SP2 Report on

Service Life Model for Calcium Aluminate Cement Based on Field Test Results

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Summary

Site specific models that predicts the rate of CAC corrosion for Sydney, Melbourne and Perth sewers were developed using field data from coupons that were installed in these cities for 30 months and of CAC cores with longer service lives from Sydney and Barwon Water (2-16 years). The model predicts the rate of corrosion based on the Al_2O_3 content of CAC and the environmental conditions, H_2S, temperature and humidity.

The model was developed based on Fick's diffusion equation. Although suitable predictions have been developed over the period of 0-16 years, the reliability of the model to predict longer service life has not been tested in this study. The corrosion results obtained in this study were subject to expansion. It appears that samples in service for 6 years were still subject to expansion. This would suggest that the models developed in this study could underestimate the rates of CAC corrosion.

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1.0 INTRODUCTION

1.0 Rate of CAC Corrosion

The progress of corrosion under diffusion controlled reaction could be approximated by the moving boundary reaction diffusion model. The shrinking core model has been used to describe the rates of corrosion of concrete where the rate of movement of the boundary is considered slower than the transport rates of the acids. Because of the slow movement of the boundary, the mass transport could be considered to be always at steady state. In case of sulphate ion attack, for example, the sulphate ion is considered to migrate inwards through the corrosion product into the boundary with uncorroded material. At the interface the sulphate ions will react with the hydration products of CAC, consisting of CAH_{10}, C_2AH_8, C_3AH_6 and AH_3) to produce $Al(OH)_3$, and dissolved Al and Ca sulphate species. The mass transport is assumed to be always at steady state and is then used to estimate the rate of progression of the corrosion interface through the concrete. The corrosion reactions can be simplistically expressed as follow:

$$C_3AH_6 + 6H^+ \rightarrow 3Ca^{2+} + 2Al(OH)_3(s) + 6H_2O \qquad (1)$$

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 et. al., 1999):

$$2Al(OH)_3(s) + 6H^+ \rightarrow 2Al^{3+} + 6H_2O \qquad (2)$$

The flux of sulphate ions is given as:

$$N = -D_i \frac{C_o}{x} \qquad (3)$$

The rate of progression of the corrosion interface is then the rate of sulphate mass transport divided by the concentration of the Al_2O_3 and CaO in CAC.

$$\frac{dx}{dt} = -\frac{N}{C_a} = \frac{D_i C_i}{C_a x} \qquad (4)$$

The solution to this equation is given as:

$$x = \left(\frac{2D_i C_o}{C_a} t\right)^{1/2} = kt^{1/2} \qquad (5)$$

Where k = $\sqrt{\frac{2D_i C_o}{C_a}}$

C_a = concentration of Al_2O_3 and CaO in CAC solid (moles/cm3)

Co = concentration of the sulphate or corresponding acid anion in the bulk solution (moles/cm^3)

X = depth of corrosion (cm)

D_i = acid anion diffusion coefficient (cm^2/s)

t = time (s)

To correlate the rate of reaction to the CAC properties and environmental conditions, the rate of corrosion were fitted to the following empirical correlation:

$$k = k_1[H_2S]^{\alpha}[T]^{\beta}[RH]^{\gamma}[Al_2O_3]^{\varepsilon} \quad (6)$$

where

H_2S = hydrogen sulphide concentration (ppm)
T = temperature (°C)
RH = relative humidity (%)
Al_2O_3 = alumina content (wt%)

2.0 EXPERIMENTAL

2.1 Material

The calcium aluminate cement used in this study was Sewpercoat sourced from Kerneos, Australia. Elemental analysis of Sewpercoat was conducted using PHILIPS PW2400 XRF with Rh end-window tube. The composition of Sewpercoat is shown in Table 1.

Table 1. Composition of calcium aluminate cement

Oxides (wt%)	Calcium Aluminate Cement
Al_2O_3	41.3
CaO	37.4
Cr_2O_3	0.13
Fe_2O_3	9.54
K_2O	0.3
MnO	0.12
MgO	0.3
NiO	0.137
SiO_2	6.97
TiO_2	1.93
V_2O_5	0.05
ZrO_2	0.14

2.2 Preparation of Calcium Aluminate Cement

The CAC cement specimens were prepared with the assistance of Mr Andrew Martins, a technical personnel from Kerneos. The water cement ratio was maintained at 0,4 by combining one 20 kg bag of sewpercoat with 3.25L of water. A high shear electric mixer was used to mix the water and dry sewpercoat powder until homegeneous. The cement mixture was shovelled into wooden moulds (25mm, 50mm and 75mm square) to give approximately 25 mm thick coupons. These were tapped with a steel bar to remove trapped air bubbles. The coupons were cured for 24 hours at 21°C in 98% relative humidity environmental chamber, demolded and cured further in the same environment for another 2 days. The specimens were then cut using a tile cutter to give a 50x50 mm coupons. The cured specimens were kept moist during storage by placing a wet cloth over the samples until their installation in the sewer.

2.3 Coupon installation

2.3.1 Installation schedule

For this study, coupons were installed in two sewer sites in three cities, Sydney, Melbourne and Perth. Coupons were installed for approximately 30 months. The coupon installation and retrieval schedule for each site are summarised in Table 2.

2.3.2 Installation method

The coupons were installed in the sewers by placing the samples in 316 stainless steel mesh baskets (see Figure 1). Coupons were secured using plastic nylon cable ties. A thin PVC sheet roof was placed above each basket to protect the coupons from acids formed on the sewer concrete pipes on which these baskets were bolted.

2.3.2 Sewer environmental conditions

Environmental conditions including H_2S concentration, temperature and humidity were monitored with time. The data reported are number average and time weighted average values. The time weighted values captures the average conditions to which the coupons were exposed to within a given time frame. The time weighted average H_2S concentration was estimated as follow:

$$Time\ weighted\ average\ H2S\ (ppm) = \frac{\sum_{t_i}^{t_f} H_2S_i t_i}{t_f - t_i} \tag{1}$$

where H_2S = concentration of H_2S (ppm) with time, t_i = time of exposure (days) and t_f-t_i = installation period (days). The environmental conditions for each sites are summarised in Tables 3 to 5. Where humidity meters are flooded, the relative humidity were taken at 99%.The time weighted average H_2S concentration and temperatures are also plotted as a function of time in Figure 3. As shown the conditions in each site fluctuated with time. It is apparent that Perth sites provided the highest H_2S concentration followed by Melbourne then Sydney. The temperature in Perth was also the highest followed by Sydney and Melbourne.

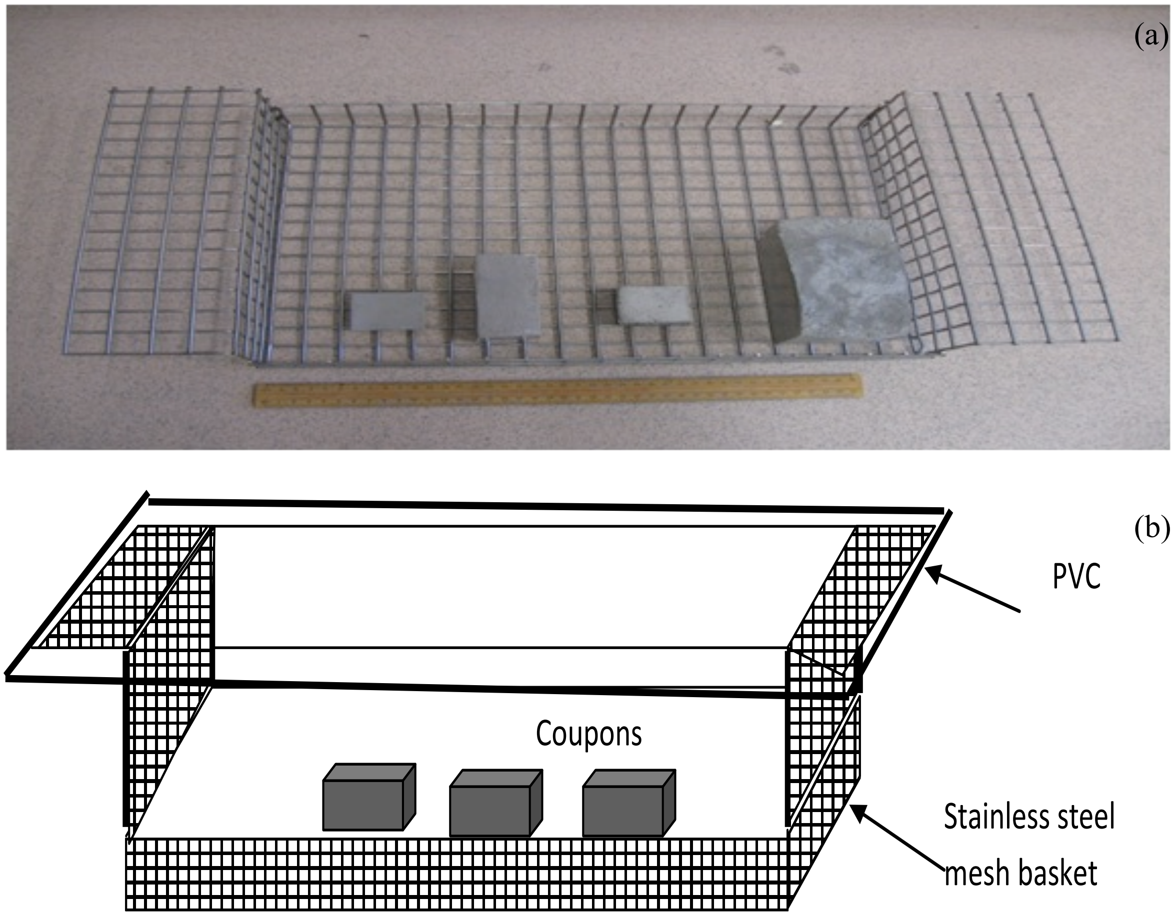
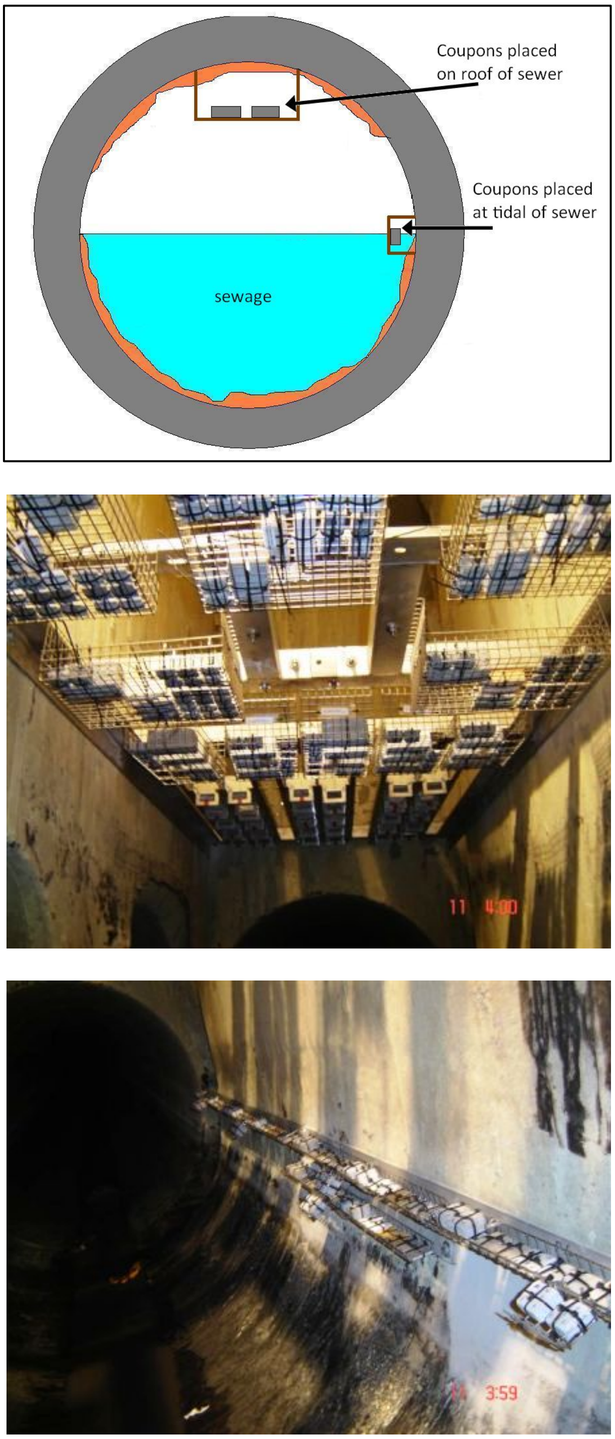


Figure 1. a) Picture and b) schematic diagram of coupon installation baskets

Coupon baskets were installed in both in the roof and tidal zone of the sewers (see Figure 2).



Schematic diagram

Sewer Crown

Tidal zone

Figure 2. Coupon installation location in Perth sewers.

Table 2. Coupon Installation and Retrieval Schedule

Location	Installation Dates		Retrieval Dates				
	Nominal Period (months)		6	12	18	24	30
Sydney	22/09/2009	24/09/2009	17/6/2010	21/9/2010	29/3/2011	19/9/2011	3/4/2012
	SWOOS South Barrel	SWSOOS North Barrel					
	Period of Installation (Days)		268	364	553	727	924
Melbourne	5/2/2010	16/2/2010	24/9/2010	22/2/2011	22/8/2011	20/2/2012	7/9/2012
	WTS	SET					
	Period of Installation (Days)		231	382	563	745	945
Perth	6/5/2010	11/6/2010	7/12/2010	28/6/2011	6/12/2011	3/7/2012	5/12/2012
	Bibra Lake	Perth MS					
	Period of Installation (Days)		215	418	579	789	944

Table 3. Environmental Conditions in Sydney Sewers

City	Sewer	Time (days)	Number Average H_2S, ppm	Time Weighted Average H_2S, ppm	Time Weighted Average Temp, °C	Relative Humidity (%)
Sydney	South Barrel	268	2.35	2.35	17.3	99.0
		364	3.86	2.75	17.7	90.88
		553	2.19	2.56	19.3	99.0
		727	3.22	2.72	19.7	99.0
		924	2.27	4.27	20.5	96.94
	North Barrel	268	1.21	1.21	17.3	99.0
		364	3.01	1.68	17.4	91.64
		553	1.78	1.72	19.1	99.0
		727	4.32	2.34	19.7	99.0
		924	4.60	3.68	20.6	95.17

Table 4. Environmental Conditions in Melbourne Water Sewers

City	Sewer	Time (days)	Number Average H_2S, ppm	Time Weighted Average H_2S, ppm	Time Weighted Average Temp, °C	Relative Humidity (%)
Melbourne	WTS	231	4.69	4.69	20.9	99.0
		382	7.15	5.66	20.5	99.0
		563	2.94	4.78	19.9	99.0
		745	7.40	5.43	20.8	99.0
		924	3.60	5.07	18.4	99.0
	SET	231	0.79	0.79	18.5	99.0
		382	1.73	1.16	18.8	99.0
		563	1.28	1.20	18.2	99.0
		745	3.00	1.64	18.7	99.0
		924	0.60	1.44	16.7	99.0

Table 5. Environmental Conditions in Water Corporation Sewers

City	Sewer	Time (days)	Number Average H_2S, ppm	Time Weighted Average H_2S, ppm	Time Weighted Average Temp, °C	Relative Humidity (%)
Perth	Bibra Lakes	215	654.3	654.3	28.5	91.35
		418	375.0	518.6	29.3	85.50
		579	329.5	466.0	27.6	93.30
		789	230.3	403.3	25.9	92.80
		944				
	Perth MS	215	68.4	68.4	26.6	99.13
		418	178.0	121.6	27.1	80.00
		579	62.6	105.2	27.5	97.70
		789	36.9	87.0	25.8	94.50
		944				

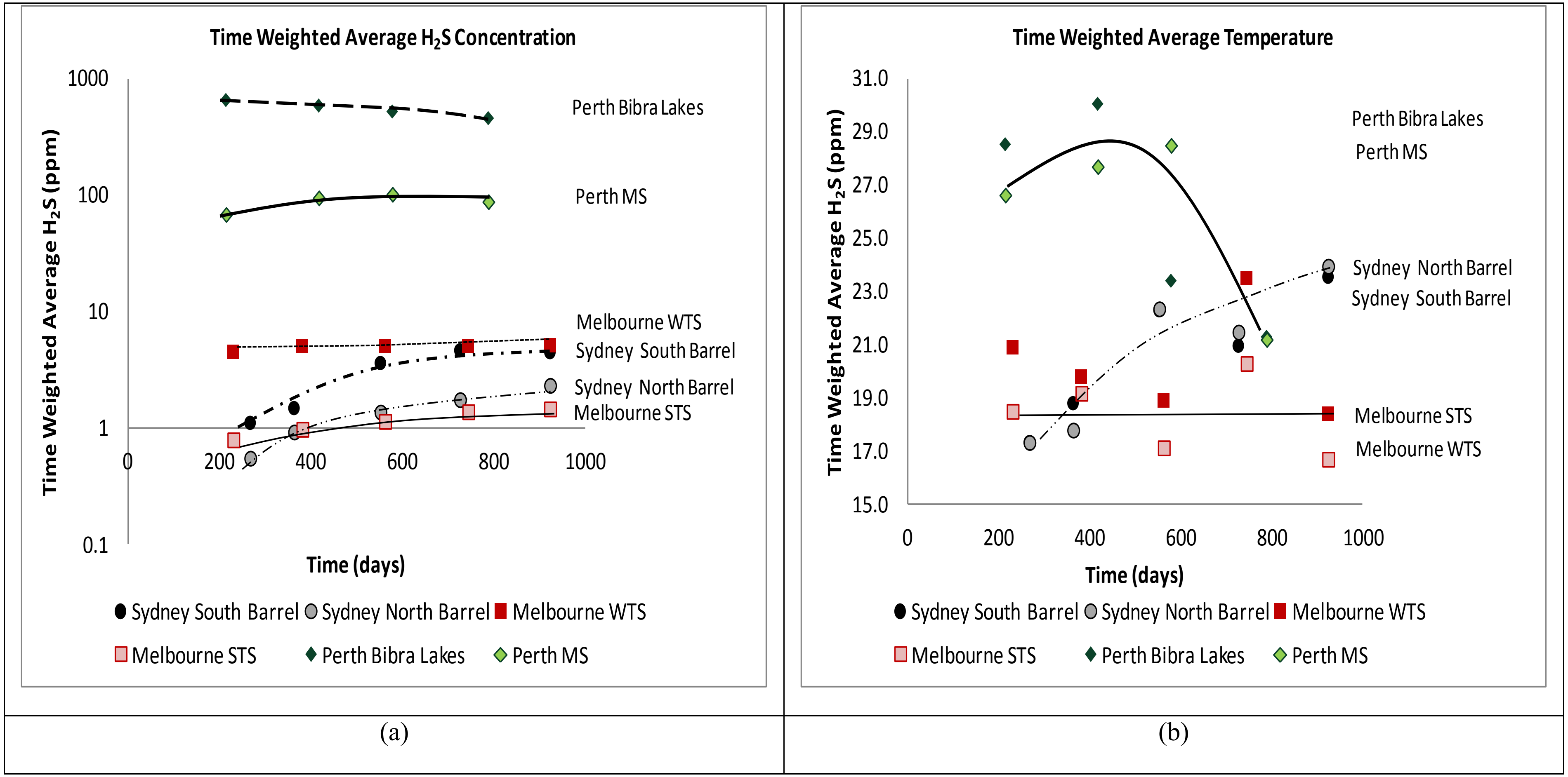


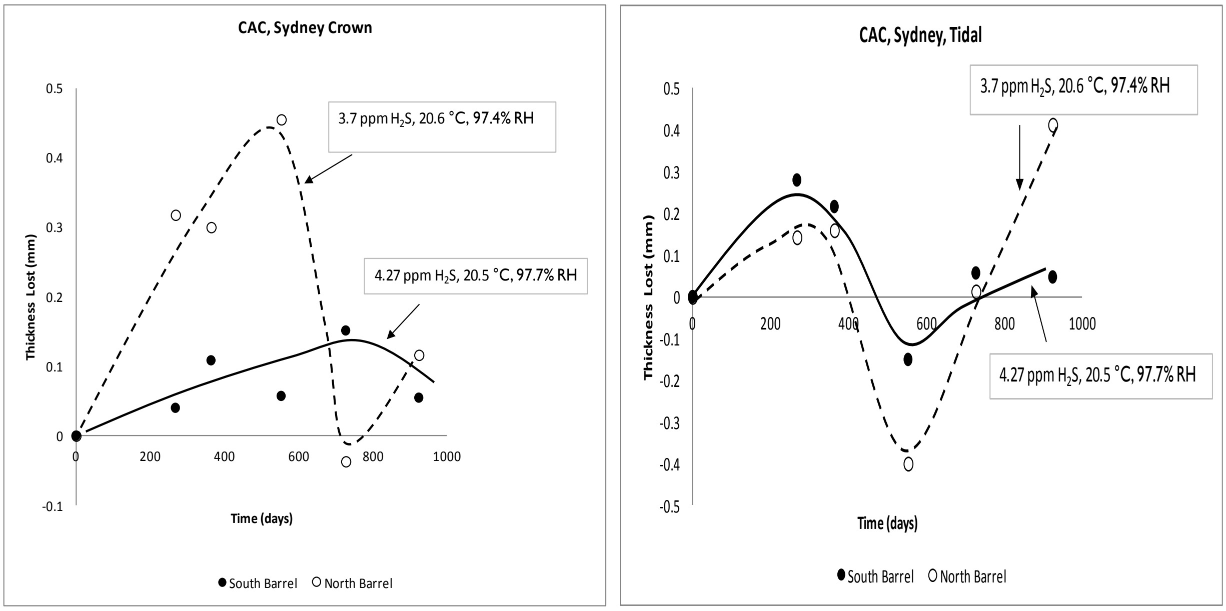
Figure 3. Time weighted average a) H_2S concentration in Sydney, Melbourne and Perth sewers.

3.0 FIELD CORROSION DATA OF CALCIUM ALUMINATE CEMENT

For the modeling purpose, two sets of samples were used in our analysis. The first are CAC coupons installed for approximately 30 months in Sydney, Melbourne and Perth sewers. The second are CAC samples with a longer field service life in Sydney and Melbourne Water sewers.

3.1 CAC coupons installed in the sewer for 30 months

The rates of corrosion of CAC (Sewpercoat) installed in the crown of the Sydney Water South and North barrel sewers in the Southern & Western Suburbs Ocean Outfall System (SWSOOS) are shown in Figure 4. As shown there is an initial loss of thickness attributed to corrosion, then followed by expansion and again by loss of thickness. This behavior was observed for CAC coupons installed in both the crown and tidal zones of the Sydney Water sewers. Coupons installed in the WTS and SET sewers in Melbourne Water (see Figure 5) and Bibra Lakes and Perth MS in Water Corporation sewers in Perth (see Figure 6) also showed similar behavior.



(a) (b)

Figure 4. Rate of corrosion of calcium aluminate cement in the a) crown and b) tidal zpne of Sydney sewers.

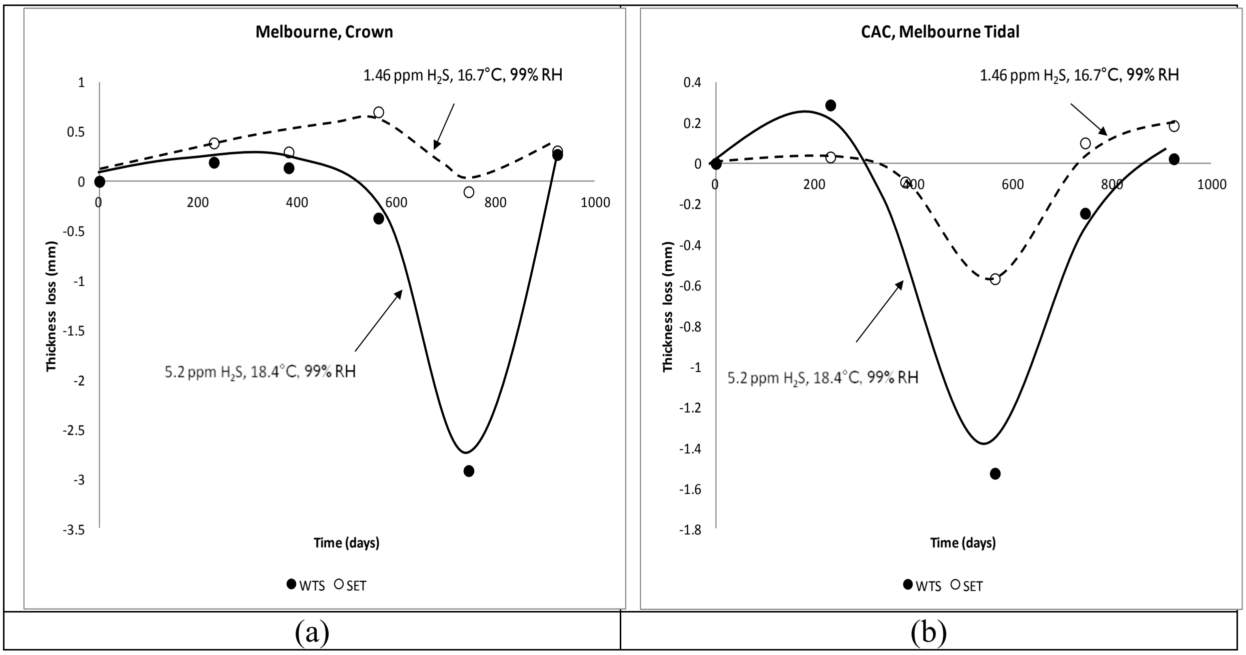


Figure 5. Rate of corrosion of calcium aluminate cement in the a) crown and b) tidal zone of Melbourne sewers.

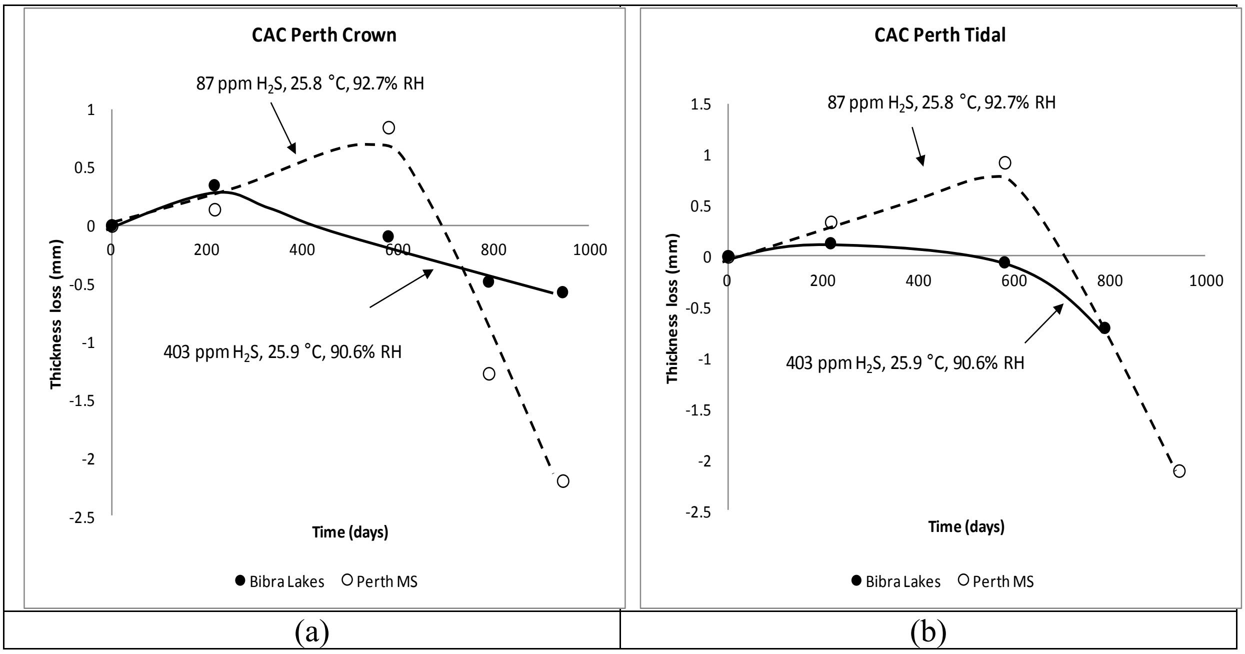


Figure 6. Rate of corrosion of calcium aluminate cement in the a) crown and b) tidal zone of Perth sewers.

3.2 CAC Cores and Long term field samples

3.2.1 Sydney Water

The CAC used for this study were obtained from the SWSOOS1 and SWSOOS for periods of 2 to 16 years. The thickness loss were derived from reports submitted SWC.

Table 6. CAC Samples from Sydney Water – Long Term Field Service

Sewer	Age (years)	Location	CAC	Environmental Conditions	Thickness loss, mm
SWSOOS1	16	Wall	Sewperspray	3-5 ppm H_2S, 17-21°C	4.5
SWSOOS2 (Hayden Pl)	2	Roof	Sewpercoat	3-5 ppm H_2S, 17-21°C	0.3-0.67
SWSOOS2 (Hayden Pl)	6	Roof	Sewpercoat	3-5 ppm H_2S, 17-21°C	0.15-0.22

It appears the thickness loss from 2 to 6 years in SWSOOS2 has decreased suggesting that CAC continued to expand to 6 years of service life.

3.2.2 Barwon Water

CAC corrosion data of long term service was obtained from Barwon Water (see Table 7).

Table 7. CAC Samples from Barwon Water – Long Term Field Service

Sewer	Age (years)	Location	CAC	Environmental Conditions	Thickness loss, mm
Hesse Street, Queenscliff	1.5	Wall	Sewperspray	25-65 ppm H_2S, 1-21°C	3
Hesse Street, Queenscliff	5	Wall	Sewperspray	25-65 ppm H_2S, 1-21°C	3.5
Hesse Street, Queenscliff	10	Wall	Sewperspray	25-65 ppm H_2S, 1-21°C	6
Hesse Street, Queenscliff	13	Wall	Sewperspray	25-65 ppm H_2S, 1-21°C	7.5

3.3 Fitting Corrosion Data to Service Model

The coupon data and core data from Figure 4-6 and Tables 6 and 7 were fitted to equations (5) and (6).

The fitted parameters are summarized in Table 8 with the regression correlation coefficient, R^2. The experimental and predicted thickness loss are plotted as a function of time in Figures 7-9 plots.

Table 8. Fitted CAC Corrosion parameters

City	k_1	α	β	γ	ε	R^2
Parameters		H_2S (ppm)	T(°C)	RH(%)	Al_2O_3 (%)	
Sydney	43.05	-0.39	3.48	-2.17	-2.40	0.98
Melbourne	13.86	-0.60	-0.49	2.35	-4.27	0.98
Perth	7.23	-0.68	22.84	-10.58	-8.12	0.99

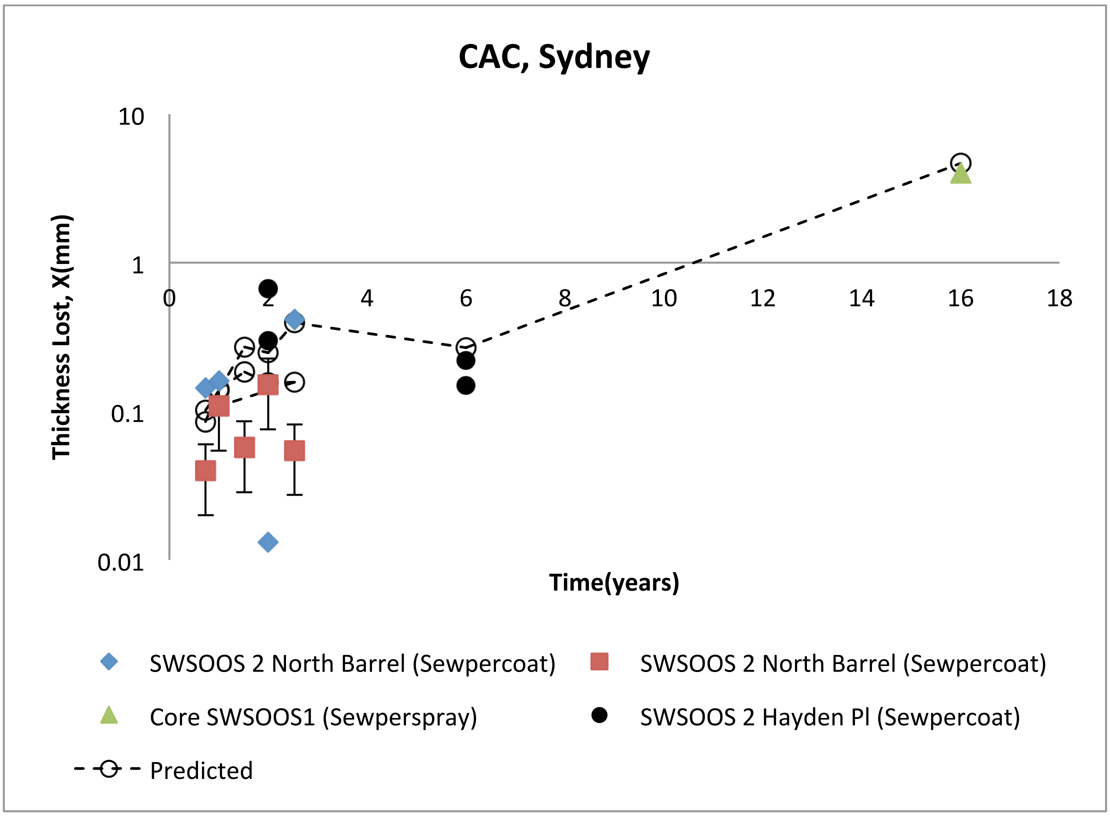


Figure 7. Experimental and predicted thickness loss of CAC in Sydney sewers.

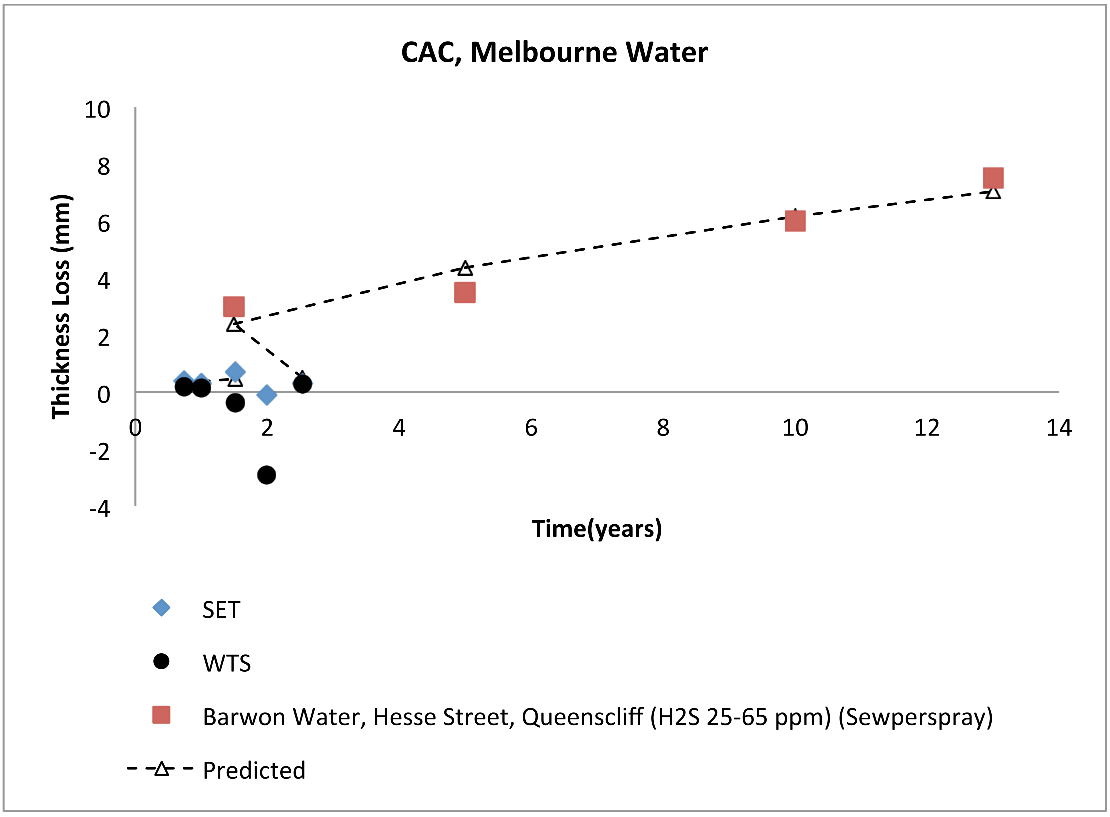


Figure 8. Experimental and predicted thickness loss of CAC in Melbourne sewers.

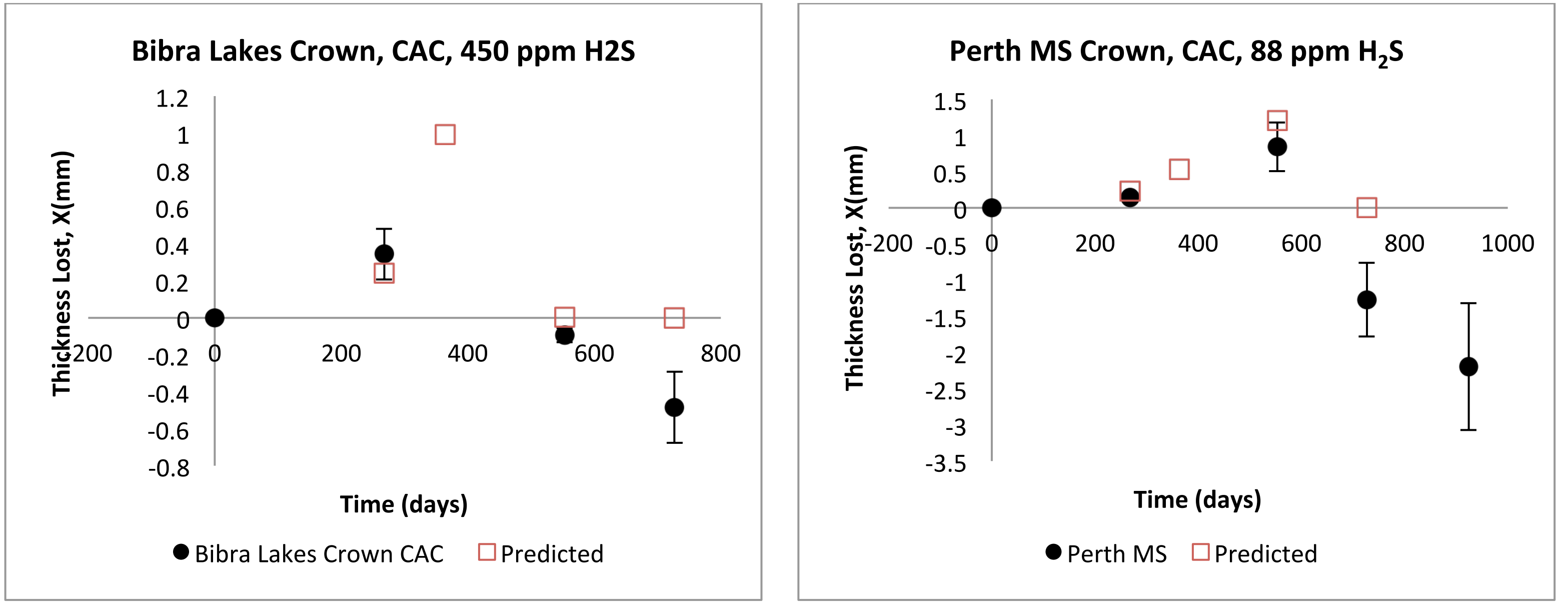


Figure 9. Experimental and predicted thickness loss of CAC in Perth sewers.