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Biogenic acids produced on epoxy linings installed in sewer crown and tidal zones

M. Valix*, K. Shanmugarajah

School of Chemical and Biomolecular Engineering, The University of Sydney, NSW 2006, Australia

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ABSTRACT

In this study the biogenic acids generated by microbes on the surface of Bisphenol A epoxy mortar coupons were investigated for up to 30 months. The epoxy coupons were installed in six sewers in three city locations, Sydney, Melbourne and Perth. Coupons were installed in both the crown and the tidal zones of the sewers to capture the effect of location within the pipe on acid production. The coupons were retrieved approximately every 6 months to provide a dynamic analysis of the biogenic acid production. Our results reveal the colonisation of epoxy mortar by the more aggressive acidophilic bacteria occurred within six months to two years of their installation in the sewer pipes. Biogenic acid generation appear to occur homogeneously from the tidal zone to the crown of the sewer pipes. The reduction in the surface pH of the epoxy lining was supported by the successive growth of microbes beginning with fungi followed be neutrophilic and heterotrophic bacteria and finally by the acidophilic bacteria and the corresponding accumulation of organic and sulphuric acids attributed to these organisms. This study also revealed the potential inhibiting effects on the microbes induced by the accumulation of metabolic products on the epoxy surface. The accumulation of organic acids and H_2S coincided with the growth and metabolism inhibition of fungi and acidophilic bacteria. These results provide insights into the microbial interaction and biogenic acids production that contribute to lining degradation and corrosion of concrete in sewer pipes.

1. Introduction

Microbiologically induced concrete corrosion or MICC is of significant concern worldwide (Okabe et al., 2007). The rehabilitation and replacement of sewer systems is expensive with estimates of the annual cost in the US alone exceeding $31 billion (O'Connell et al., 2010). An earlier estimation provided an annual cost of both water and wastewater asset concrete corrosion in the US at $36 billion (Koch et al., 2002) reflecting the growing escalation of the problem. In addition failure of wastewater collection system lead to health and environmental problems (Davis et al., 1998). MICC results from the metabolism of biogenic acids by microbes that thrive on the sewer wall and crown. The account of the involvement of sulphur oxidising bacteria (SOB), *Acidithiobacillus thiooxidans* or as formerly known as *Thiobacillus thiooxidans*, to concrete corrosion was first reported by Parker (Parker, 1945). Sulphuric acid that is generated by these microbes reacted with the alkaline components of concrete to form ettringite and gypsum, which have little or no hydraulic property and thus no structural integrity (Mehta, 1983). Since then the role of SOB and other microbes in concrete corrosion has been corroborated by other studies (Davis et al., 1998; Islander et al., 1991; Mori et al., 1991; Sand and Bock, 1991).

More recently the cooperative activity of the sewer microbes has been described as the successive growth of organism and their production of various biogenic acid and gases (Islander et al., 1991; Mori et al., 1992; Okabe et al., 2007; Valix et al., 2012). This occurs because organisms have specific pH growth range and pH growth optimum. Acidophiles, such as *A. thiooxidans* and *Acidithiobacillus ferrooxidans*, which oxidise H_2S and sulphur compounds (e.g., S_2O_3 and S) to sulphuric acid, have their growth optimum at pH 0.0 to 5.5 (Hernandez et al., 2002; Okabe et al., 2007); neutrophiles such as *Thiobacillus thioparus*, *Starkeya novella* (formerly *Thiobacillus novellus*), *Halothiobacillus neapolitanus* (formely *Thiobacillus neapolitanus*) and *Thiomonas intermedia* (formerly, *Thiobacillus intermedius*), which promote the conversion of thiosulphate to elemental sulphur grow optimally at pH 5.5 to 8.0 (Islander et al.,

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* Corresponding author.
E-mail address: marjorie.valix@sydney.edu.au (M. Valix).

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1991; Kelly et al., 2000; Kelly and Wood, 2000), and fungi such as *Aspergillus niger*, produces various organic acids, grow at pH 4.0 to 6.0 (Cho and Mori, 1995; Gu et al., 1997; Valix et al., 2012), although acidophilic fungi may also tolerate pH down to 1.6 (Johnson, 1998). Heterotrophic bacteria such as *Mycobacterium* sp. will also generate organic acids optimally within pH of 3.0–6.0 (Cho and Mori, 1995; Davis et al., 1998; Nica et al., 2000; Vincke et al., 2001). Fresh concrete has a pH of approximately 12.0. Each strain of organisms will need to work cooperatively by growing and generating their specific biogenic acids successively to bring down the pH of concrete. Sewer gases including H_2S, CO_2, NH_3, and SO_2 also play an important role in reducing the concrete pH particularly when it is still very alkaline and is less supportive to the growth of corrosion inducing microbes. Ammonia is oxidised to nitrite by *Nitrosomonas* and nitrite is oxidised to nitrate by *Nitrobacter* (Muller et al., 1995). When hydrolysed in humid sewer environments these sewer gases will form both weak and strong acids, specifically H_2CO_3, HNO_2, HNO_3 and H_2SO_3 (Sand, 1997). Because these hydrolysis gases and H_2S originate from the sewage, they will contribute to the corrosion of the crown and walls of concrete sewer pipes regardless of the concrete surface pH and microbe population on its surface. Controlling the corrosive effects of MICC will therefore require an understanding of this successive growth and the metabolism of these microbes. As shown this is quite a complex process and despite the advances provided by molecular methods in assessing the population distribution of MICC (Hernandez et al., 2002; Okabe et al., 2007) we still have limited understanding of the interactions of these microbes.

Various mitigation strategies have been in use around the world to control MICC, which include chemical treatment to reduce the concentration of the dissolved H_2S in wastewater with caustic soda, ferric chloride, ferrous or ferric chloride blends, ferric nitrates, hydrogen peroxides, oxygen injections and sodium nitrates (Redner et al., 2004; Scrivener et al., 1999), the use of acid resistant coatings including polymeric mortars (Redner et al., 2004) and cement lining materials (Scrivener et al., 1999) and spraying with magnesium hydroxide to raise the pH level of concrete (Sydney et al., 1996). These techniques have all showed promise in reducing corrosion. However there are significant challenges in their application, with many of these technologies proving to be costly and with inadequate control in most cases. With coatings, there are two specific technical gaps, these relates to understanding of the microbial system and their interaction with the coating materials and insufficient knowledge in predicting their performance and durability in real sewer environments. Much of the studies devoted in assessing the performance of lining materials have been based on simulated sewer environments that involve using reagent acids (e.g., sulphuric acid) and biochambers (Hewayde et al., 2007; Redner et al., 2004; Valix et al., 2011; Vipulanandan and Liu, 2005). Although these provide insights to the resistance of the coatings to acidic environment, these results are often difficult to translate to actual service life in unique and complex sewer environments. Reported field data are scarce and the results suggest great variability in coating performance and that some currently used coatings are unable to match the service conditions that continue to become more aggressive with time (Nixon, 1997; Parker, 1945).

Efforts to design protective systems for wastewater collection facilities based on lining materials will be ineffective without adequate fundamental understanding of microbial colonisation of coatings. Although significant studies have been carried out on microbial communities in sewers, much of these have focused on microbes that grow only on the surface of concrete (Cho and Mori, 1995; Davis et al., 1998; Gu et al., 1998; Hernandez et al., 2002; Islander et al., 1991; Milde et al., 1983). While the study of microbes colonising lining materials remains scarce (Gu, 2003; Pagaling et al., 2014). In addition, although the microbial analysis may detect the presence and concentration of acid generating microbes, accurate assessment of their corrosive ability will require an analysis of the metabolic acidic products generated. The aim of this study was to examine the microflora and biogenic acidic products that are generated, which contribute to the degradation of protective polymeric lining in sewers. Of specific interest are the effect of environmental conditions and period of service on the nature and concentrations of these acids.

2. Material and methods

2.1. Polymeric coating

Commercially available diglycidyl ether of Bisphenol A epoxy resin cured with cycloaliphatic amine curing agent was used for this study. The epoxy mortar was prepared and cured according to the manufacturer's instruction and coupons of 50 mm × 50 mm x 10 mm were prepared by casting them in molds. The XRF analysis of the composition of the filler and LOI or loss on ignition of the polymeric lining is shown in Table 1.

2.2. Coupon installation and sewer site environmental conditions

Field testing involved the installation of the epoxy coupons in sewers in Sydney, Melbourne and Perth. Two sewers were chosen in each city to reflect the variable corrosive conditions. The sites and their environmental conditions are summarised in Table 2. The Sydney and Melbourne sites represent low H_2S environment and moderate temperatures, whilst Perth sewers represent highly elevated H_2S concentrations with slightly higher temperatures. All humidities were high (>90% RH) with the exception of Perth MS. Coupons were installed both in the crown and tidal zone of each sewer (see Fig. 1) to reflect the potential variability in microbial activity at these two locations. Coupons on the crown reflect largely the microbial activity in the gas phase of the sewer with little or no contact with the sewage. Whilst coupons in the tidal zone, as the term implies, would experience intermittent contact with the sewage flow. The coupons that were installed in the tidal zones would have been subjected to cyclic flooding. Under regular operations, the coupons would be flooded during heavier sewage flow in the morning until midnight. However, with heavy rainfall, the tidal zone would have been constantly flooded. Removal of solid build on the bottom of the pipe as they are cleaned may lower the tidal zone leaving the installed samples above the sewage flow. Based on the flow of sewage through the pipes, the coupons on the tidal zone would have been submerged at 30–40% of the period they were installed. As such it would be anticipated the microbiological activity on the walls and coupons at this location would have been disrupted by removal of microbes and neutralisation of biogenic acids by the alkaline sewage (~pH 7.0–8.0), whilst the supply of potential nutrients were replenished. The effect of cyclic flooding cannot be decoupled, however the installed coupons should capture the cumulative effect on microbiological activity imposed on the sewer wall in the tidal zone. The coupons installed on the roof would have also closely reflected the actual environmental conditions and moisture content experienced by the sewer concrete on the crown. The air flowrates though these sewer are, high from 4 to 6 kL/s and would have maintained a high convective heat transfer through the pipe. The high relative humidity within the sewer environment meant air and dew point temperatures were similar with some sewers experiencing about 0.5–2 °C difference. Condensation on the walls and on the coupons installed in the crown were observed at retrieval supporting the fact that the walls and samples reached temperatures below the dew point of