-C <sub>2</sub> AH <sub>8</sub>	1950	(Scheller 1974)
C <sub>3</sub> AH <sub>6</sub>	2529	(Lager, Armbruster et al. 1987)
Brownmillerite (C <sub>4</sub> AF)	3684	(Colville and Geller 1971)
Ettringite (C <sub>6</sub> A S <sub>3</sub> H <sub>32</sub> )	1775	(Struble 1986)
Stratlingite C <sub>2</sub> ASH <sub>8</sub>	1940	(Kuzel 1976)
Al(OH) <sub>3</sub>	2420	Mineral web

### Conversion

- Conversion increases the rate of corrosion of corrosion of CAC. The extent of conversion depends on the temperature of the sewer environment and the moisture that is available from the sewer and that generated as a result of the conversion reaction.
- Conversion tends to be higher closer to the sewer front, where there is an abundance of moisture, and is reduced in CAC closer to the concrete substrate (see Figure 6).

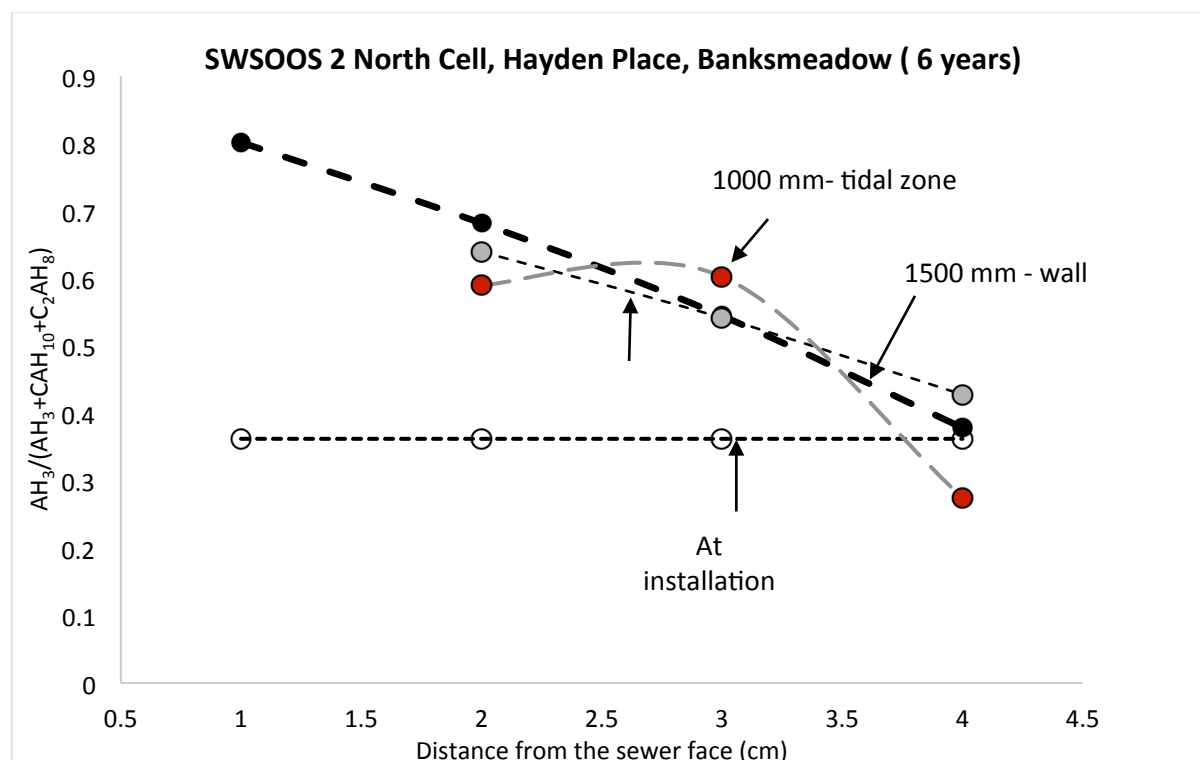


Figure 6. Conversion across CAC.

## Carbonation

- Carbonation reduces the pore pH of CAC reducing its ability to resist acid corrosion.

## Shelf Life

- CA has a shelf life of one year

## 1.7 Further Information

ARC Linkage Final Report- Field Testing of Cement Based Coatings for Sewer Application

MSc Thesis: Zamri, D. (2012), Biogenic and Chemical Corrosion of Calcium Aluminate Cement in Sour Media, submitted to the University of Sydney.

MSc Thesis: Sio, J. (2013), Effect of Pozzolanic Material in the Mineralogy and Corrosive Behaviour of Calcium Aluminate Cement to be submitted to the University of Sydney.

## 1.8 Case Studies

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Wubben., R. (2008). Assessment of Service Life Performance by Core Sampling on Kerneos 'Sewperspray' Application, ConCorr Pty. Ltd. (submitted to Kerneos Aluminate Technologies).

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