# Evaluation of acid diffusion behaviour of amine-cured epoxy coatings by accelerated permeation testing method and prediction of their service life

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## ARTICLE INFO

## ABSTRACT

Epoxy coatings are used as barriers to protect concrete sewer pipes from the ingress of corrosive biogenic acids. To establish the relative performance of coatings in sewer environments, this study investigated the diffusion and mass transfer of sulphuric acid through two industrial coatings, epoxy F and epoxy Novolac, using accelerated permeation tests. Weight uptake data fitted to Fick's second law and revealed diffusion coefficients of $1.42 \times 10^{-10}$ cm²/s and $1.66 \times 10^{-11}$ cm²/s for 10 wt.% sulphuric acid diffusion in epoxy F and epoxy Novolac, respectively. The results were used as a basis for examining the use of the Crank equation in estimating the service life of the coatings in sewer environments. The Crank equation predicted the depth of acid permeation at specific service life that were within 96–98% of depth measured by elemental sulphur mapping by SEM-EDS. These findings demonstrated the use of accelerated immersion testing and the Crank equation in assessing the performance of coating and in predicting the service life of epoxy coatings.

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## 1. Introduction

Degradation of concrete structures in sewers as a result of micro-organism activity, known as microbiologically induced corrosion (MIC), is an important problem affecting the performance and lifetime of underground wastewater facilities [1–3].

Various micro-organisms that grow under the tidal zone and in the crown and wall surface of sewer pipes are responsible for corrosion of concrete. As a result of the successive growth of organisms in these sites various metabolites are generated. The anaerobic conditions in the tidal zone promote the activity of sulphur reducing bacteria (SRB) for example the genus *Desulfovibrio* and *Desulfobulbus* in converting the sulphate and other sulphur compounds to hydrogen sulphide ($H_2S$). It is well known that other sewer gases including $CO_2$, $NO_2$, and $SO_2$ are also generated. Sewer gases have limited solubility in water and considerable portion of these gases escape to the sewer atmosphere. In the sewer walls and roof, $H_2S$ is converted by sulphur oxidising bacteria (SOB) including *Acidithiobacillus thiooxidans* or as formerly known as *Thiobacillus concretivorus thiooxidans* to sulphuric acid [4]. Whilst $CO_2$, $NO_2$, and $SO_2$ are hydrolysed in humid sewer environment to form weak acids, specifically $H_2CO_3$, $HNO_3$ and $H_2SO_3$ [5]. $H_2S$, $H_2CO_3$, $HNO_3$ and $H_2SO_3$ also play an important role in reducing the concrete pH. Fungi that are present on walls such as *Aspergillus niger*, will also produce various organic acids [3,6]. Among these metabolic acids, however, sulphuric acid is considered to be the most destructive, as this acid is able to dissociate completely and pH values below 1.0 are known to be generated in the sewer. For this study, experiments were performed with sulphuric acid as a test case metabolic acid.

Different types of polymeric coatings have been developed, as a mitigation strategy, to protect concrete surfaces against MIC [7]. Amongst the protective liners used in sewers epoxy based resins and mortars are used commonly. Epoxies are an important class of thermosetting polymers that exhibit high tensile strength, excellent chemical and corrosion resistance, and good dimensional stability. Despite their known corrosion protection properties, epoxy coatings continue to show variable performance in corrosive sewer environments [8–10]. This is attributed to the presence of nano-voids and hydrophilic groups in their polymeric network that has affinity to polar groups such as moisture and biogenic acids [11–13]. Additionally, in harsh environments like sewers, different acids and corroding gases penetrate into the polymer structures contributing to enhanced degradation rates [14]. Understanding the rate of acid diffusion and predicting the acid

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**(a) Bisphenol F**
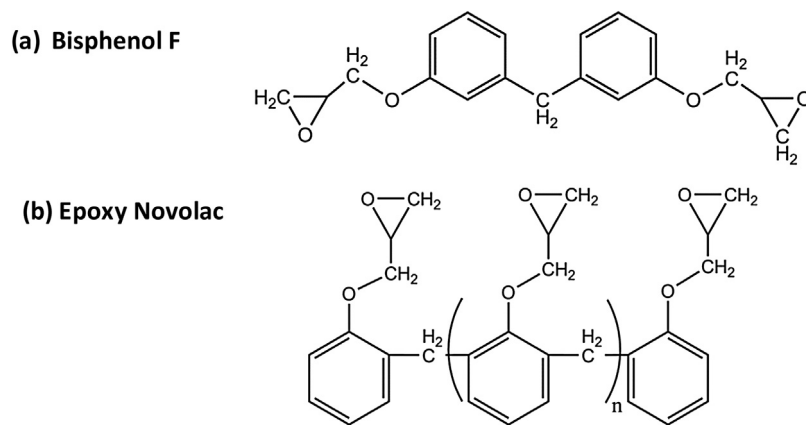
**(b) Epoxy Novolac**

**Fig. 1.** The generalised structure of: (a) epoxy F and (b) epoxy Novolac monomers.

breakthrough time in epoxy coatings is of paramount importance in designing and selection of protective coatings.

The process of solution and gas diffusion into polymers has been investigated by various techniques [15–17]. These studies have led to theoretical definitions and models for describing the diffusion in polymers in different environments [18,19]. These models were developed based on different physical conditions including obstruction effects, hydrodynamic interactions and free volume theory and/or their combinations [20]. It is assumed that Fick's first and the second laws model the steady-state and non-steady state diffusion in polymers, respectively [21]. In other word, if the diffusion rate is slower than the stress relaxation of the polymer structure then it is considered as Fickian diffusion but if the segmental relaxation rate is slower than the diffusion rate then it is considered non-Fickian or anomalous diffusion [23,24]. Shen and Springer [25] study showed moisture permeation into graphite-epoxy composites followed the Fickian diffusion model. Rao et al. [26] found water diffusion into fibre reinforced epoxy composites also fitted the Fickian model. Bonniau and Bunsell [27] investigation showed moisture and water diffusion into three types of glass epoxy composites followed two different diffusion models for each composite. Epoxy with diamine hardener followed a single phase absorption in which water diffused into the epoxy matrix by capillary action. While epoxy with dicyandiamide hardener followed a two phase behaviour indicative of non-Fickian diffusion involving hydrogen bond formation between water and epoxy hydrophilic sites. Current studies have centred on examination of water and moisture transport into polymers, whilst very little study has been conducted on the diffusion and mass transport behaviour of biogenic acids found in sewers into epoxy liners.

For the purpose of developing a method for assessing the performance of industrial coatings in acidic media, the mass transfer behaviour of sulphuric acid into two types of industrial epoxy coatings is investigated in this study.

## 2. Experimental

### 2.1. Materials and sample preparation

The epoxy resins used in this study are two-part commercially available bisphenol-F and epoxy Novolac resins with amine hardener. Fig. 1 illustrates the generalised chemical structure of these resins. Epoxy Novolac has a higher temperature resistance and greater chemical stability compared to epoxy F. However this is achieved at the expense of increased brittleness and reduced toughness and flexibility. The coatings were prepared following the manufacturer's instructions. Appropriate quantities of resin and

hardener were mixed and poured into steel moulds. The epoxy was cured at room temperature for at least 24 h prior to testing. After curing, the epoxy slabs were cut into coupons with dimensions of 50 mm × 50 mm × 5 mm. The extent of curing was confirmed by measuring the hardness of the epoxy using an analog Teclock Durometer GS-702G hardness tester. After curing, epoxy F and epoxy Novolac have hardness of 85 and 80, respectively. These are consistent with reported hardness range of these coatings once cured [28,29].

### 2.2. Immersion test

The dynamic acid sorption measurement was carried out by gravimetric method. In this method rectangular (50 mm × 50 mm × 5 mm) epoxy coupons were immersed in 10 wt.% sulphuric acid at constant temperature of 23 °C. The temperature condition considered for this study was the average of sewer temperatures observed in Australian sewers that vary from 17 °C to 30 °C. At appropriate time intervals, the samples were removed from the acid bath, wiped with paper towel and then weighed on an analytical balance with four decimals accuracy. The acid uptake $M_t$ was calculated according to Eq. (1).

$$M_t (\%) = \frac{w_t - w_d}{w_d} \times 100 \tag{1}$$

where $w_t$ and $w_d$ are the weight of the specimen at time t and the dry weight of the specimen respectively. At specified periods some samples were also removed from the container for destructive characterisations such as SEM-EDS.

### 2.3. SEM analysis

The estimated acid penetration depth predicted by the Crank equation was validated by measurement of the acid penetrated depth in the acid treated specimen. The depth of sulphuric acid penetration was measured by mapping the sulphur (S) element through the cross section of specimen using SEM-EDS. This was carried out using Zeiss EVO-50 Scanning Electron Microscopy (SEM) and Oxford Instruments Aztec integrated EDS system.

## 3. Diffusion model

Moisture uptake with constant diffusivity can generally be modelled with the application of Fick second law of diffusion. This model assumes the penetrant concentration gradient is the driving force for diffusion. Similar assumptions were used in measuring the dif-