SP2 Report

on

Part 1: Relative Performance of Epoxy Coatings– Based on Accelerated Tests

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Summary

Acids are generated in sewers as a result of microbial activity resulting in the corrosion of concrete sewer pipes. Protective polymeric coatings provide a barrier that isolates the pipe from the corrosive environment. The service life of the coating would therefore depend on its thickness and the rate of acid permeation. This is selecting such protective coatings, it would be of interest to establish the relative rates of acid permeation.

This study reports the relative rates of acids through various commercially available coatings. Seven coatings were examined, three epoxy A, two Epoxy F, one novolac and one polyurethane. The polyurethane acid absorption could not be decoupled from the acid absorption of the backing material. The result presented are therefore only of the epoxy coatings. The tests were conducted in three acids, citric, nitric and sulphuric acids at concentration from 1 to 20 (g/ml)% at 26°C for up to 600 days.

The results demonstrated the following:

- Novolac epoxy demonstrated the greatest resistance to acid permeationfollowed by epoxy F then epoxy A type coating. This ranking was consistent with all acids and concentrations tested.
- The acid permeation is characterized by two stages, rapid uptake followed by slower rate of permeation. This is consistent with the dual phases found in epoxy, with soft and hard phases.
- Stronger acids, sulphuric and nitric acids were found to have greater rates of acid permeation compared to citric acid. In some tests the difference is about 600 to 700% suggesting that bacteria are likely to generated greater challenge to protective liners.
- Although field observation suggests that thinner coatings (<5mm) in general are unable to provide suitable protection, our results suggests that thinner coating provides a much reduced rate of acid permeation compared to thicker coating. Epoxy A type coating with mortar demonstrated 500% higher rate of acid permeation in 20 mm coating compared to 5 mm coating. This suggests that thicker coatings does not appear to provide greater protection as anticipated. This is with the exception of Fernco Ultracoat, which demonstrate similar rates of acid permeation regardless of the coating thickness.
- The relative effect of coating thickness becomes more significant at the acid concentration and strength increases. The acid uptake for 10% sulphuric acid is 6.0 (g/m^2)/mm at 537 days and 0.096(g/m^2)/mm at 537 for weak acid.

1.0 Introduction

Protective coating will have been considered to have failed once the acid has fully permeated through the coating and/or if the coating delaminates. This study focuses on the resistance provided by the coatings to acid permeation and other permeates. This reports the assessment results of the acid resistance of various polymeric coatings. The tests were carried out by accelerated testing by immersion of coating is various acids reflecting the biogenic acids generated by fungi and bacteria in the sewers.

2.0 Experimental

2.1 Polymeric Coatings

The seven commercially available polymeric based coating based primarily on epoxy and one polyurethane coatings tested in this study are listed in Table 1.

2.2 Acid Uptake

The acid uptake were carried out using gravimetric method based on the modified water absorption method described in the ASTM D570-98 method (ASTM-D570-98 2010). Coupons of 5 cm x 5cm x t (t or thickness of 3 to 20 mm) were immersed in various acids. These acids included 1, 5 and 10% nitric and citric acid and 5, 10 and 20% sulphuric acid. The initial mass (W_o) of each coupon were determined prior to immersion. The coupons were immersed in acid and kept under a constant temperature environment of 26°C±0.5. After a predetermined time interval, each coupon was withdrawn, blotted to remove excess acid, immediately weighed (W_t).

The acid uptake was measured from the weight difference after a certain interval and normalised by the external surface area of each coupon:

$$Acid\ uptake\ \left(\frac{g}{m^2}\right) = \frac{W_t - W_o}{External\ surface\ area\ (m^2)}\, x\, \frac{Acid\ concentration\left(\frac{g}{100ml}\right)\%}{100} \qquad (1)$$

Table 1. Polymeric coatings for sewer application

Coating Name Plate	Type of Polymeric Materials (Manufacturer's TDS)	Advantages (Manufacturer's TDS)	Manufacturer	Type of Polymer
Sikadur 41	This is 3-component thixotropic mortar based on a solvent free epoxy resin with aggregates	Chemical resistant	Sika Australia Pty Limited	Epoxy mortar Bispheno A (10-30%) and Bisphenol F (10-30%)
Sikadur 31	Thixotropic adhesive mortar based on a 2 component solvent free epoxy resin containing filler	Chemical resistant and insensitive to moisture during application, cure or whilst in service	Sika Australia Pty Limited	Epoxy mortar Bispheno A (10-30%) and Bisphenol F (10-30%)
Sikagard 63N	This is a two component solvent-free high build thixotropic protective coating based on epoxy resin.	Excellent chemical resistance	Sika Australia Pty Limited	Epoxy (100% epoxy) Novolac (25-50%) Bisphenol F (2.5-10%)
Nitomortar ELS	Nitomortar ELS is a solvent free, two component system consisting of epoxy resins and chemicals, incorporating a special blend of chemical resistant fillers.	Chemical and biologically resistant	Pharchem Construction Supplies	Epoxy mortar Bispheno A (10-30%) and Bisphenol F (20-40%)
Hychem TL5	This is a two component solvent-free high thixotropic protective coating based on epoxy resin	Chemical resistant	Hychem International Pty Ltd.	Epoxy (100% epoxy) Novolac (100%)
Polibrid 705E	This is a two component solvent free elastomeric urethane coating with geotextile fabrics (100% polypropylene) embedded within the coating to produce reinforced, bonded geomembrane linings	Chemical resistant	International Protective Coating (Akzo Nobel)	Polyurea
Fernco Ultracoat S310	This is a two component solvent-free high build thixotropic protective coating based on epoxy resin.	Chemical resistant	Fernco Australia Pty Ltd	Epoxy (100%)

2.3 Results

2.31 Relative Acid Permeation Resistance Various Epoxy Coatings

The various types of epoxy used as protective coatings include:

i) Epoxy A (Bisphenol A epoxy resin)

Bisphenol A results from the reaction of phenol and acetone. The reaction of bisphenol A with epichlorohydrin forms diglycidylether bisphenol A resin or DGEBA. The molecular weight on DGEBA can be increased by adding more phenol.

ii) Epoxy F (Bisphenol F epoxy resin)

Bisphenol F results from the reaction of phenol and formaldehyde. The resulting phenolic monomer does not have the two methyl group present between the two benzene rings as found in bisphenol A. The reaction of bisphenol F with epichlorohydrin forms diglycidylether bisphenol F (DGEBF) resins. Because of the missing two methyl groups results in a higher proportion of trifunctional epoxide group increasing the functionality from 1.9 to 2.1, thus greater chemical resistance compared to bisphenol A resin.

iii) Novolac epoxy resin

Novolac is a modification of Epoxy F resin achieved by adding greater quantities of phenol. This increases its functionality from 2.1 to 2.5-6 that forms a highly crosslinked polymer network displaying high temperature and chemical resistance, but low flexibility.

Figures 1, 2 and 3 demonstrate the relative acid uptake in three types of epoxy, epoxy A (Sikadur 31, Sikadur 41 and ELS), epoxy F (Sikagard 63N) and novolac (Hychem TL5). The nature of epoxy in Fernco ultracoat was not known, but is appears to be a high molecular weight epoxy consistent with epoxy F. It is clear that the ranking in the resistance to acid uptake is novolac > Epoxy F> Epoxy A.

From the trendlines of the acid uptake, it is apparent that the rate of acid uptake is subjected to two rates, first a rapid rate followed by a slower rate of acid permeation. This is consistent with the dual phases, soft and hard phase, proposed for the epoxy structure. Where the soft phase is considered to promote rapid acid permeation and the hard phase a slower rate of acid permeation.

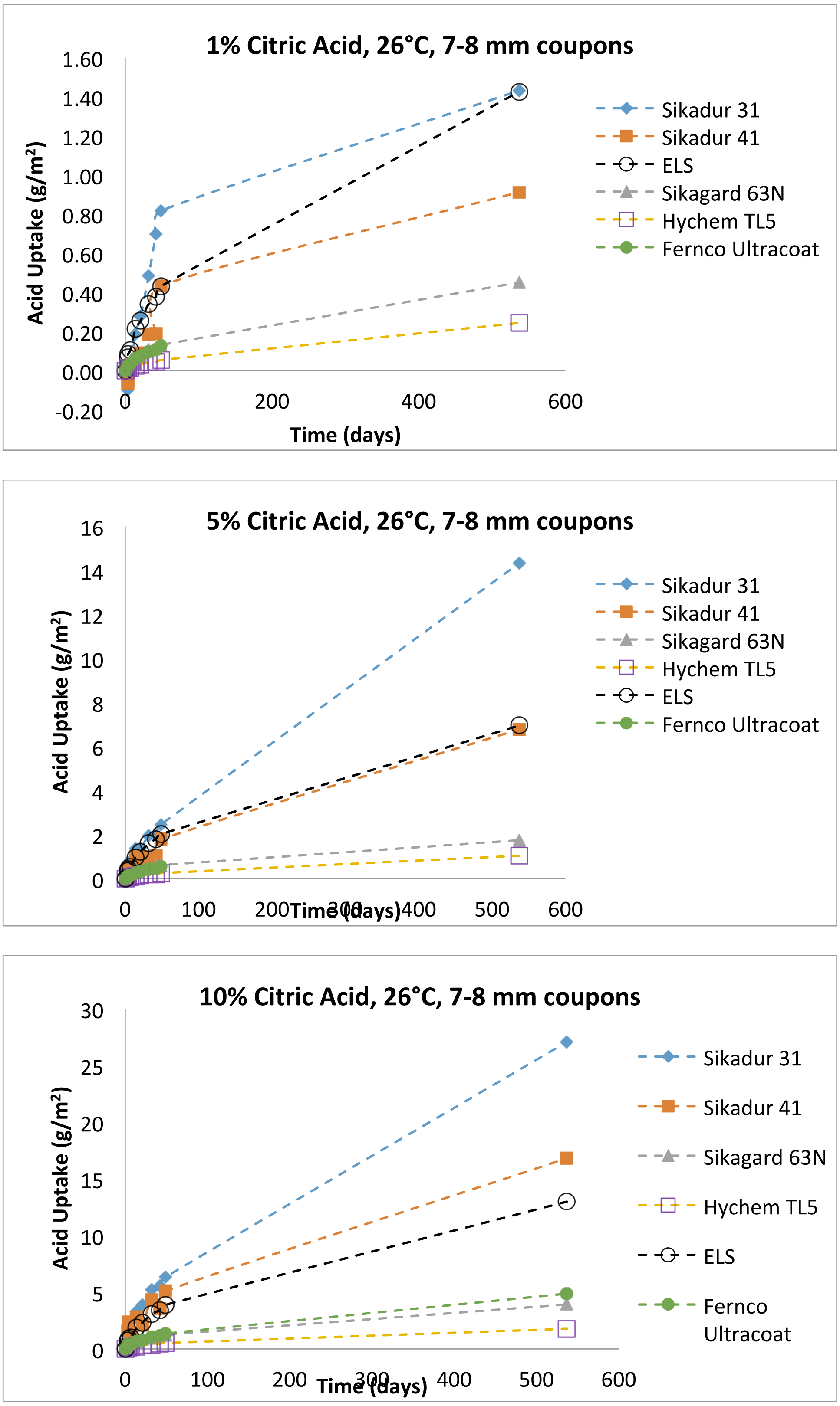

Figure 1a. Relative acid uptake of 1, 5 and 10% citric acid in various polymeric coatings (0-537 days)

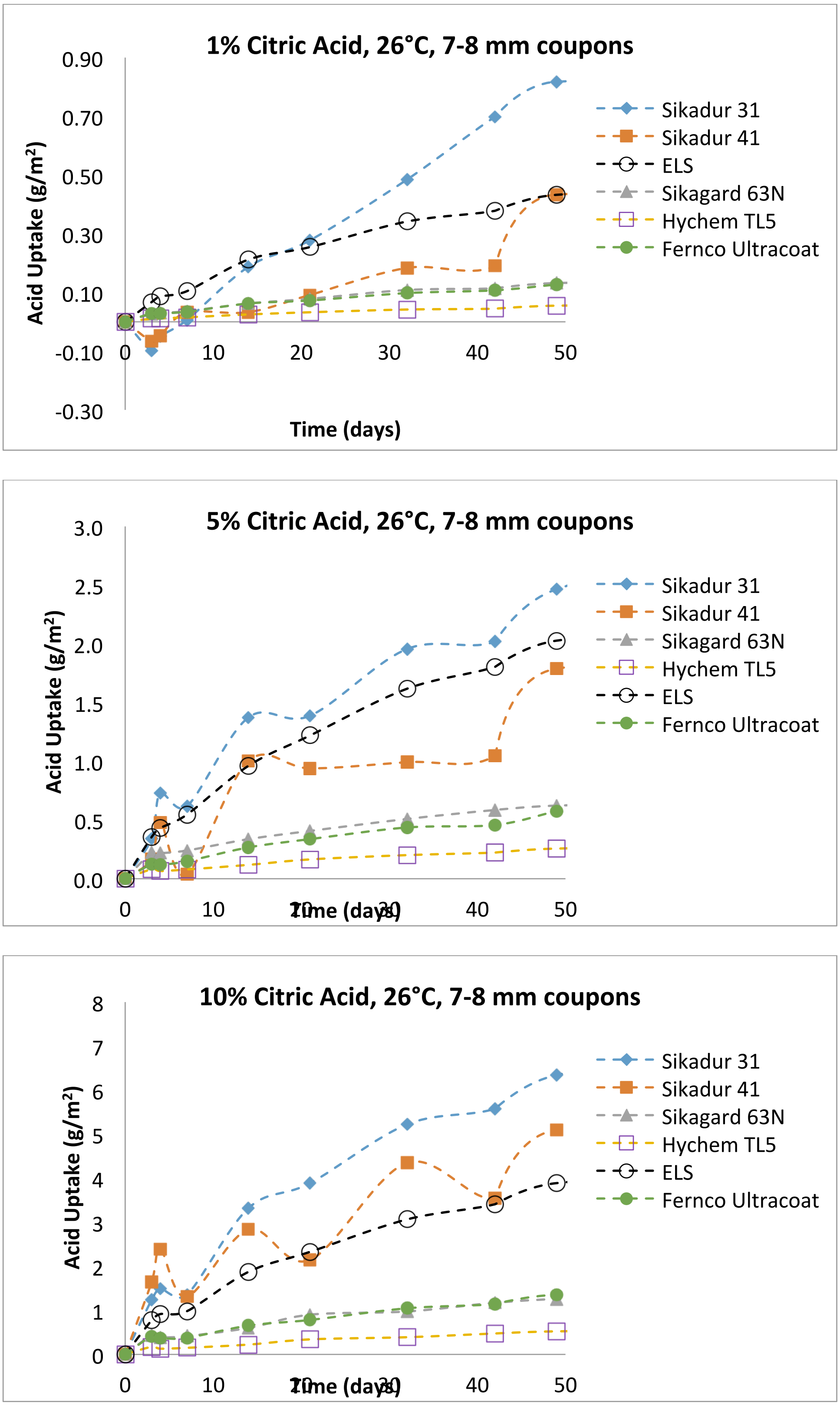

Figure 1b. Relative acid uptake of 1, 5 and 10% citric acid in various polymeric coatings (0-60 days)

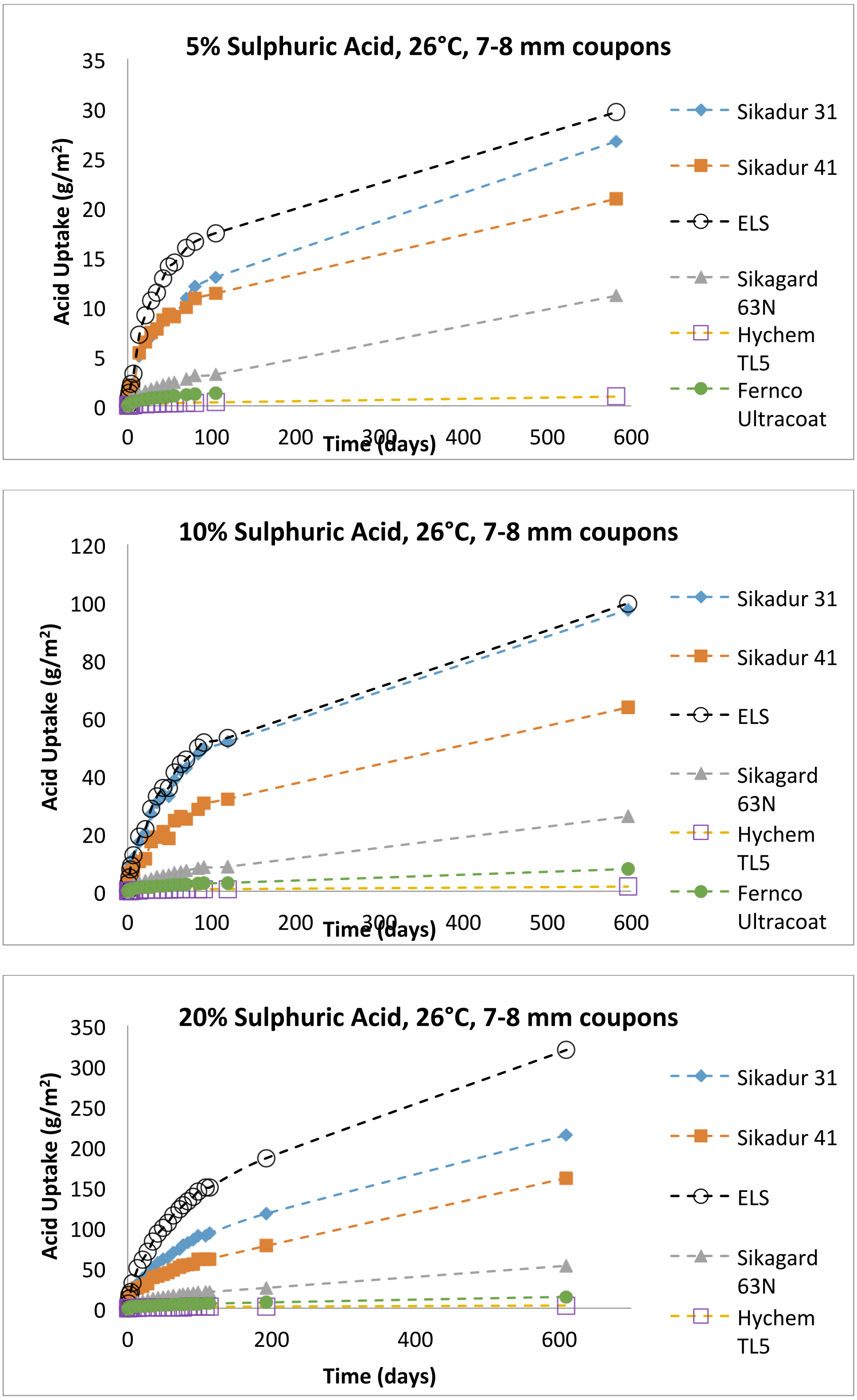

Figure 2a. Relative acid uptake of 5, 10 and 20% sulphuric acid in various polymeric coatings (0-537 days)

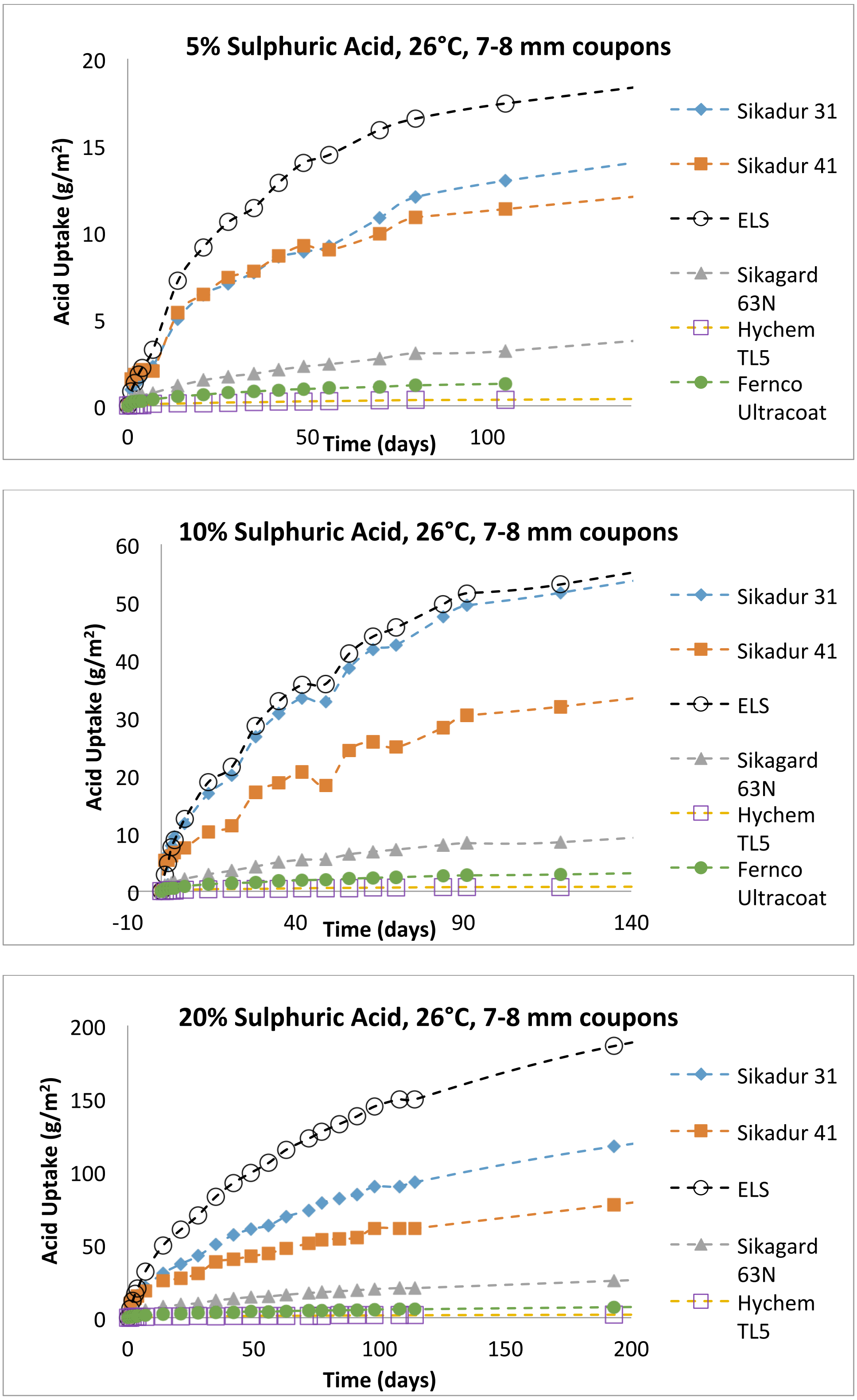

Figure 2b. Relative acid uptake of 5, 10 and 20% sulphuric acid in various polymeric coatings (0-200 days)

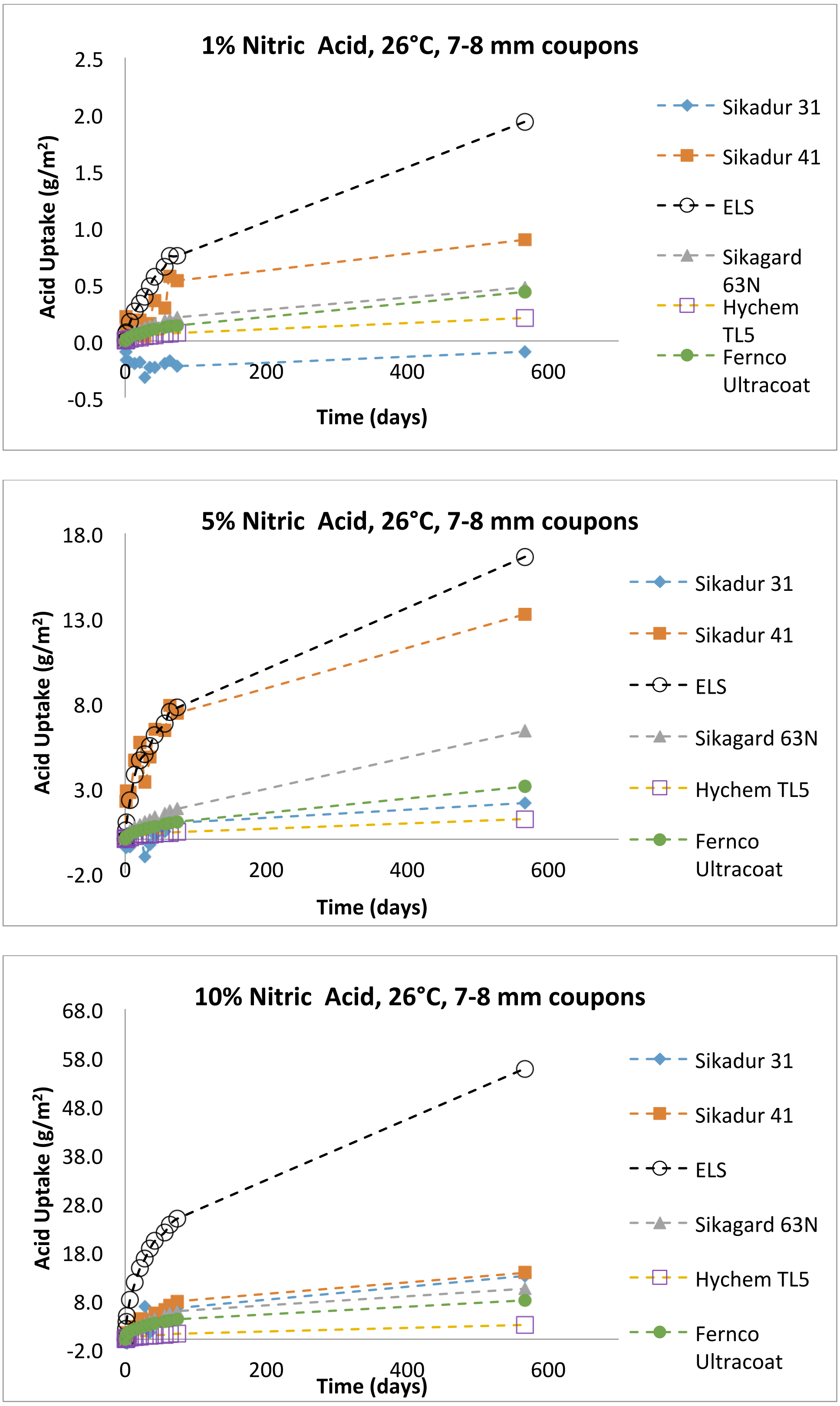

Figure 3a. Relative acid uptake of 1, 5 and 10% nitric acid in various polymeric coatings (0-537 days)

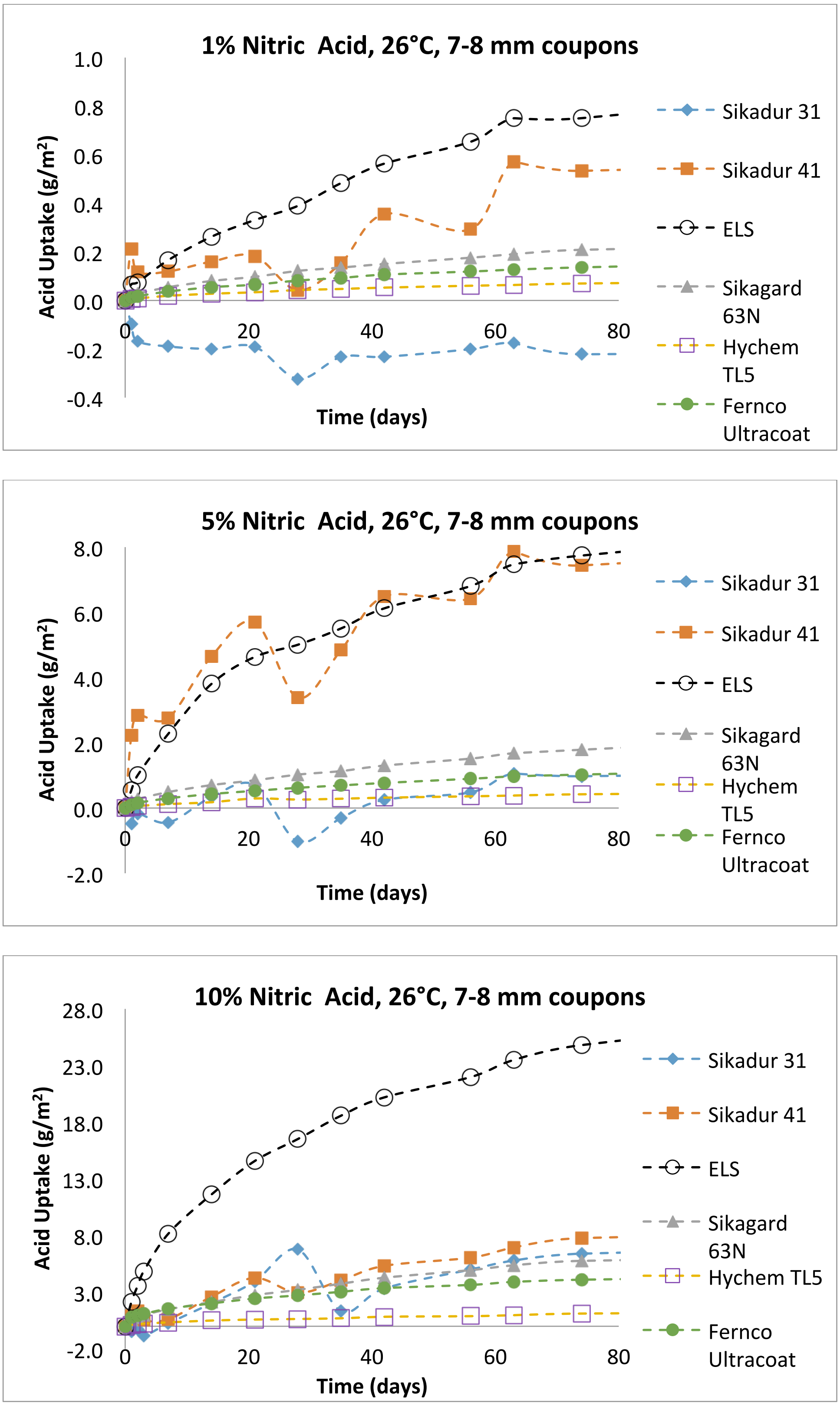

Figure 3b. Relative acid uptake of 1, 5 and 10% nitric acid in various polymeric coatings (0-60 days)

2.3.2 Relative acid uptake based on the acid type in epoxy coatings

Three types of acids were considered in these tests, citric, sulphuric and nitric acid. These were chosen to represent the types of biogenic acids generated by fungi, sulphur and nitrate oxidising bacteria. Both sulphuric and nitric acid acids are mineral and strong acids. Citric acid is organic, complexing and a weaker acid.

Figure 4-7 shows the relative uptake of these acids in four polymeric coatings. It is apparent that in most of the coatings, both sulphuric and nitric acids showed the highest rate of permeation, with the exception of Hychem, where there appears very little difference in acid uptake. This appear to suggests the acid permeation is dependent on the strength of the acids. Thus bacteria are likely to promote greater rate of acid permeation and damage to the epoxy lining than fungi.

The difference in the acid uptake are notable in the Epoxy A types of coating (Sikadur 41 and ELS) where the difference between citric and sulphuric acid is between 600 to 700% difference.
In the novolac and higher molecular weight epoxy (Hychem TL5 and Fernco Ultracoat), it appears the types of acid does not significantly affect the rate of acid uptake. It should be noted Hychem and Fernco coatings do not have high quantities of fillers as the Epoxy A types of coatings. This could partially affect the acid uptake.

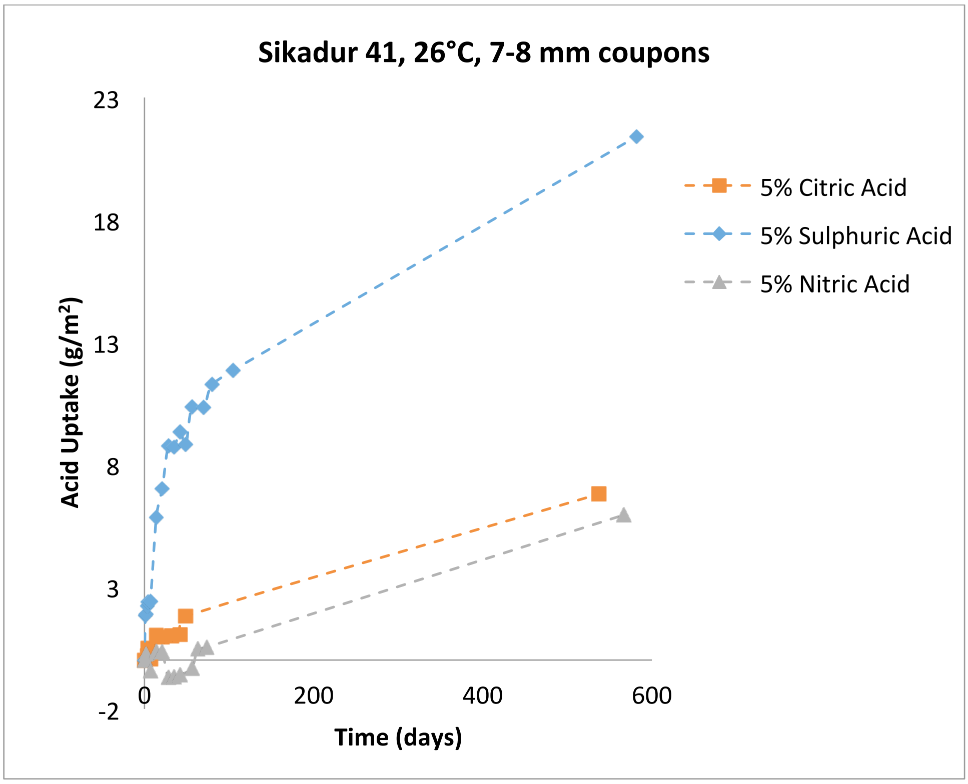

Figure 4. Relative uptake of 5% citric, nitric and sulphuric acid on Sikadur 41

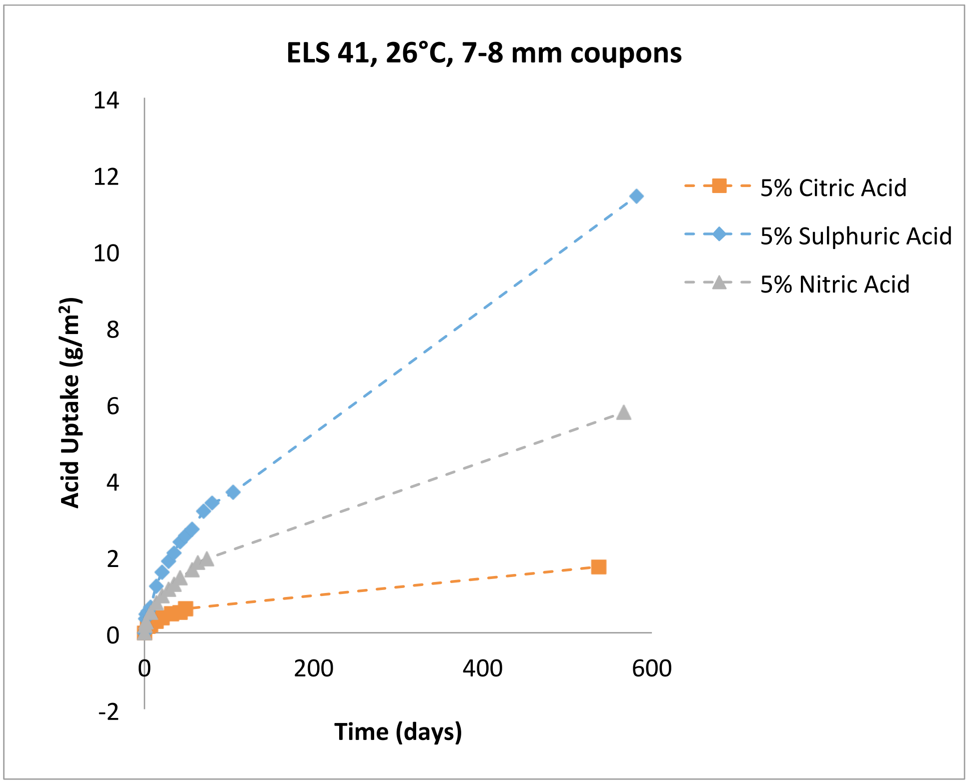

Figure 5. Relative uptake of 5% citric, nitric and sulphuric acid on ELS

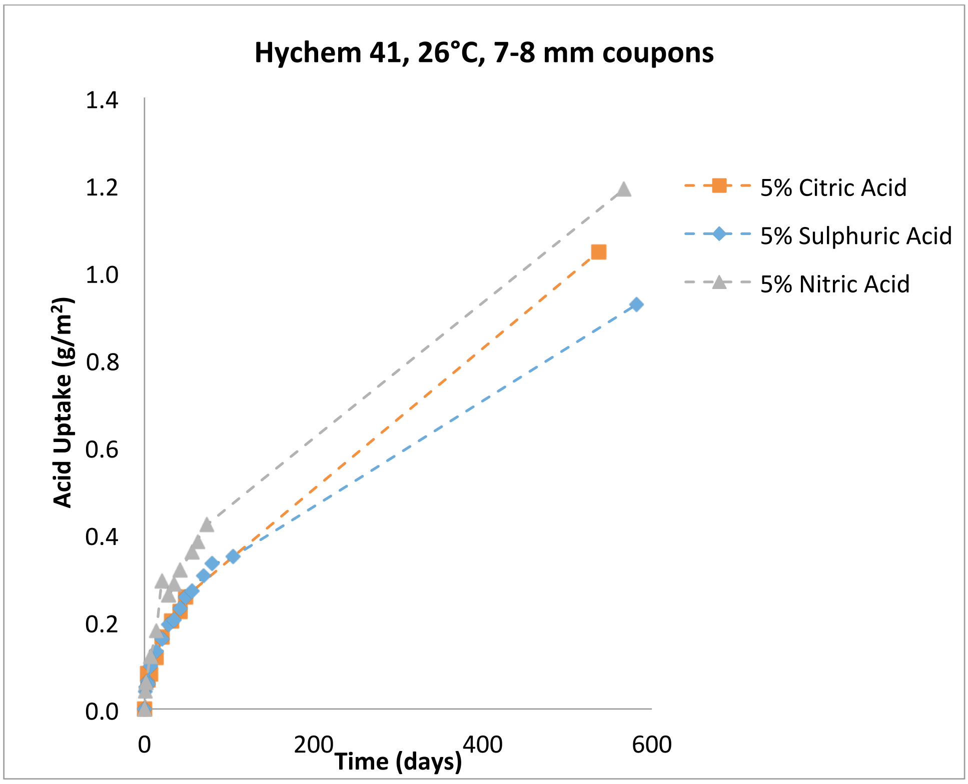

Figure 6. Relative uptake of 5% citric, nitric and sulphuric acid on Hychem

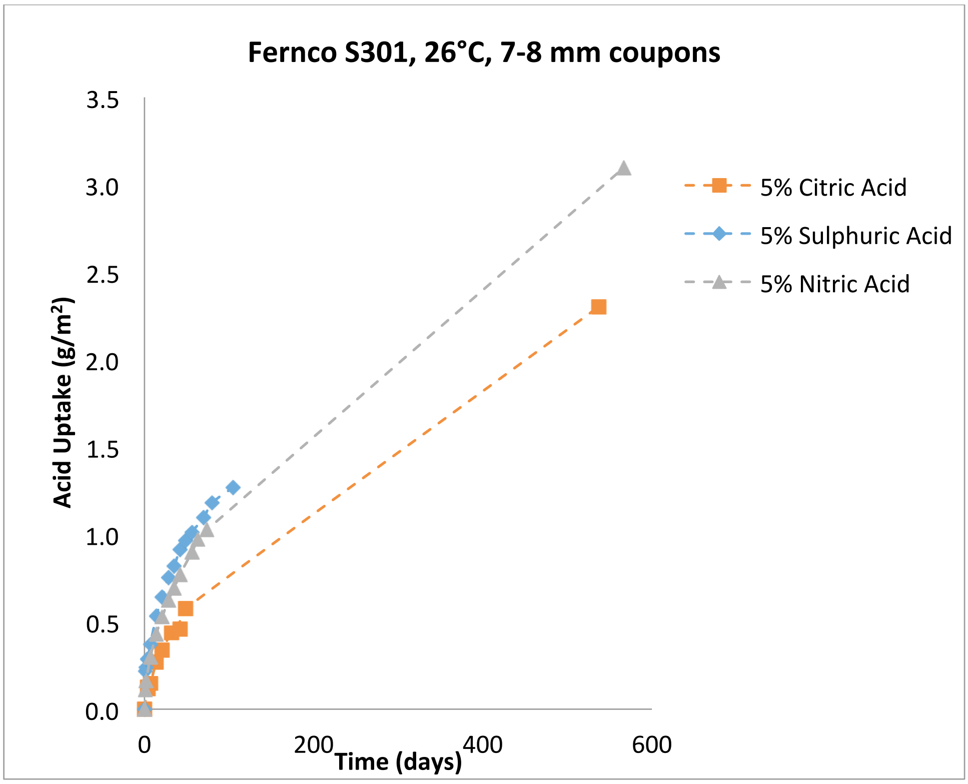

Figure 7. Relative uptake of 5% citric, nitric and sulphuric acid on Fernco Ultracoat

2.3.3 Effect of coupon thickness on the acid uptake in polymeric coating

The thickness that must be applied has always been a contentious issue. In general most industries have observed that thinner polymer lining (< 5mm) are unable to provide adequate protection in the more aggressive conditions found in Australian sewers today (Wubben 1999) (Sydney-Water 2009). Prior to 1992, Sydney Water applied < 2mm epoxy coatings. These have failed by delamination prematurely (< 2 years) despite claims from suppliers that these would last 10-15 years SW Survey response, 2009). Since then SW have used various thicknesses, from 10-30 mm, with a preference for 20 mm thick linings(Sydney-Water 2009), however performance continue to be variable (see Appendix C for coating performance).

Melbourne Water applied 0.5-1.0 mm epoxy tar coating prior to 1999 on concrete surface of manholes and related structures, which performed well, but there after demonstrated significant deterioration over time because of increased aggressiveness of the gas environment (Wubben, 1999). Melbourne Waters began applying 3 mm and 5 mm thick Hychem TL5 in 1995. Condition assessment of these coating in 2004 revealed the thicker 5 mm coating, which was also one year younger than the 3 mm coating, provided better performance than the thinner coating(Connell-Wagner 2004). Both coatings were found to have suffered localised delamination and blisters, but the occurrence of defects in the 3 mm coating was greater than the 5 mm coating.

It was therefore of interest to establish the effect of coating thickness on the rate of acid permeation and the optimal thickness that should be used in various corrosive conditions. The effect of coating thickness on the uptake of citric acid at various concentrations in Sikadur 41, Hychem TL5 and Fernco ultracoat is shown in Figure 8. It is apparent that increasing the thickness of coating increased the rate of acid permeation through the epoxy A (Sikadur 41) and novalac (Hychem TL5) coatings. Increasing the acid concentration of the acid increased the difference in rates between thinner and thicker coating. Fernco ultracoat however demonstrated similar acid uptake regardless of the thickness, although increasing the acid concentration also increased the acid uptake.

The difference in the acid uptake between the 20 mm and 5 mm coating in Sikadur 41 is 500%, which suggests the use of thicker coating may not provide greater protection and life than a thinner equivalent coating.

A relative comparison of the effect of coating thickness on the uptake of a weaker acid 1% citric acid and stronger acids on all coatings in Figures 9 and 10 respectively. Both shows scattered but a linear results demonstrating the effect of increasing the coating thickness on acid permeation. Of particular interest is that the effect of coating thickness becomes more important when the aggressiveness of corrosion increases.

The slope of Figure 9 for 1% citric acid is 0.096 $(g/m^2)/mm$
The slope of Figure 10 for 10% sulphuric acid is: 6 $(g/m^2)/mm$

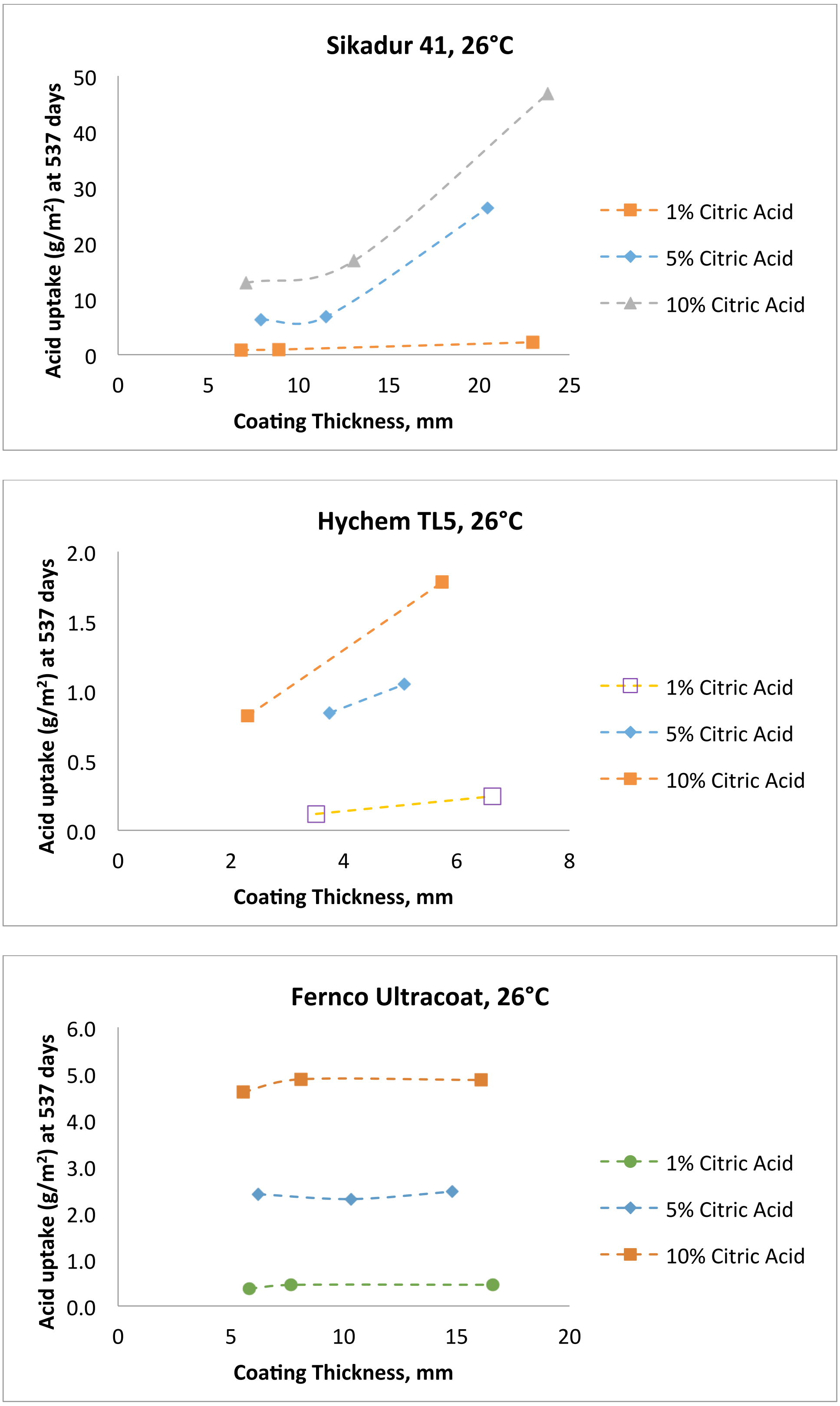

Figure 8. Effect of coupon thickness in the uptake of 1, 5 and 10% citric acid in polymeric coatings

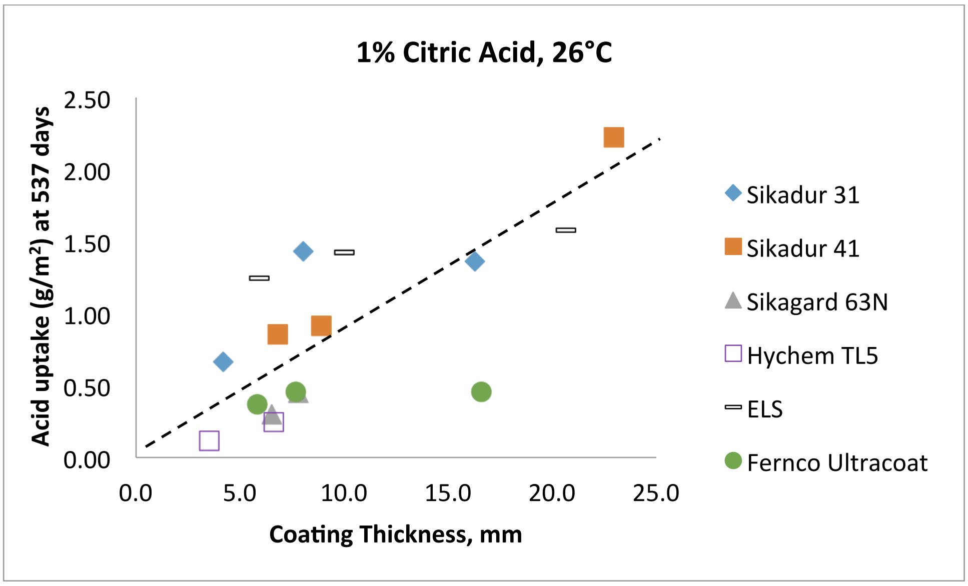

Figure 9. Effect of coating thickness on the uptake of 1% citric acid in various polymeric coatings.

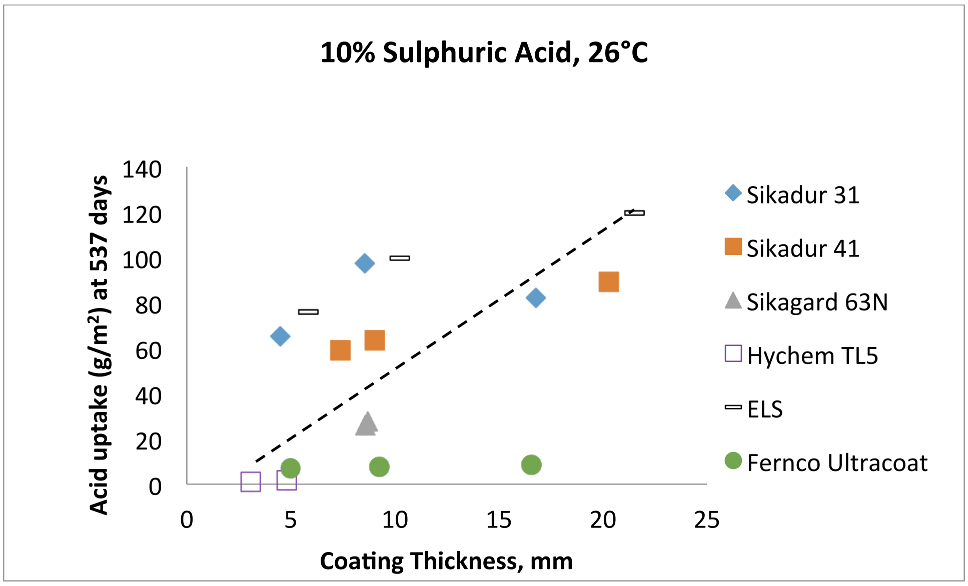

Figure 10. Effect of coating thickness on the uptake of 10% sulphuric acid in various polymeric coatings.

References

1. ASTM-D570-98. 2010. Standard Test Method for Water Absorption of Plastics
2. West Conshohocken, PA: ASTM International.
3. Connell-Wagner. 2004. Review of Epoxy Sewer Lining. Melbourne: Connell Wagner Pty Ltd. . Report no.
4. Sydney-Water. 2009. Epoxy Projects, (spreadsheet). Report no.
5. Wubben R. 1999. Evaluation of Lafarge 'Sewper Mortars' for Aggressive Sewer Environments. ConCorr Pty. Ltd. (submitted to to Lafarge Aluminates). Report no.