SP2 Report

on

Part 3: Predicting Service Life of Epoxy Coatings–

Based on Modelled Accelerated Rate of Acid Permeation

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Summary

This report outlines the basic principal used in developing models to predict the rates of acid permeation based on accelerated acid immersion test on various polymeric coatings.

The reason for conducting accelerated testing is attributed to the difficulty in maintaining and replicating the conditions in live sewers and in accessing and sampling of coating materials that are currently in service. Accelerated testings were conducted to provide a greater control on the environment and also a more systematic analysis of the effects of these environment on the acid permeation.

Tools were developed that could be used to predict the performance of coatings under various acidic environments and thus compare their relative performance. The acidic environment considered were citric, oxalic, sulphuric and nitric acids. These acids represent the biogenic acids that are generated by fungi and acidophilic bacteria known to colonise sewer walls.

In developing the service models, the following were taken into consideration:

1) Mechanism of acid permeation

In this study, the mechanism of acid diffusion suggests the presence of dual density, a soft or less dense phase and harder of more dense phase. It was established that acid diffusion occurs primarily through the soft phase while the harder phase, being more hydrophilic acted as sink for the acid. That is the harder phase tended to absorb greater quantities of acid, but demonstrated high resistance to acid permeation. Based on this analysis, the acid permeation tests were fitted to the modified Jacob-Jones Model which assumes the diffusion process and sorption processes are controlled by the different density phases in the resin. The Jacob-Jones model provides a measure of the mass transport parameters, diffusion coefficients (D) and acid absorption (M) in both phases.

2) Empirical correlation of mass transport parameters coating properties and environmental conditions

To develop generic tools that relate the properties of the coatings and environmental conditions to acid permeation, a series of empirical models were developed to correlate the mass transport parameters derived from the Jacob-Jones model to the coating properties and environmental conditions. The coating properties considered included polymeric content, filler size, wetting property and thickness. The environmental conditions considered included acid type and concentration.

3) Service life model

The predicted service lives were then predicted using the modified Crank equation. The Crank equation provides a breakthrough curve or an estimate of the acid concentration profile as a function of position in the coating. This provides a tool for measuring the time for the acid to permeate through certain thickness of coating. This time is also referred to

as "time-to-corrosion" which will be used to estimate the service life of polymeric coatings.

4) Validation of the models

The models developed were validated using statistical analysis and by comparing the relative performance of the coatings predicted by the models with the rate of acid permeation observed in field samples.

The final models were based on the modified Jacob-Jones model, the Crank equation and a series of empirical models were developed to correlate the effects of coating properties and environmental conditions on the rate of acid permeation. These equations formed the basis for this tool – to predict the service life of coating based on accelerated tests.

It should be noted that because a simulated corrosion environment was used in this study, the service life that is predicted by the mass transport models in this study can only be used to compare the relative performance of coatings and can only applied under the conditions used in the testing.

1.0 INTRODUCTION

Various coatings systems are available today suitable for maintaining and protecting sewer pipes. Polymeric coatings based on epoxy, polyurea and polyurethane substrates with and without 'inert' fillers have been utilised widely. In particular epoxy and epoxy mortar. It is well established that corrosion of the concrete substrate would be initiated due to the penetration of acidic metabolites, moisture and H_2S through protective polymeric coatings. The time needed for this process has been referred to as "breakthrough time", "initiation time" or "time-to-corrosion" and the time during which corrosion can propagate in the presence of the corroding agents and reach a critical level of damage is named "propagation time".

The service life of the coatings would therefore equate to time it would take for the acids to permeate fully through the coating to initiate the corrosion of the concrete substrate. Estimating these times requires an understanding of the process of mass transfer through the polymer network.

The following examines two approaches considered in this study, the first based on the assumption the rate of acid permeation follows Fick's law and the second based on non-Fickian models.

1.1 Fick's Law and Cranks Equation to Estimate Service Life

The basic principle that will be used to estimate the service life of polymeric coatings will be presented here. Permeates (the material permeating e.g., acid) absorption is generally considered to be independent of acid concentration. The diffusion of acid into cured epoxy resin is generally considered to obey Fick's law (Crank 1956):

$$\frac{M_t}{M_\infty} = 4 \left(\frac{Dt}{\pi b^2} \right)^{\frac{1}{2}}$$

(1)

Where Mt is the permeate uptake with time, M∞ is the maximum permeate uptake in the sample mass, D is diffusivity of the permeate and b is the sample thickness. The process of acid permeation follows Fick's law if plotting its M_t/M_∞ vs $t^{1/2}$ generates a linear relationship. The diffusion coefficient of the permeate is obtained by plotting M_t/M_∞ vs $t^{0.5}$. As an example the permeation of 10 wt% sulphuric acid through Sikadur 41 is shown in Figure 1. As shown Fick's law is followed by sulphuric acid over the time it was tested because the plot is relatively linear.

The diffusion coefficient that was derived using equation (1) can be used to determine the breakthrough time of this acid using Crank's equation (Crank J., and Park G.S. 1968). If the

acid content at the boundary is constant, the acid content of the polymer as a function of position in a semi-infinite medium can be estimated by the following equation (Crank 1975):

$$u = u_{x=0} - (u_{x=0} - u_0)erf\left(\frac{x}{\sqrt{4Dt}}\right) \qquad\qquad (2)$$

Where u is the moisture content with position , $u_{x=0}$ is the epoxy moisture content at the boundary or the equilibrium moisture content and u_0 is the initial moisture content of the epoxy.
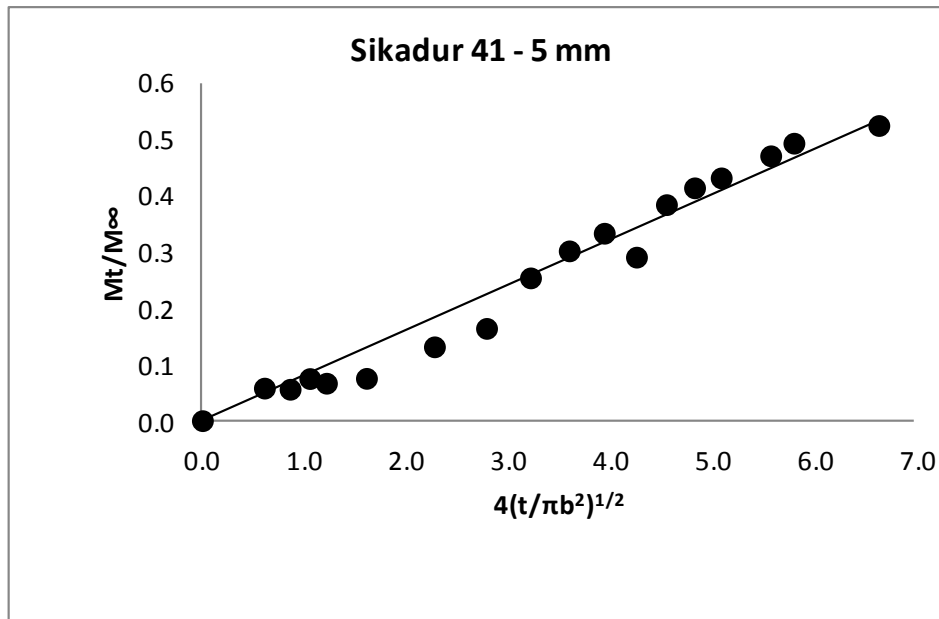

Figure 1. Estimating diffusion coefficient of 10 (wt%) sulphuric acid in sikadur 41.

A series of sulphuric acid vs position profiles were predicted for various times of exposure using Crank's equation. These are shown in Figure 2. These correlations could be used to estimate the time it would take for the acid through given thickness of coating. For example, in one year, sulphuric acid as shown has permeated through 10 mm of the coating. This means the time to corrosion for a 10 mm Sikadur 41 would be one year.

Because of the non-homogeneous network of the polymer, parts may be more dense than other sections, the rate of acid permeation may not follow Fick's law. The next section will present a more detailed analysis of other models that captures these form of mass transfer. These are also referred to as non-Fickian models. The principle by which these models are used will be similar to that presented here.
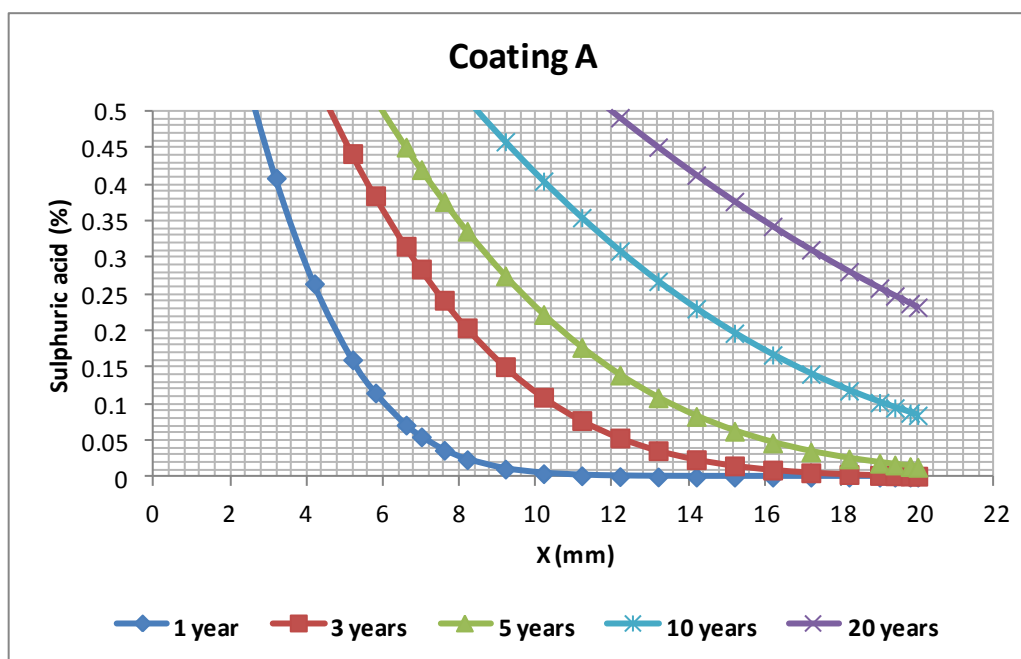
Figure 2. Permeation of moisture through Sikadur 41 estimated though Crank's equation.

2.0 FACTORS INFLUENCING THE TRANSPORT OF MOISTURE THROUGH EPOXY COATINGS

Epoxy resins are widely used as substrate for structural composite materials, adhesives, and organic coatings for high corrosive system due to their good mechanical properties and corrosion resistance. However, it is well known that these properties can be strongly affected by environmental permeates including moisture, biogenic acids, gases (e.g., carbon dioxide, H_2S), solvents and other organic pollutants (Gu J. D. et al. 1996, Gu X. H. et al. 2005, Maggana and Pissis 1999). The absorption of these permeates can causes plasticization(Ellis et al. 1984, Moy P. and Karasz 1980), lowering, the glass transition temperature,(Ellis et al. 1984, McKague et al. 1978, Moy F. H. and Kamal 1980) and may diminishes the mechanical strength of the resin (McKague et al. 1978). In addition, the presence of these permeates will also affect curing (Gu X. H. et al. 2005). Among these permeates only the effect of moisture diffusion has been examined in detail. Little has been done in the study of biogenic acid permeation in epoxy and such study has been limited in the permeation of H_2SO_4 only as this is considered the primary corrodent in the sewer (Milde et al. 1983, Monteny et al. 2001, Redner 2004)

The transportation of permeates are strongly influenced by two key factors, the chemical composition, or the number of polar groups present in the coating, and its micro-structure (Maggana and Pissis 1999), which is determined by the presence of free volume, crystallinity of the epoxy, the presence of distinct phases or the density of cross-linked structure and the

properties of the fillers(Apicella et al. 1988, Feng et al. 2004, Lu et al. 2001, Maggana and Pissis 1999).

Over the years, a few aspects of the moisture transport process in epoxies have become clear. The most significant development was realizing the role of polarity in determining the ultimate permeate uptake (e.g. water) (Bellenger et al. 1987, Soles and Yee 2000). Water is a polar molecule and capable of hydrogen bonding with other polar species such as hydroxyls and amines functional groups in the epoxy. In addition to polar interactions, the structure or porosity of the resins, or its chain topology must be considered in a discussion on the absorption process (Soles et al. 1998). Different molecular configurations can result in a more "open" structure or free volume, which should influence how much permeate is absorbed. The essence of this idea of openness is captured by the free-volume arguments. Researchers have tried to relate both the equilibrium uptake and diffusion coefficient to the free-volume content of the materials. It has been observed that there are distinct differences in the properties of coatings that have been desiccated (relatively dry environment) and soaked samples, supporting the possible inducement of structural changes by the permeate and aging(Gupta et al. 1985). Although the exact nature of this change has not been completely identified, previous investigations offered explanations related to the microvoiding and crazing of the polymer or by assuming a dual state of the water in cured epoxy. Micro-voiding is characterised by the formation of a significant number of small voids in the resin cured at elevated temperature. These micro-voids are typically less than 500μm diameter. Although individual void do not significantly affect, the sum of the effects of numerous microvoids can have sufficient effect on the structural integrity of the resin (Jin et al. 2011). Crazing is a network of fine cracks. It is differentiated from a crack in that crazes are able to support load. This often occurs in highly amorphous and brittle polymers (Wang et al. 2007, Yang J. et al. 2011).

Studies on the sorption of permeates through epoxy have focussed primarily on the permeation of water. The transport of water in epoxies generally follow two approaches. On the one hand, some researchers emphasize the role of hydrogen bonding between water and the epoxy network (Bellenger et al. 1989, Jelinski et al. 1985, Zhou and Lucas 1999). For others, the structure of the epoxy is considered to be the primary factor governing sorption and transport (Apicella et al. 1988, Barrie et al. 1984, Gupta et al. 1985, Maggana and Pissis 1999, Vanlandingham et al. 1999).

Various studies have been conducted to examine the nature of bonding of water with specific functional groups in epoxies and the resulting effect on the properties of the epoxy from such interactions (Bellenger et al. 1989, Jelinski et al. 1985, Zhou and Lucas 1999). Water may be present in the epoxy as bound or hydrogen bonded to polar groups or as "free water," that is water molecules that are not hydrogen-bonded. In a series of papers, Soles *et al.* carefully examined the role of free volume or "nanopores," concluding that transport is primarily governed by the hydrogen bonding of water to the epoxy (Soles and Yee 2000, Soles et al.

2000, Soles et al. 1998). However, they did not consider the two phase structure of epoxies in their analysis.

In addition to free volume, one must consider both heterogeneous nature of cured epoxies and its crystallinity. It is well-known that amorphous epoxies exhibit two phases after curing (Bellenger et al. 1989, Feng et al. 2004, Jelinski et al. 1985, Zhou and Lucas 1999). This two phase structure consists of a hard phase of high crosslink density in a matrix of low crosslink density. This structure has been proposed to occur via initial formation of microgels, which deplete their immediate neighbourhood of reactants. At the later stages of cure the regions between the microgel particles crosslink to form the soft phase. This two phase structure and its chemical nature, have been shown to have a significant influence on the mechanical properties and diffusion coefficient of moisture through epoxy ((Feng et al. 2004, Vanlandingham et al. 1999). It is considered that in this dual system, the hard phase is impermeable, and thus diffusion only occurs through the second phase (low crosslink density phase). That is the hard phase acts as an obstacle for the diffusing water molecules, effectively slowing their advance (Feng et al. 2004). In amine-rich or polar rich resins, although the fraction of hard phase decreases with increasing functional ratio, the diffusion coefficient is found to decrease correspondingly. This is attributed to the higher number of polar groups that fixes water or the permeate through hydrogen bonding (Soles and Yee 2000).

In one case an analytical model for moisture diffusion in epoxies explicitly accounts for the heterogeneous morphology, although in that case the hard phase was arbitrarily identified as being hydrophilic and the soft phase as being hydrophobic (Maggana and Pissis 1999). This means the adsorption through the softphase occurs primarily by diffusion and in the absence of permeate (water) and epoxy interaction. Whilst in the hard phase, the water is considered to be bound primarily to the polar functional groups.

While there has been extensive work describing moisture sorption for conventional epoxies, there is only limited information available regarding diffusion in liquid crystalline epoxies. It has found that the moisture permeation process for both the conventional epoxy system and the liquid crystalline epoxy system follows Fick's law. The high cross-linking density is responsible for this behavior. The liquid crystalline epoxy network was found to exhibits higher barrier properties to moisture permeation than the conventional epoxy network. This is associated with greater packing effect of the mesophase of the liquid crystalline thermoset (LCT) resulting in reduced free volume. Thus providing a higher resistance water permeation (Feng et al. 2004).

As shown, the focus in the analysis of permeate transport in epoxy has been on the individual role of the permeate-epoxy interaction and epoxy structure. In only a few cases are the two effects considered together. Adamson identified three distinct stages of water sorption, and postulated that those stages correspond to water first entering the free volume, then water becoming bound to hydrogen-bonding sites, and finally water entering the more densely crosslinked phase (Adamson 1980).

3.0 TRANSPORT MECHANISM

3.1 MODELS (Sorption Mechanisms)

Although diffusion of water into epoxy-based adhesives and epoxy based composites has been well documented in the literature, there has been little work done on the permeation of biogenic acids on epoxy, as would be found on the sewers. Various models have been proposed to describe the kinetics of water diffusion (Carter and Kibler 1978, Crank J. 1975, Marsh et al. 1984). This has included Fick's law(Crank J. 1975), the Langmuir two phase model (Bonniau and Bunsell 1981, Carter and Kibler 1978), Jacob-Jones model (Jacobs and Jones 1989a, b), modified Jacob-Jones model which takes into account the sorption or hydrogen bonding of the permeate(Maggana and Pissis 1999) and multiphase model (Marsh et al. 1984). In general researchers have come to agree that there is no universal model to cover all types of water diffusion. In most cases, each model is found to be only relevant to a particular material under a particular set of conditions. This is believed to be due to the complexity of the molecular interactions between water and the resin, as well as the consequence of those interactions.

Complex expressions, which take into account parameters, such as the formation of hydrogen bonds(Apicella et al. 1988, Cotinaud et al. 1982, Karner et al. 1994), the heterogeneity of the epoxy resin system(Jacobs and Jones 1989a, b), relaxation phenomena during hydration (Berens and Hopfenberg 1978) degradation of epoxide material (Xiao and Shanahan 1997) the depression of Tg (Vrentas and Vrentas 1992) and the formation of clusters, crazes, and microcracks during hydration, have been proposed by many authors(Illinger and Schneider 1980, Jacobs and Jones 1989a).

Adamson (Adamson 1980) has proposed the transport of permeate below the glass transition temperature involves a three-stage process in which the permeate first occupies the free volume. In the second stage, water becomes bound to network sites, causing swelling. Finally, water enters the densely crosslinked regions. Yang et al.(Yang F. et al. 1986) and Carfagna (Carfagna et al. 1982) both proposed the relative importance of hydrogen boding of polar permeates on the polar functional groups of the resin (especially hydroxyls produced during curing reactions or amine groups when there is an excess of the curing agent) and the unoccupied volume of the epoxy resin.

This section will present the method for dynamic acid absorption and models to describe the transport process through epoxy resins.

3.2 Dynamic Acid Absorption

Testing of water permeation has been carried out principally by the gravimetric method to monitor the dynamic water absorption (Bonniau and Bunsell 1981, Carter and Kibler 1978, Ellis et al. 1984, Maggana and Pissis 1999). The dynamic acid sorption measurements in this study has followed similar methodology. These were carried out by immersion of dry square epoxy mortar coupons into appropriate concentration of acid. The dimensions of the specimen are shown in Figure 3, where n is the width, l is the height and b is the thickness of the coatings to. At appropriate intervals, the samples were removed from the acid bath, blotted dry, and weighed on an analytical balance. The acid content of the epoxy with time, Mt, was calculated as follows:

$$M_t = \frac{w_t - w_d}{w_d} x100 \qquad (3)$$

Where w_t and w_d are the weight of the specimen at time t and the weight of the dry specimen respectively.
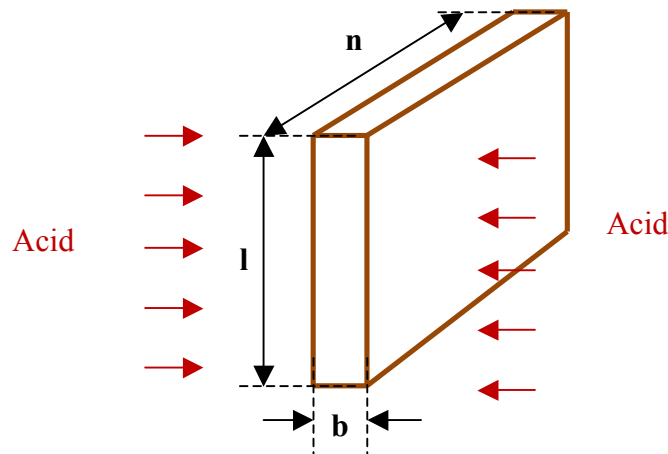

Figure 3. Geometry of Epoxy Coating Specimens

3.3 Fick's Theory

In most of the cases, the kinetics of permeate absorption is described by the one-dimensional Fick's second law, expressed as follows:

$$\frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial x^2} \qquad (4)$$

where c is the concentration of the diffusing substrate, x is the distance through plate thickness, t is the time, and D is the diffusion coefficient in the direction of absorption (x-direction normal to the plate surfaces). D is considered to be independent of the permeate content. That is Fick's laws as described above *can* only be applied in the *case* when the permeate and polymeric molecules do not interact. Such interactions could for instance be the adsorption of permeate molecules in hydrophilic components of the matrix, in impurities or in reactive epoxy groups, and the consequence would be that the trapped permeate is no longer available for the diffusion mechanism.

The one-dimensional case of Fick's second law implies that the material is exposed to the environment on one side only, or on two sides with both sides being parallel, as Figure 3 shows. To determine the diffusivity, equation (4) is integrated with the following boundary conditions:

$$c = c_i \quad 0 < x < b \quad t \leq 0 \tag{5}$$

$$c = c_a \quad x = 0; x = b \quad t > 0 \tag{6}$$

where c_i and c_a are the permeate concentrations at the initial time T_i (t<0) and at infinite time T_a (t>0) respectively, to give(Crank J., and Park G.S. 1968):

$$\frac{M_t}{M_\infty} = 4 \left(\frac{Dt}{b^2}\right) \left(\frac{1}{\pi^2} + 2 \sum_{n=o}^{(\infty}(-1)^n ierf(\frac{nb}{2(Dt)^2})\right) \tag{7}$$

The uptake is considered to be a diffusion process controlled by a constant diffusion coefficient, D, and $M\infty$ is the equilibrium sorption attained theoretically after infinite time. The value of D can be deduced from an observation of the initial gradient of a graph of M_t/M_∞ as a function of $(t/b^2)^{1/2}$.

Short period approximation
This observation is made easier by the fact that, for a constant diffusion coefficient, the graph for a sorption experiment is a straight line. To within the normal limits of experimental error, for M_t/M_∞ as much as about 50 percent, most observed correlations are linear. That is, at short times, where M_t/M_∞ is less than 0.5, equation (5) can be approximated by the following equation (Crank J., and Park G.S. 1968):

$$\frac{M_t}{M_\infty} = 4 \left(\frac{Dt}{\pi b^2}\right)^{\frac{1}{2}} \tag{8}$$

Longer period approximation
For moderate and longer periods of time, sorption can be approximated by the following equation:

$$\frac{M_t}{M_\infty} = 1 - \left(\frac{8}{\pi^2}\right)\left(\sum_{m=0}^{(\infty)} exp\left[-\frac{D(2m+1)^2\pi^2 t}{b^2}\right]\right) \qquad (9)$$

Which can be approximated to give:

$$\frac{M_t}{M_\infty} = 1 - \frac{8}{\pi^2}e^{-\frac{D\pi^2 t}{b^2}} \qquad (10)$$

The diffusion coefficient can be obtained by plotting $ln(1-M_t/M_\infty)$ vs (t/b^2) to give a slope of $D\pi^2$.

3.4 Edge Effects

For samples where edge effects needs to be considered, that is permeation through the edges, Shen and Springer (Shen and Springer 1976) proposed the following correction factor:

$$D_x = D\left(1 + \frac{b}{l} + \frac{b}{n}\right)^{-2} \qquad (11)$$

where D_x is the corrected diffusion coefficient and *b, l* and *n* are the thickness, length and width of the specimen (see Figure 3).

3.5 Non-Fickian Models

The kinetics of water absorption in epoxy resins is usually assumed to be a concentration-independent Fickian diffusion process (Deneve and Shanahan 1993, Nicholson 1997, Theocaris et al. 1983, Zheng and Morgan 1993). Often it has been observed that Fick's diffusion model fails to describe the whole sorption phenomenon (Illinger and Schneider 1980, Karner et al. 1994). To address this, researchers have attempted to explain the deviation from Fick's model using the Langmuir type diffusion process,(Bonniau and Bunsell 1981, Carter and Kibler 1978, Karner et al. 1994) in which the permeate (water) diffuses as a mobile phase whilst some are strongly bound on the polar functional groups of the epoxy (Apicella et al. 1988, Bonniau and Bunsell 1981, Cotinaud et al. 1982). Moisture absorption-desorption in these systems (epoxy and epoxy mortar) is considered a quasi-reversible process, the kinetics of which are non-Fickian (Type II) and dependent on prior permeation history. The multi-staged sorption and transport behavior are interpreted in terms of multiphase models (Marsh et al. 1984). Other authors have proposed the existence of two phases within the epoxy structure, each differentiated by the different crosslinking densities(Jacobs and Jones 1989a, b). Changes in the structure of the material during the moisture exposure, such as plasticization and formation of cavities have also been considered (Gupta et al. 1985, Hayward et al. 1997). Two of the models that have been proposed, the

Jacob-Jones model(Jacobs and Jones 1989a, b), the modified Jacob-Jones models(Maggana and Pissis 1999) and two phase Langmuir models (Bonniau and Bunsell 1981, Carter and Kibler 1978) are described below.

3.5.1 Jacob Jones Model or Two Phase Model

The analysis of Jacobs and Jones model proposes the existence of two phases within the epoxy material, one dense and one less-dense phase (Jacobs and Jones 1989a, b). They proposed that diffusion proceeds by parallel Fickian processes in both phases as described by equation 4. Using this assumption, the percentage permeate composition as a function of time M_t can be calculated from the equation:

$$M_t = G(M_\infty - M_i) + M_i \tag{12}$$

where Mi is the initial percentage of moisture content of the sample, M_∞ is the percentage of moisture content at equilibrium, and G is a time dependent parameter that is obtained by solving equation (1) and the given boundary conditions (see equations 5 and 6). The result of the integration is given as follows:

$$G = \frac{M_t - M_i}{M_\infty - M_i} = 1 - \frac{8}{\pi} \sum_{j=0}^{\infty} \frac{\exp\left[-(2j+1)^2 \pi \left(\frac{Dt}{b^2}\right)\right]}{(2j+1)^2} \tag{13}$$

G is obtained by integrating the solution of equation (4) over the plate thickness b. An analytical approximation for G is given as follows:

$$G = 1 - \exp\left[-7.3\left(\frac{Dt}{b^2}\right)^{0.75}\right] \tag{14}$$

A nominal diffusion coefficient (D) can be estimated from the slope (s) of the plot of M_t vs $t^{1/2}$ using the following equation:

$$D = \pi \left(\frac{sb}{4M_\infty}\right)^2 \tag{15}$$

This diffusion coefficient can be corrected for edge effects using equation (9). To take into account the presence of the two phases, the normalised permeate content $M(t) = M_t/M_\infty$ as a function of time can be described by the following morphology dependent equation (Jacobs and Jones 1989a, b) :

$$M(t) = V_d\left\{1 - exp\left[-7.3\left(\frac{D_d t}{b^2}\right)^{0.75}\right]\right\} + (1 - V_d\left\{1 - exp\left[-7.3\left(\frac{D_l t}{b^2}\right)^{0.75}\right]\right\} \tag{16}$$

Where D_d and D_l are the diffusion coefficients in the dense and less dense phase respectvively and V_d is the volume fraction of the dense phase. The values of the diffusion coefficients can be estimated from the equilibrium permeate concentrations of the dense and less dense phase, M_d and M_l. The value of M_l is estimated by extrapolating the slope of the plot of M(t) as a function of $t^{1/2}$ in region II of the less dense back to the M(t) axis (see Figure 4). M_d is estimated by subtracting M_l from M_∞. The diffusion coefficients from the dense and less dense phase can be estimated using the following equations:

$$D_d = \pi \left(\frac{s_d b}{4(M_\infty - M_l)} \right)^2 = \pi \left(\frac{s_d b}{4M_d} \right)^2 \qquad (17)$$

And

$$D_l = \pi \left(\frac{(s_x - s_l)/d}{4(M_l)} \right)^2 = \pi \left(\frac{s_l b}{4M_l} \right)^2 \qquad (18)$$
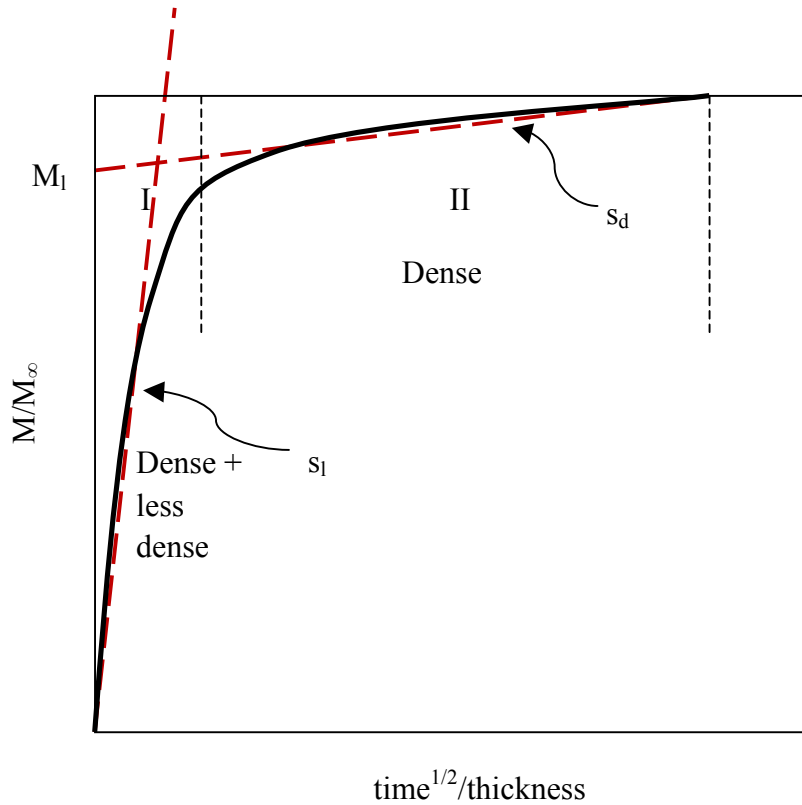
Figure 4. Permeate sorption curve of resin demonstrating two phase structure of a mixture of dense and less dense phases (Region I) and dense phase alone (Region II).

3.5.2 Modified Jacob-Jones Model – Diffusion and sorption through two phase system

The Jacobs–Jones model accepts that in each phase, the diffusion process is controlled only by the density of that phase and neglects the possible sorption of permeate (e.g., water) on polar groups of the resin. Maggana (Maggana and Pissis 1999) proposed the modification of the Jacob-Jones model. Their model also considers the epoxy as a two phase system

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consisting of a master phase (phase 1), where the major part of water is absorbed, and of a second phase (phase 2), with a different density or/and hydrophilic character than phase 1. The modified Jacobs–Jones model is given as follows:

$$M_t = M_1 \left\{ 1 - e^{\left[-7.3 \left(\frac{D_1 t}{b^2} \right)^{0.75} \right]} \right\} + M_2 \left\{ 1 - e^{\left[-7.3 \left(\frac{D_2 t}{b^2} \right)^{0.75} \right]} \right\} \quad (19)$$

Where D_1, D_2, M_1 and M_2 are the diffusion coefficients and percentage of permeate absorbed at saturation on the two phases respectively. M_∞ equals $M_1 + M_2$. The first term of equation (19) is related to the diffusion of the permeate in the homogeneous and non-polar phase 1 (mode1). That is the permeate is transported by diffusion in the absence of permeate and resin interaction by sorption. The second term of equation (19) expresses the contribution of permeate absorption in phase 2 (mode 2) to the whole diffusion procedure. That is D_1 measures the diffusion coefficient in the less dense phase. D_2 is the diffusion in the dense phase where the permeation should be more restricted by the higher cross-linking but water sorption should be higher because of the greater concentration of polar groups.

3.5.3 Two phase model based on the Langmuir equation

Humidity and other polar permeates such as acids induces changes to the physicals properties and stress characteristics of epoxy-composite structures. Long term absorption results that are principally analysed and are assumed by most workers to fit the simple (Fickian) diffusion theory may give anomalous results. A slightly generalized but linear model which involves sources and sinks of diffusing water molecules have been proposed based on the Langmuir model (Bonniau and Bunsell 1981, Carter and Kibler 1978). The Langmuir two phase model considers a free diffusion phase and a second combined phase which does not involve diffusion. This model is based on diffusion theory and Fick's law which consider that the driving force of diffusion is the permeate concentration gradient. With this model the weight gain M_t as a function of time t is written in terms of four parameters, the diffusion coefficient D, weight gain of permeate at saturation M_∞, the probability α a molecule of water passing from a combined state to the free phase and the probability β of a molecule of water passing from the free to the combined phase(Bonniau and Bunsell 1981, Carter and Kibler 1978).

For

$$\alpha \ll \frac{D \pi^2}{b^2} \text{ and } \beta \ll \frac{D \pi^2}{b^2} \quad\quad\quad\quad (20)$$

The normalised permeate content as a function of time can be written as:

$$\frac{M_t}{M_\infty} = 1 - \frac{\beta}{\alpha + \beta} e^{-\alpha t} - \frac{\alpha}{\alpha + \beta} \cdot \frac{8}{\pi^2} \sum_{n=0}^{\infty} \frac{1}{(2n+1)^2} e^{\left[-\frac{Dt}{b^2} \pi^2 (2n+1)^2 \right]} \quad (21)$$

For $Dt/b^2 > 0.05$, this reduces to:

$$\frac{M_t}{M_\infty} = 1 - \frac{\beta}{\alpha+\beta}e^{-\alpha t} - \frac{\alpha}{\alpha+\beta}\cdot\frac{8}{\pi^2}e^{\left[-\frac{Dt}{b^2}.\pi^2\right]}$$
(22)

For $Dt/b^2 < 0.05$, this reduces to:

$$\frac{M_t}{M_\infty} = \frac{\alpha}{\alpha+\beta}\cdot\frac{4}{\pi}\sqrt{\frac{Dt}{h^2}}$$
(23)

Estimation of the diffusion coefficient and the parameters α and β are conducted by fitting the data to equations 22 and 23 using solver in Excel.

3.0 Experimental

3.1 Coating Materials
Eight types of coating materials were tested in this study and a list are shown in Table 1.

3.2 Acid Permeation Tests
The acid permeation tests were performed at 25-27°C in acids including citric, oxalic, nitric and sulphuric acid at concentrations of 1, 5, 10 and 20 wt%.

4.0 RESULTS
The rate of acid permeation can influence the service life of polymeric coatings. The aim of this aspect of the study is to develop models that could be used to predict this rate of permeation and thus develop a tool that could be used to compare the performance of various coatings. In this study two aspects are considered, the first is the mechanism of acid permeation through epoxy and the second considers the factors that affects the rate of acid permeation.

4.1 Mechanism of Acid Permeation

The choice of the diffusion model that needs to be used to analyse the permeation of acid will depend on the mechanism of acid diffusion. In this section, the mechanism of acid permeation was examined. The absorption of acids through the epoxy and epoxy mortar coating were monitored by immersion tests. Graphs of M_t as a function of $(t/b^2)^{1/2}$ of 1% citric in various coatings are shown in Figure 5. For simplicity most researchers assume the permeate absorption is a concentration-independent Fickian diffusion process. However, as shown in Figure 5, although Fick's law may describe the first phase of the process, it cannot describe the whole transport process, that appears to be characterised by two slopes. As suggested in the review, researchers have attempted to explain this behaviour using the Langmuir model (Bonniau and Bunsell 1981, Carter and Kibler 1978) in which the absorbed material can be divided into mobile and strongly-bound types. Whilst others assume epoxy coating with two-phase structure, comprising areas of differing density, which may influence

Table 1. Polymeric coatings for sewer application

Coating Name Plate	Type of Polymeric Materials (Manufacturer's TDS)	Advantages (Manufacturer's TDS)	Manufacturer	Website	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	www.sika.com.au	Epoxy A and F (mortar)
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	www.sika.com.au	Epoxy A (mortar)
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	www.sika.com.au	Epoxy F (100% epoxy)
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	**www.parchem.com.au**	Epoxy A (mortar)
Hychem TL5	This is a two component solvent-free high thixotropic protective coating based on epoxy resin	Chemical resistant	Hychem International Pty Ltd.	www.hychem.com.au	Novolac (100% epoxy)
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)	www.international-pc.com	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	www.fernco.com.au	Epoxy

the diffusion characteristics of the system as a whole(Jacobs and Jones 1989a, Maggana and Pissis 1999). The absorption data in Figure 5 demonstrate the features of this two phase structure. Phase I is characterised by rapid diffusion of acid into the resin and phase II the diffusion process is considerably slower reflecting the transport through the more dense phase.

In this study, further analysis of acid absorption on the epoxy and epoxy mortars were analysed using the modified Jacobs–Jones model as proposed by Maggana (Maggana and Pissis 1999). Their model considers the epoxy as a two phase system consisting of a master phase (phase 1), where the major part of eluent is absorbed, and of a second phase (phase 2), with a different density or/and hydrophilic character than phase 1.

To examine the mass transport through the two phases, the diffusion coefficients and permeate absorption of 1% citric acid through Sikadur 41 of various thickness were estimated using equation (19). The measured diffusion coefficients (D_1, D_2) and percentage of permeate absorbed at saturation on the two phases (M_1 and M_2) are plotted as a function of thickness in Figure 6. The reported corrected diffusion coefficients have been corrected for the edge effects introduced by the different thickness of the coatings.

As shown, the hard phase is shown to be impermeable with relatively lower diffusion coefficients compared to the soft phase. Thus diffusion appears to only occur through the soft phase with its low crosslink density. Whilst the hard phase acts as an obstacle for the diffusing acid molecules, effectively slowing their advance (Feng et al. 2004). However the permeate absorbed in the hard phase is higher than the soft phase. The **hard phase** is arbitrarily identified as being **hydrophilic** whilst the **soft phase as being hydrophobic** (Maggana and Pissis 1999). This means the transport of the through the softphase occurs primarily by diffusion. Whilst in the hard phase, the permeate is considered to be bound primarily by the polar functional groups. This feature is also apparent in Figure 5, where there is an initial rapid uptake of acid in the soft phase, albeit the quantity is lower, followed by slower but overall higher permeate absorption in the second (hard) phase. The increase in the permeate uptake with thickness suggests the concentration of polar groups in the dense phase increases with coating thickness. It is also apparent the diffusivity in both the soft and hard phase increased with thickness of the coating.

4.2 Service Models Based on Accelerated Acid Permeation

As established above, the acid permeation through the epoxy coating is subjected to the effects of the dual crystallinity or phases in the coating. It appears the acid permeation is best analysed using the models that reflects these properties, such as the Jacob Jones model.

The mass transport parameters, diffusion coefficients and permeate absorption could be used in the Crank's equation to establish the service life of the coating based on the breakthrough profile (acid concentration vs coating position) of the permeate through the epoxy:
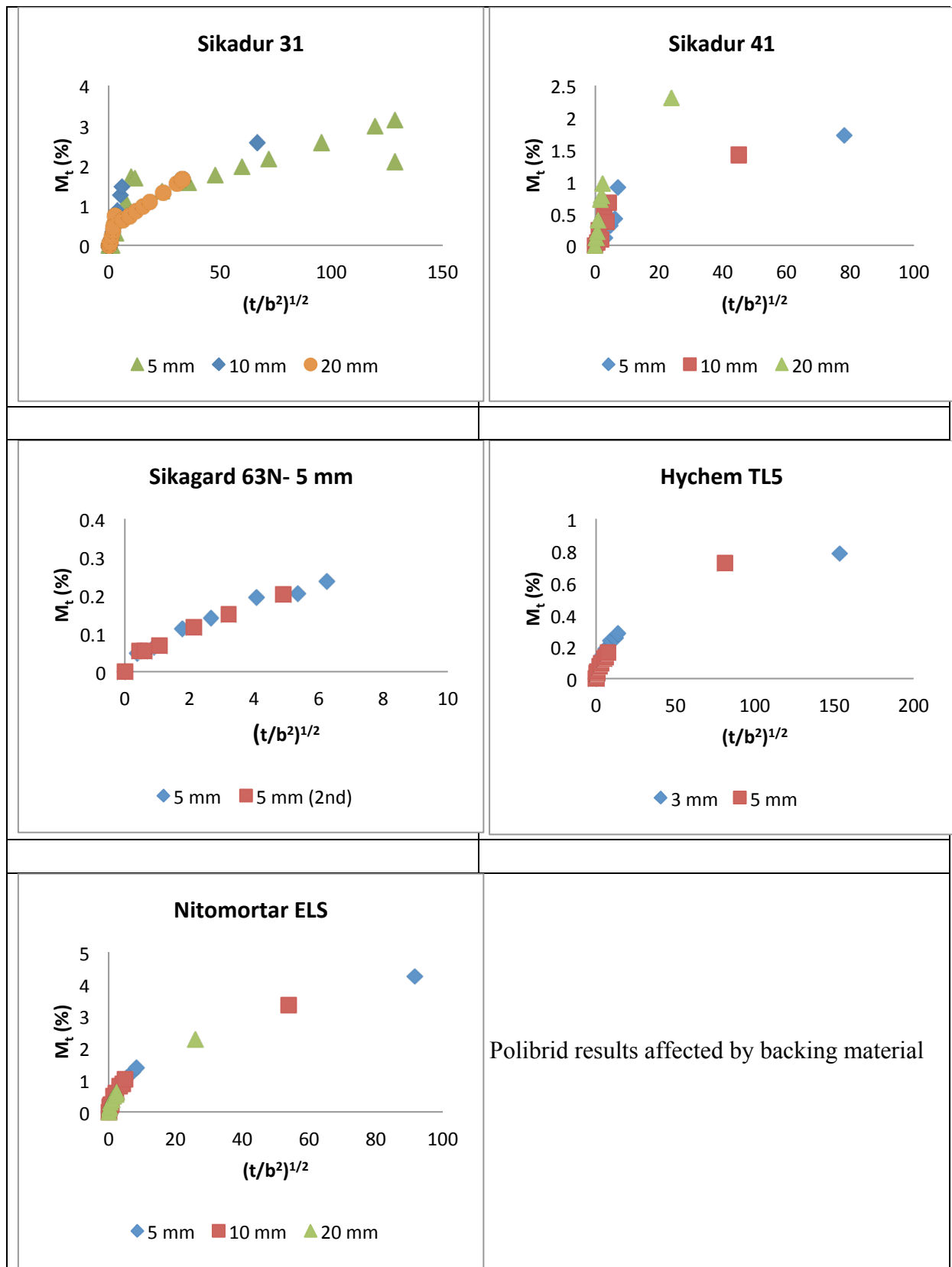
Figure 5. Experimentally determined absorption of 1% citric acid in various epoxy coatings at 26°C.
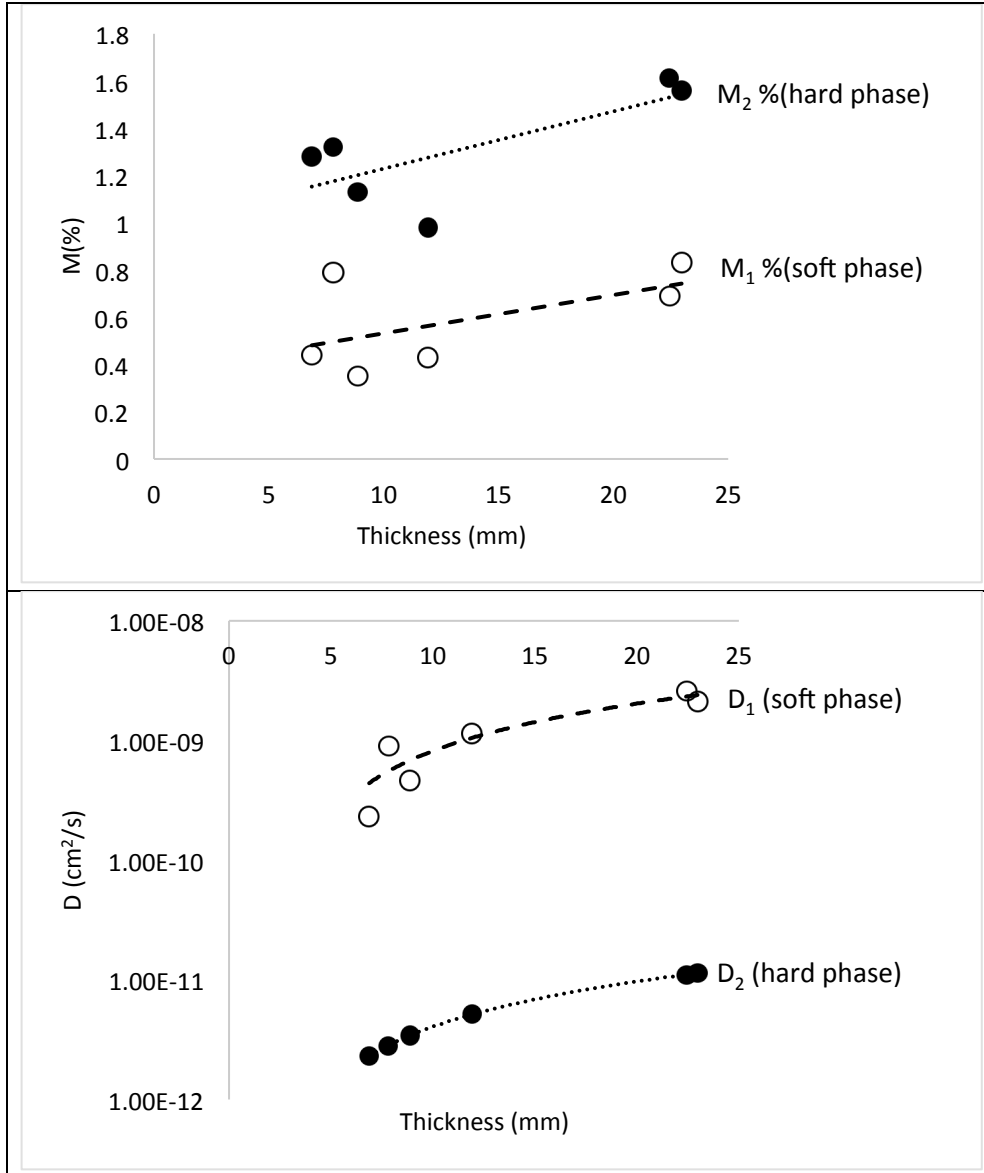
Figure 6. Diffusion coefficients and percentage permeates of 1% citric acid through the amorphous and dense phases of Sikadur 41.

$$M_t(\%) = \left\{ M_1 - M_1 erf\left(\frac{x}{\sqrt{4D_1 t}}\right) \right\} + \left\{ M_2 - M_2 erf\left(\frac{x}{\sqrt{4D_2 t}}\right) \right\} \tag{24}$$

4.2.1 Factors affecting the rate of acid permeation

To obtain a more general equation to predict the breakthrough profile of coating, as series of empirical equations were developed to correlate the mass transfer parameters to factors that affects acid permeation. SP2 Report 3, Part 2 analysed the chemical factors that influences

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the rate of acid permeation. On the basis of this study, the following factors were correlated with the mass transport parameters of equation (24).

i.   Environmental conditions

Acid type: Reflects difference in molecular size and polarity

Acid concentration: (g/100ml)%

Temperature: all tests were conducted at 25-27°C, the typical temperature in most sewers, however the effect of temperature differences should also be considered in future studies.

ii.   Chemical properties of coatings

LOI: (loss of ignition) represents the percentage of polymeric component of the coating. This is established from XRF testing of the coating.

D: number mean particle size of the filler (μm), established by microscopic examination of the coating

H: wetting property or hydrophilicity, measured from ratio of the peak height of the OH to benzene functional groups established by FTIR

iii.   Physical properties

t :   coating thickness (mm)

These factors were fitted to the mass transport parameters using the following empirical equations.

$$M_\infty = k_1 [LOI]^{\alpha 1} [D]^{\beta 1} [H]^{\gamma 1} [t]^{\delta 1} [C]^{\tau 1} \qquad (25)$$

$$M_d(\%) = k_2 [LOI]^{\alpha 2} [D]^{\beta 2} [H]^{\gamma 2} [t]^{\delta 2} [C]^{\tau 2} \qquad (26)$$

$$D_1 = k_3 [LOI]^{\alpha 3} [D]^{\beta 3} [H]^{\gamma 3} [t]^{\delta 3} [C]^{\tau 3} \qquad (27)$$

$$D_2 = k_4 [LOI]^{\alpha 4} [D]^{\beta 4} [H]^{\gamma 4} [t]^{\delta 4} [C]^{\tau 4} \qquad (28)$$

The fit of the model were established by comparing the predicted with the experimental parameter using the measured coefficient of determination, R^2 for each acid tested (see Figures 8-11). Adjusted R^2 were also measured to take into account potential bias that is introduced by the multiple factors in the model. The measured R^2 and adjusted R^2 were from 0.77 to 0.99 indicating the models adequate describe the correlation between the chemical, physical, environmental factors to mass transport parameters. These fit were found for all the coatings examined with the exception of Fernco Ultracoat and Polibrid (non-epoxy) coating. . The corresponding model parameters are shown in Tables 2-5
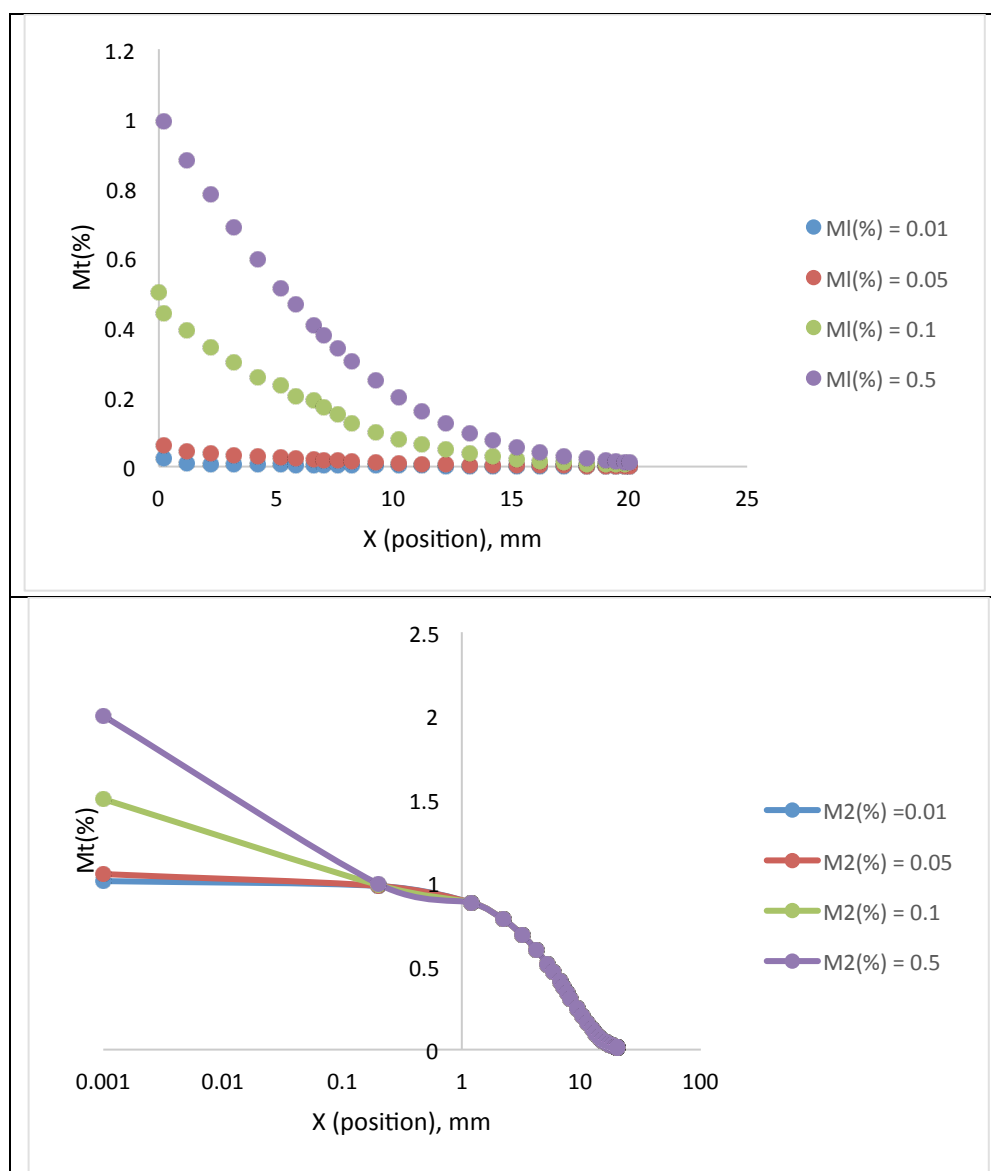
Figure 7. Effect of permeate absorption in the soft phase (M1) and hard phase (M2) on the rate of acid permeation.
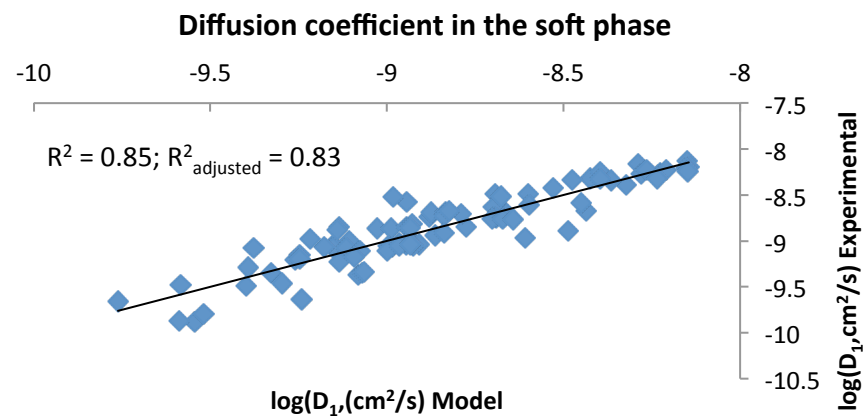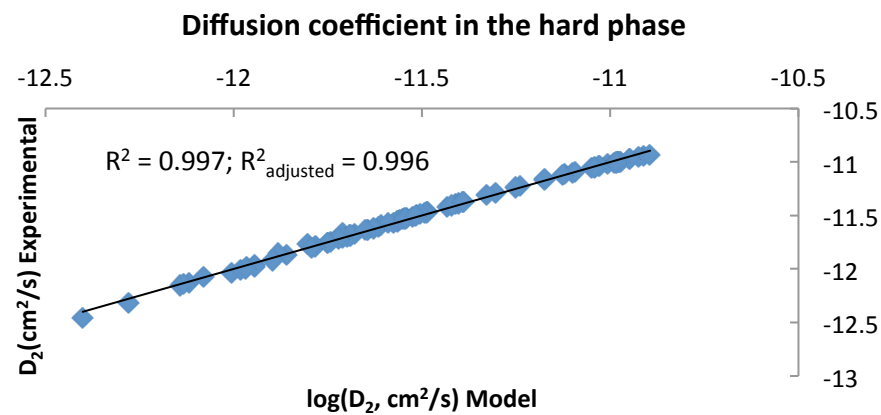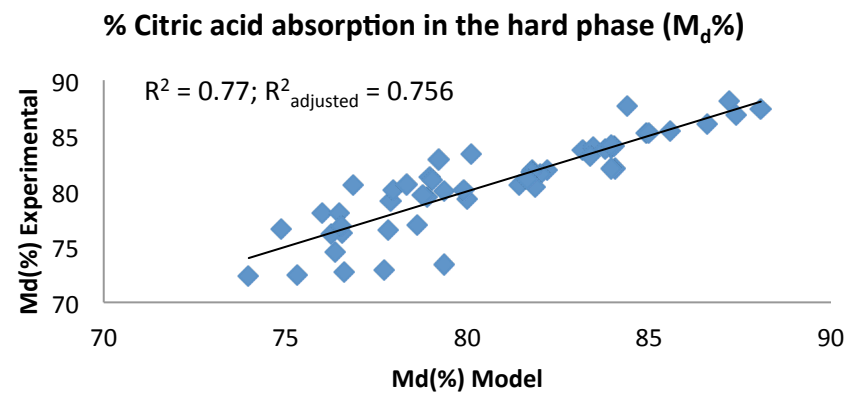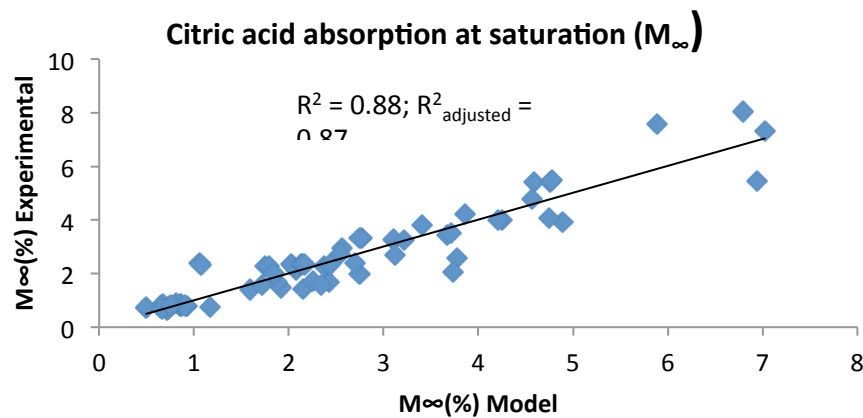
Figure 8. Correlation of experimental and predicted mass transport parameters for citric acid.
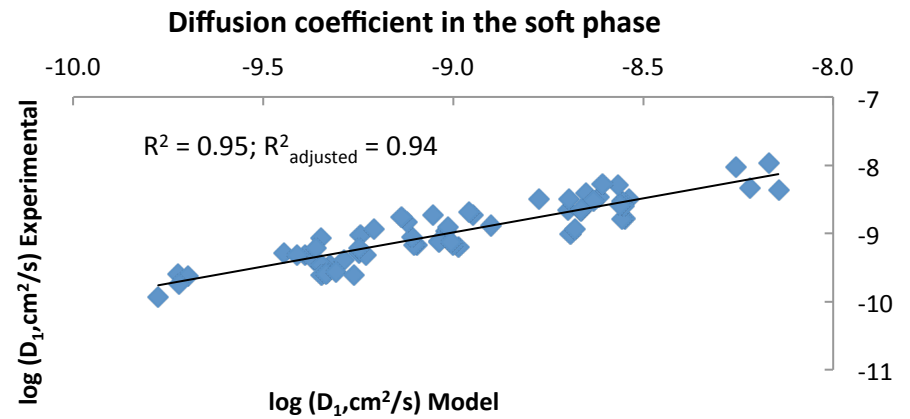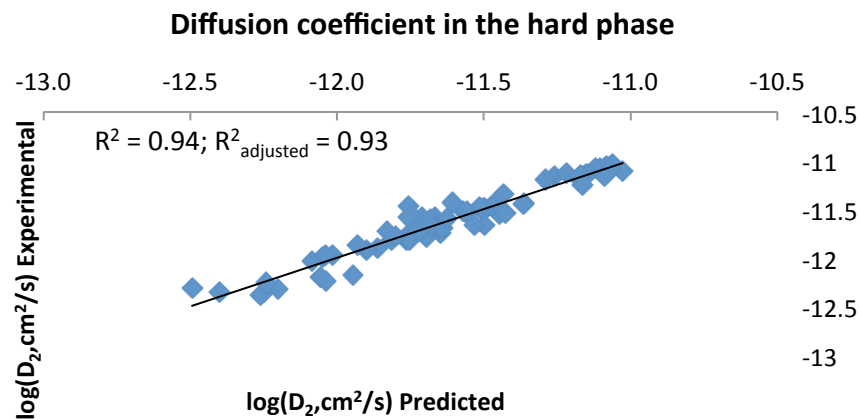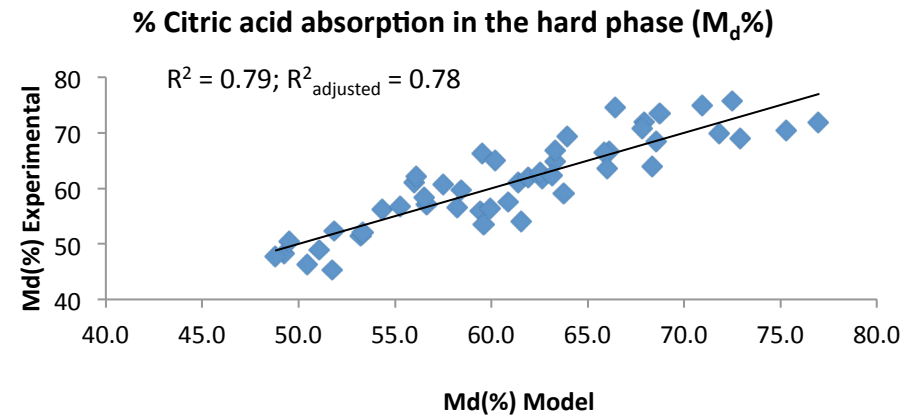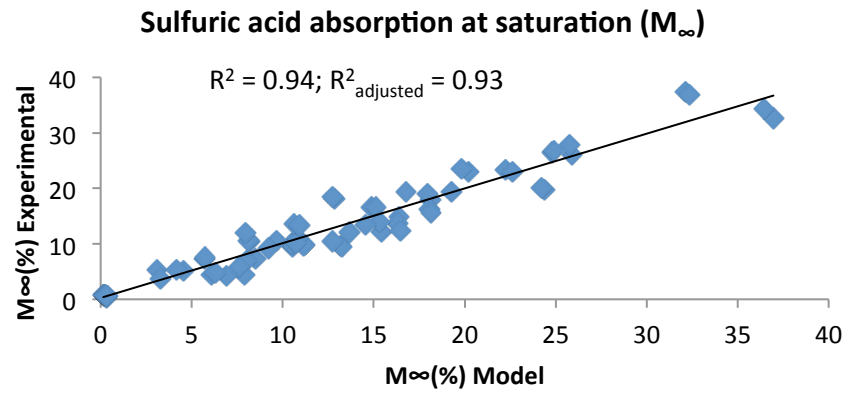
Figure 9. Correlation of experimental and predicted mass transport parameters for sulphuric acid.
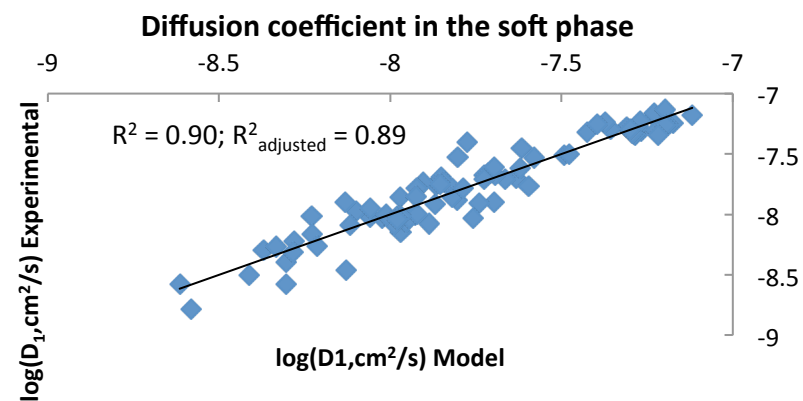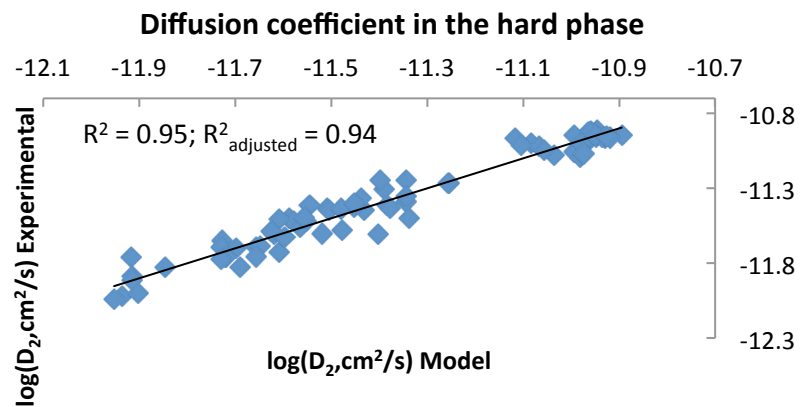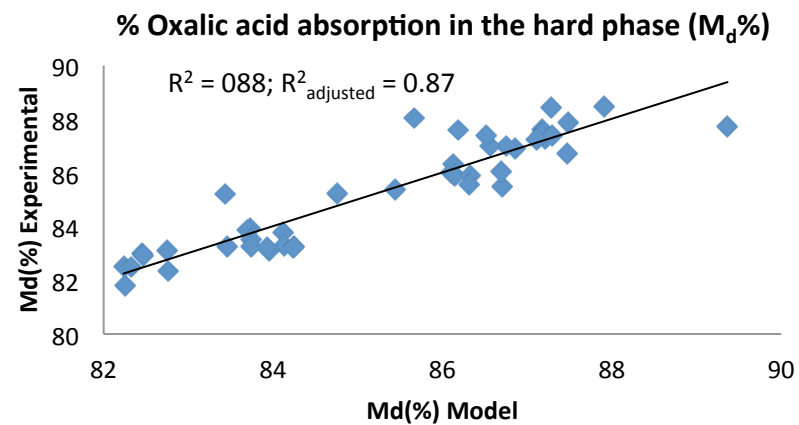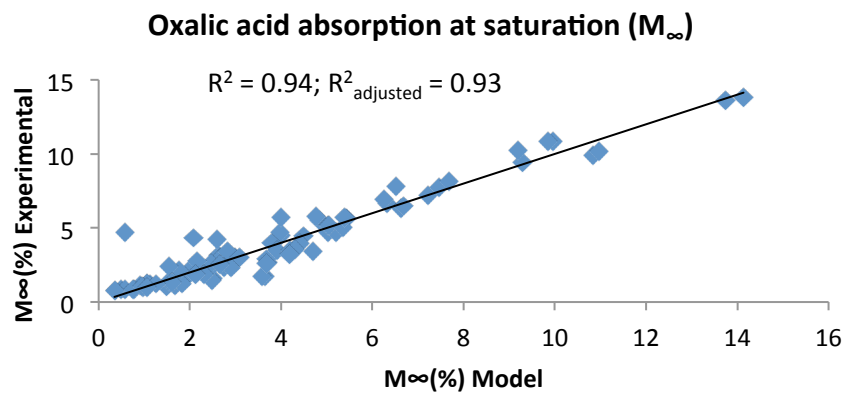
Figure 10. Correlation of experimental and predicted mass transport parameters for oxalic acid.
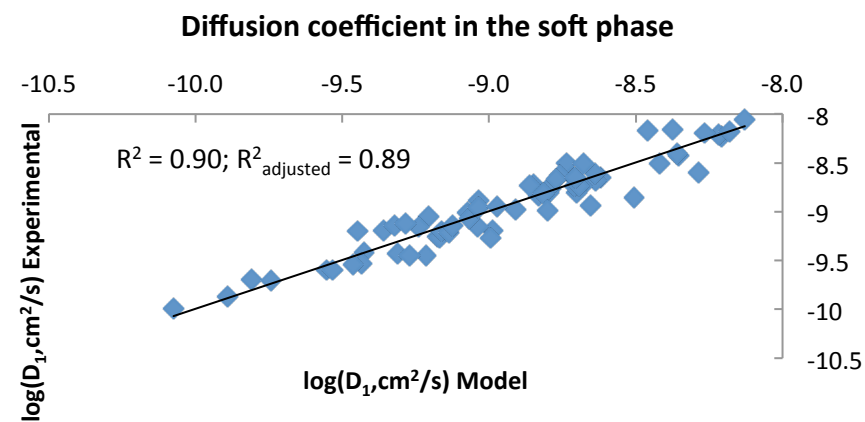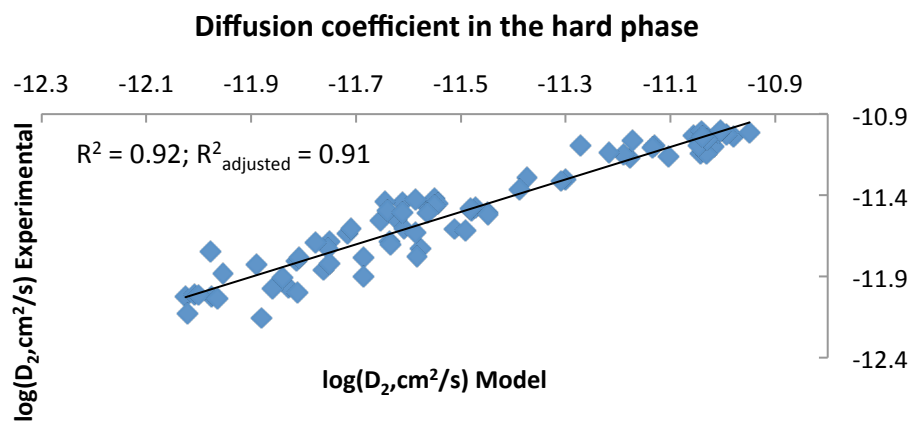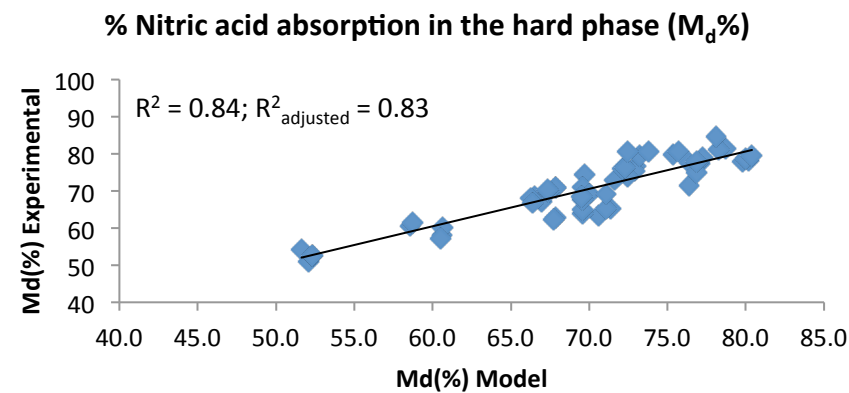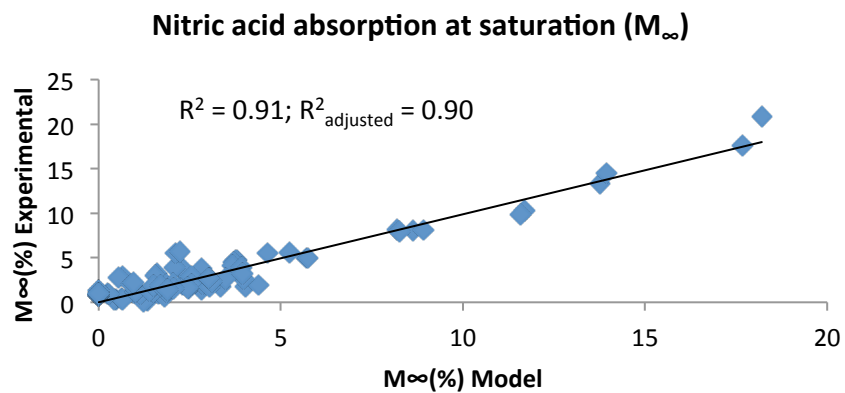
Figure 11. Correlation of experimental and predicted mass transport parameters for nitric acid.

Table 2. Model parameters for citric acid fitted diffusion coefficients and acid absorption

Models	Model Parameters					
	Chemical Properties of Coatings			Physical	Environmental Cond	
	α	β	γ	δ	τ	k
	LOI (%)	D (μm)	Hydrophilicity	t (mm)	Acid Conc %(g/100ml)	
M_∞	0.90	1.87	1.76	-0.63	0.09	1.55×10^{-5}
$M_{d\%}$	-0.01	-0.01	-0.07	0.07	0.01	7.27×10^{1}
D_1	-0.0069	0.0011	0.0021	-0.0757	-0.0137	-10.8
D_2	0.0001	0.0000	-0.0079	-0.0538	0.0001	-12.9

Table 3. Model parameters for sulphuric acid fitted diffusion coefficients and acid absorption

Models	Model Parameters					
	Chemical Properties of Coatings			Physical	Environmental Cond	
	α	β	γ	δ	τ	k
	LOI (%)	D (μm)	Hydrophilicity	t (mm)	Acid Conc %(g/100ml)	
M_∞	0.88	1.61	8.07	-0.30	0.46	9.81×10^{-5}
$M_{d\%}$	-0.05	-0.04	-0.48	0.16	0.07	4.91×10^{1}
D_1	-0.0081	0.0098	0.0296	-0.0755	0.0011	-10.5
D_2	-0.0011	0.0007	-0.0226	-0.0504	-0.0010	-12.9

Table 4. Model parameters for oxalic acid fitted diffusion coefficients and acid absorption

Models	Model Parameters					
	Chemical Properties of Coatings			Physical	Environmental Cond	
	α	β	γ	δ	τ	k
	LOI (%)	D (μm)	Hydrophilicity	t (mm)	Acid Conc %(g/100ml)	
M_∞	0.45	0.22	5.10	-0.60	0.41	8.32×10^{-1}
$M_{d\%}$	0.00	0.00	-0.07	0.00	0.01	8.43×10^{1}
D_1	-0.0009	0.0008	-0.0032	-0.0821	-0.0047	-9.3
D_2	-0.0050	-0.0003	0.0448	-0.0544	-0.0012	-13.2

Table 5. Model parameters for nitric acid fitted diffusion coefficients and acid absorption

Models	Model Parameters					
	Chemical Properties of Coatings			Physical	Environmental Cond	
	α	β	γ	δ	τ	k
	LOI (%)	D (μm)	Hydrophilicity	t (mm)	Acid Conc %(g/100ml)	
M_∞	0.48	0.32	18.05	-0.61	0.53	5.5×10^{-1}
$M_{d\%}$	0.17	-0.02	-0.09	0.04	0.00	3.50×10^{1}
D_1	0.0001	0.0023	0.0056	-0.0758	-0.0245	-10.8
D_2	-0.0020	-0.0007	0.0667	-0.0538	-0.0003	-13.2

4.3 Validation of the Models

A summary of the coating parameters of the various coatings tested in this study are shown in Table 6. Based on Crank's equation (equations 24) and the corresponding empirical models of mass transport parameters (equations 25-28) and the coating properties in Table 6, mass transport behaviours of citric, sulphuric, oxalic and nitric acid could be predicted for these coatings. This provides a tool that could be used to compare the relative performance of protective coatings.

Table 6. Chemical properties of epoxy and epoxy mortar coatings

Coatings	LOI(wt%)	Psize(μm)	Hydrophilicity
Sikadur 31	26.34	350	0.90
Sikadur 41	12.06	350	0.95
Sikagard 63N	65.8	85	0.93
Hychem TL5	71.17	100	0.61
Nitomortar	58.7	200	0.98
Fernco S301	80	1	0.98

Validation of the model was conducted by comparing the experimental uptake of 5% citric acid through various coatings in Figure 12 and 5% sulphuric acid in Figure 14 are compared to the predicted acid profile through the coatings after 527 days in Figure 13 and Figure 15. As shown the permeate absorption at 537 days obtained experimentally are comparable, with greater amount of acid being taken up for example in Sikadur 41 compared to both Sikagard 63N and Hychem TL5. Figure 16 shows the relative permeation of the acids through the coating and as shown these are comparable to the relative rates of permeation observed from

field samples in Figure 14 and 15. Although the actual extent of permeation are not similar, it does show that for example both Sikagard 63N and Hychem demonstrated greater acid resistance compared to Sikadur 41 and this is consistent with the observed acid permeation in Figures 14 and 15.
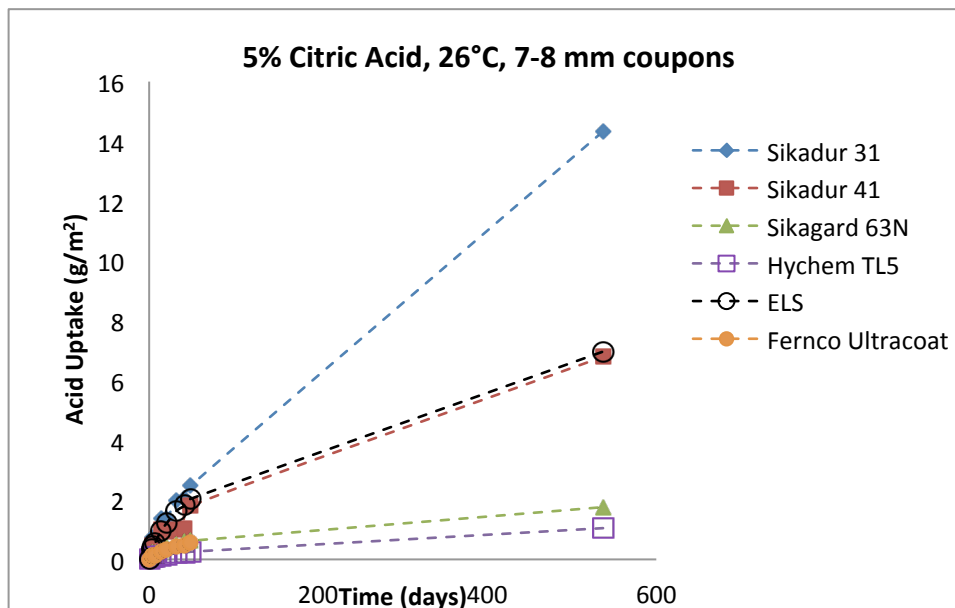

Figure 12. Experimental data comparing the acid uptake of 5% citric acid in Sikadur 31, Sikagard 63N and Hychem TL5 up to 537 days of immersion.
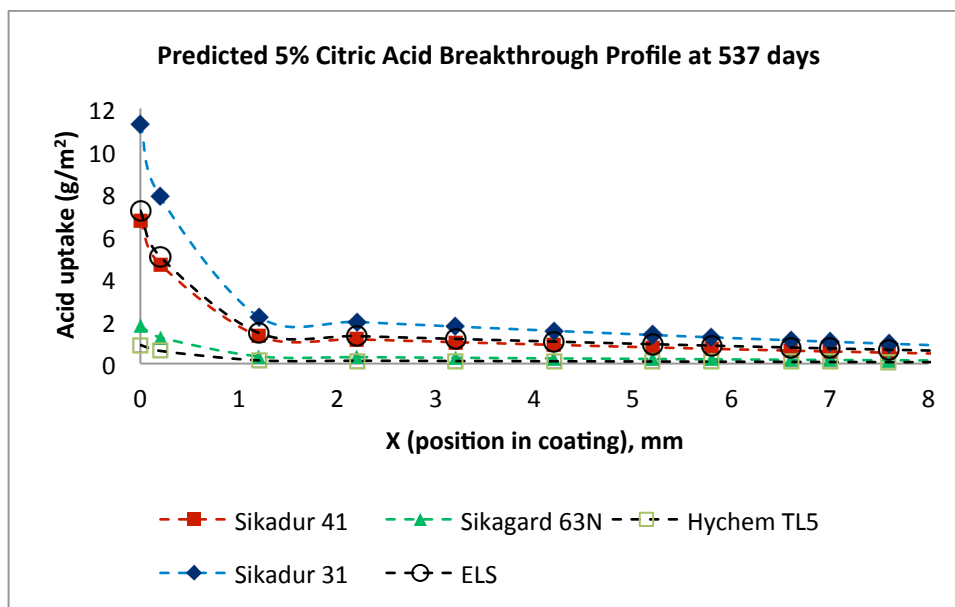

Figure 13. Predicted breakthrough profile of 5% citric acid through Sikadur 31, Sikagard 63N and Hychem TL5 after 537 days.
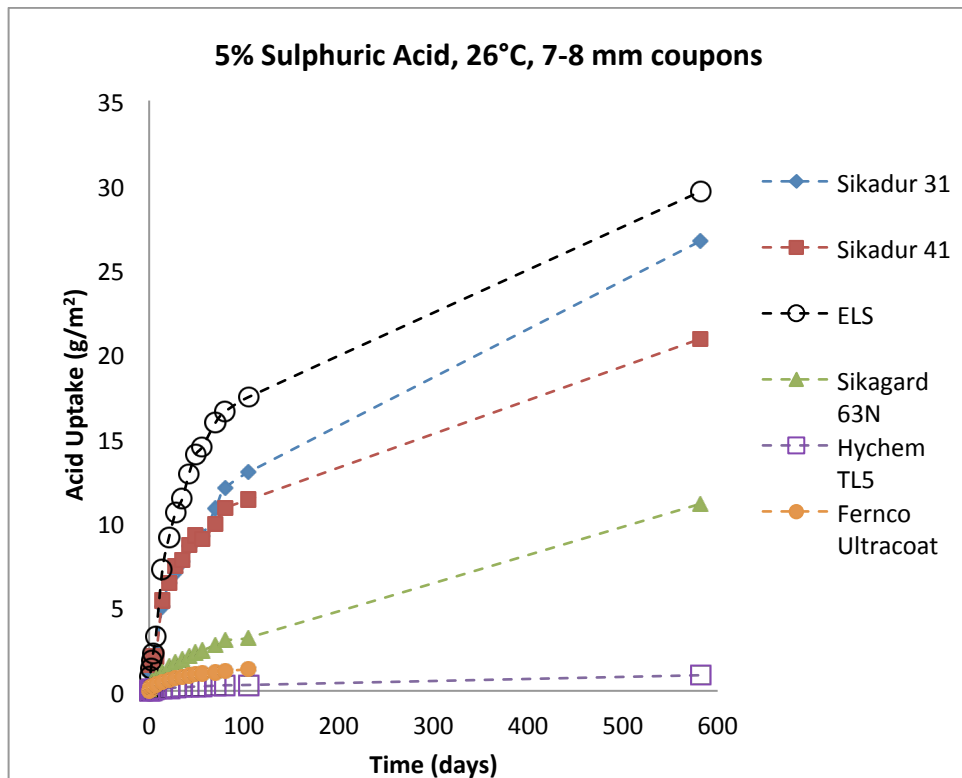
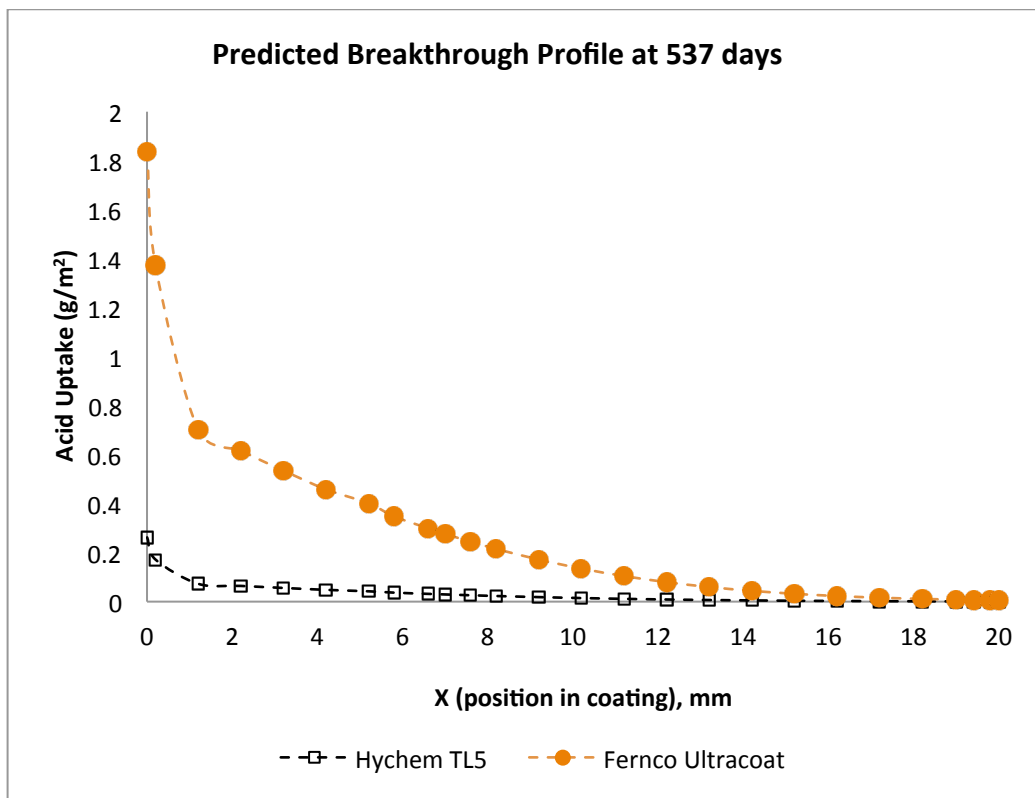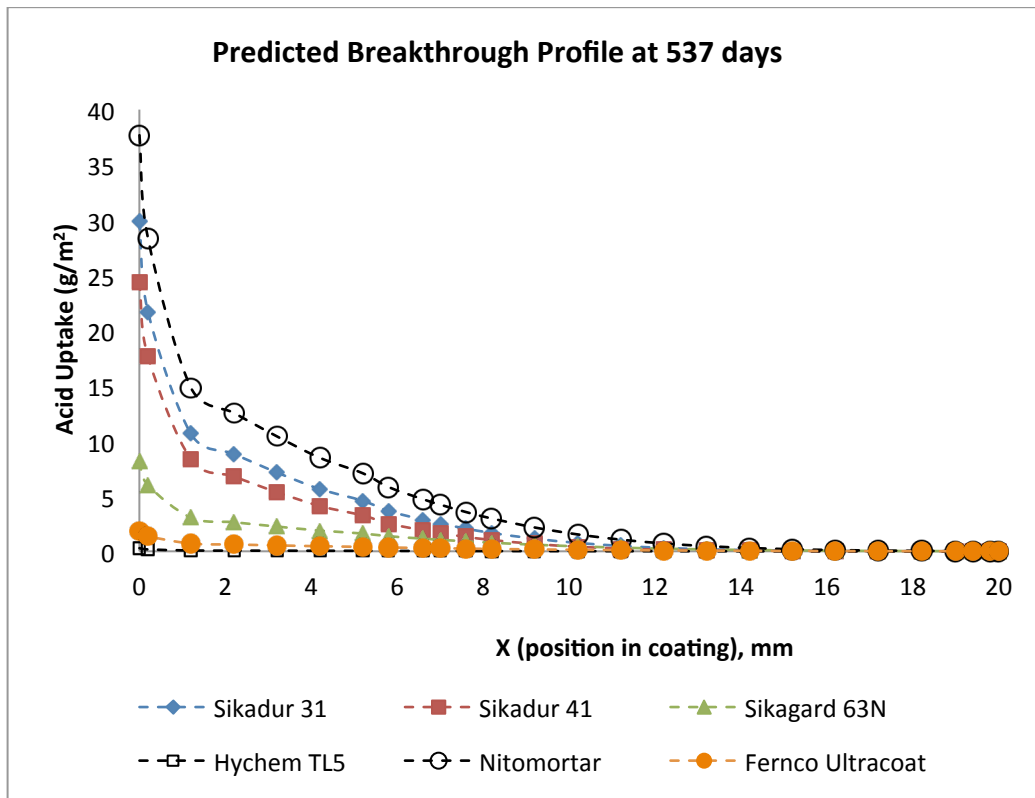Figure 14. Experimental data comparing the acid uptake of 5% sulphuric acid in various epoxy coatings to 537 days of immersion.

Figure 15. Predicted breakthrough profile of sulphuric acid in various epoxy coatings to 537 days of immersion.
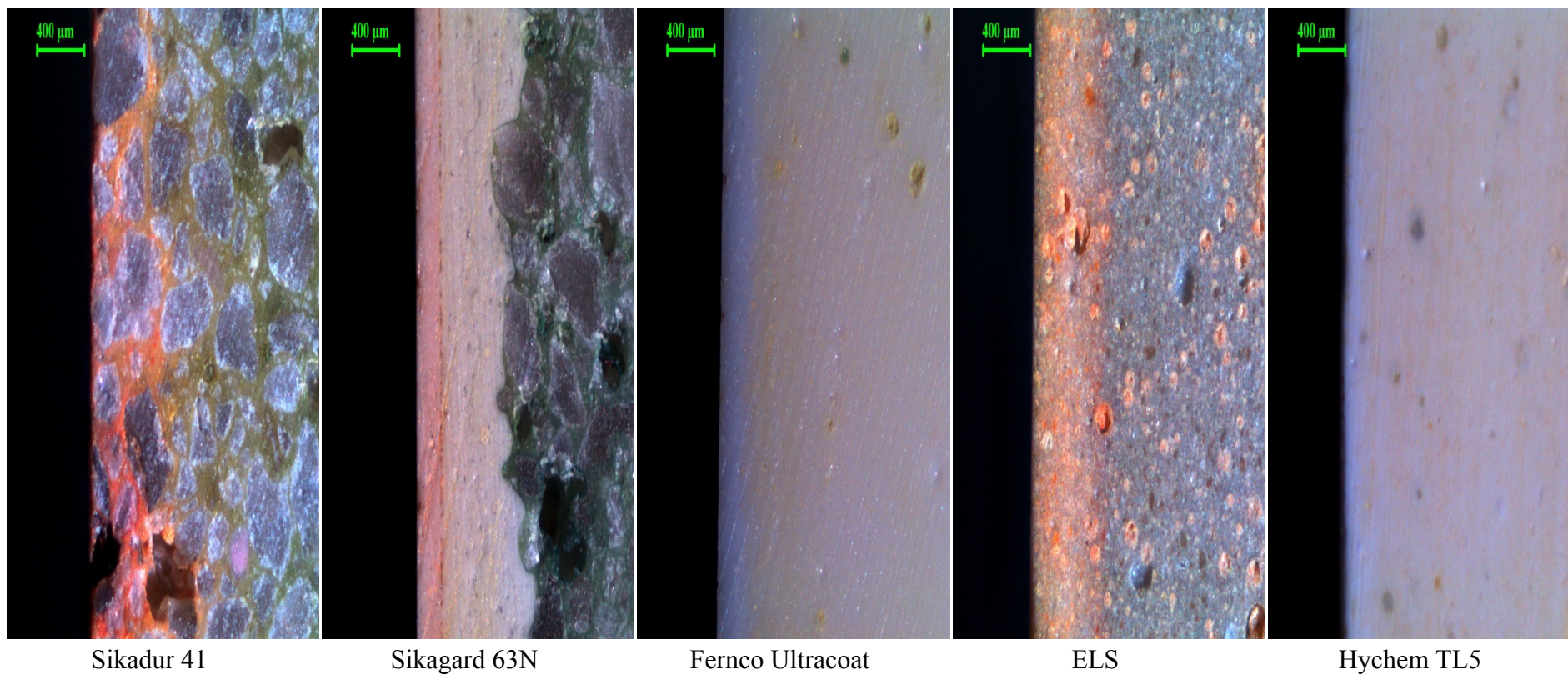
| Sikadur 41 | Sikagard 63N | Fernco Ultracoat | ELS | Hychem TL5 |

Figure 16. Acid permeation through coatings after (537 days ~18 months) in Sydney Water South Barrel.

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