

SP2 Report on

Service Model of Calcareous Aggregate Cement Based on Field Test

Author and Chief Investigator: M. Valix

Summary

This is a service life model based on the kinetic analysis of calcareous aggregate corrosion in the field for 30 months. Coupons of the concrete were installed in Sydney, Melbourne and Perth sewers. The rate of corrosion was modeled assuming a diffusion controlled reaction based on Fick's 2nd law. An empirical model was developed to correlate the kinetic constant with the environmental conditions (H_2S , temperature and relative humidity)

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1.0 INTRODUCTION

Calcareous aggregate cement is a Portland cement with limestone aggregates. The alkalinity of the limestone is used to impart a higher acid neutralisation capacity on the Portland cement thus potentially extending its life.

The aim of this study was to develop a kinetic model for the rate of calcareous aggregate cement. Coupons of the cement were installed in the Sydney, Melbourne and Perth sewers for 30 months. The conditions of these sewers are given in the CAC report.

1.1 Cement Hydration

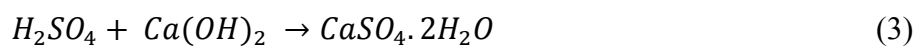
The hydration of Portland cement involves the reaction of the silicate and aluminate phases with water to form hydrates phases. The result of hydration is an interlocking mass, with specific properties such as porosity, compressive strength and chemical resistances based on the cement composition and the amount of water added (Newman and Choo 2003). Water reacts with C_3S and C_2S to form an amorphous calcium silicate hydrate also known as C-S-H gel. This hydrate acts as a binder or 'glue' which binds the aggregate particles together. The reactions of C_2S and C_3S are shown below:



Both alite and belite form the C-S-H gel with water, while the excess calcium is precipitated out as portlandite ($Ca(OH)_2$). C_3S goes through a dormant state after initial reaction with water, and this characteristic is what allows cement to be placed and compacted before the hardening process occurs.

1.2 Rate of Concrete Corrosion

The progress of corrosion was examined under diffusion controlled reaction mechanism where it 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 the cement to $CaSO_4$. Concrete corrosion mainly occurs due to the chemical reaction of acid with the free lime, $Ca(OH)_2$ that is present in the concrete. The C-S-H bond loses strength due to decalcification. Biogenic acids (e.g., sulphuric acid) that is produced by sulphur oxidizing bacteria (SOB) reacts with $Ca(OH)_2$ to produce gypsum ($CaSO_4 \cdot 2H_2O$).



The flux of sulphate ions is given as:

$$N = -D_i \frac{C_o}{x} \quad (4)$$

The rate of progression of the corrosion interface is then the rate of sulphate mass transport divided by the concentration of the Ca(OH)_2 .

$$\frac{dx}{dt} = -\frac{N}{C_a} = \frac{D_i C_i}{C_a x} \quad (5)$$

The solution to this equation is given as:

$$x = \left(\frac{2D_i C_o}{C_a} t \right)^{1/2} = k t^{1/2} \quad (6)$$

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

C_a = concentration of CaO in cement solid (moles/cm³)

C_o = concentration of the sulphate or corresponding acid anion in the bulk solution (moles/cm³)

X = depth of corrosion (cm)

D_i = acid anion diffusion coefficient (cm²/s)

t = time (s)

To correlate the rate of corrosion of calcareous aggregate cement to environmental conditions, the following empirical correlation was fitted to the corrosion data:

$$k = k_1 [\text{H}_2\text{S}]^\alpha [\text{T}]^\beta [\text{RH}]^\gamma \quad (7)$$

where

H_2S = hydrogen sulphide concentration (ppm)

T = temperature (°C)

RH = relative humidity (%)

2.0 MATERIALS AND EXPERIMENTAL METHODS

The method for preparing the calcareous aggregate cement is given in the thesis by Jamaludin, In (2010), Corrosion Properties of Calcareous Aggregate Cement, Honours thesis submitted to the School of Chemical and Biomolecular Engineering, The University of Sydney.

3.0 RESULTS

3.1 Corrosion Data

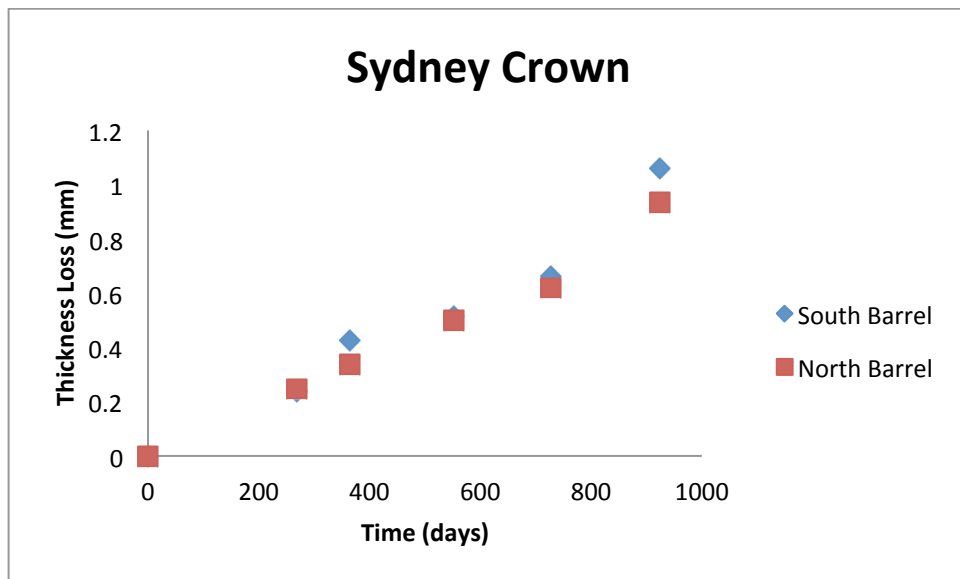


Figure 1. Calcareous aggregate cement corrosion data in Sydney sewer.

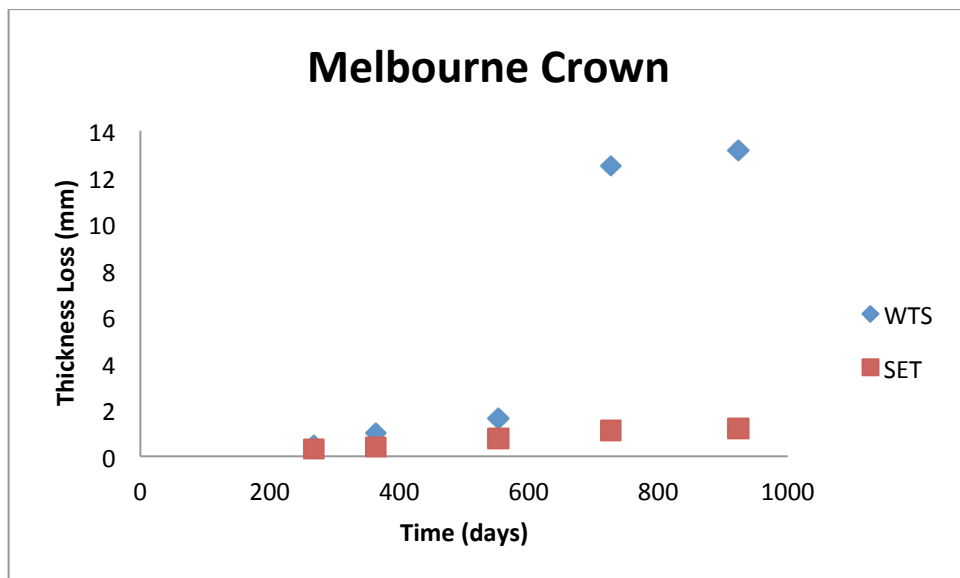


Figure 2. Calcareous aggregate cement corrosion data in Melbourne sewer

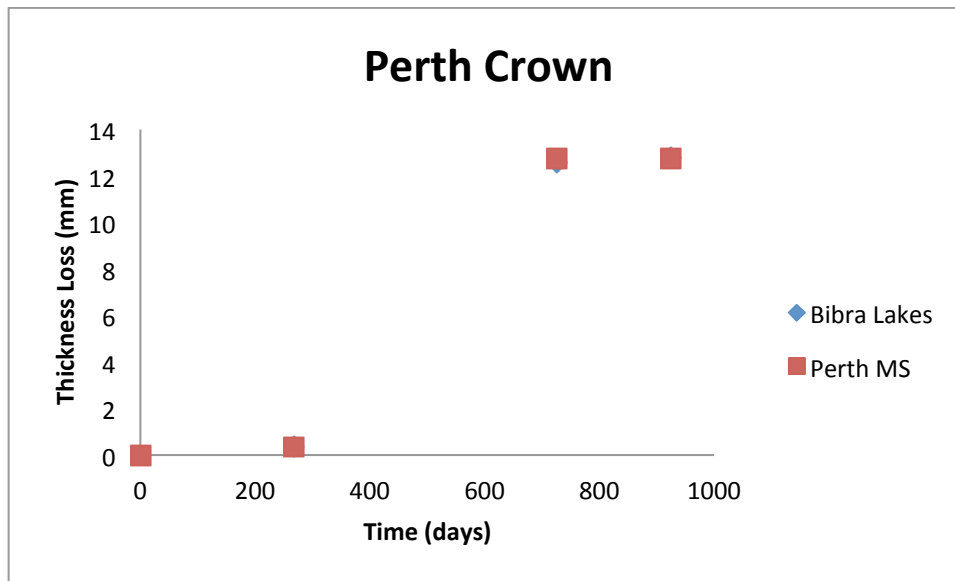


Figure 3. Calcareous aggregate cement corrosion data in Perth sewer.

3.2 Fitting Corrosion Data to Service Model

The coupon data and core data from Figures 1-3 were fitted to equations (6) and (7). The fitted parameters are summarized in Table 1 with the regression correlation coefficient, R^2 .

Table 1. Fitted Calcareous aggregate cement corrosion parameters

City	k_1	α	β	γ	R^2
Parameters		H ₂ S (ppm)	T(°C)	RH(%)	
Sydney	4.02×10^{-6}	0.196	1.42	0.92	0.87
Melbourne	1829	0.757	-3.89	-0.09	0.98
Perth	2.55	0.53	-11.6	6.77	0.78

References

Newman, J. and B. S. Choo (2003). Advanced Concrete Technology: Constituent Materials, Butterworth-Heinemann.