ABSTRACT

The paper reviews the performance of cementitious materials under conditions of biogenic corrosion of concrete sewer pipes. It draws on data from samples analysed in the laboratory and also installed in an experimental sewer in South Africa, as well as data from sewers in France and work from simulation chambers in Germany. Cementitious materials, including supplementary cementitious materials (SCMs), have been used widely in sewer networks to counter different mechanisms of deterioration, with varying success. However, under certain conditions, sewage that is conveyed through outfall sewers becomes septic and hydrogen sulphide gas is generated and biogenically converted to sulphuric acid, which reacts with the acid-soluble components of concrete causing it to corrode. The concrete sewer pipe materials under review comprise those made with Portland Cement and Calcium Aluminate Cement. Results indicate that the formation of alumina gel, as a product of a chemical reaction between the acid and certain cementitious materials, and densification of the concrete matrix, have a significantly positive impact on the rate of deterioration of concrete sewer pipes. The experimental scope of a related current research project is previewed, focusing on the expected outcomes.

Keywords: concrete sewers, biogenic acid generation, biogenic corrosion, cementitious materials.

1 INTRODUCTION

Concrete sewer pipe deterioration due to biogenic sulphuric acid (H$_2$SO$_4$) attack is not a new problem. As far back as 1918, attempts were made to combat corrosion in a range of sewers in Cairo [1] and since then, researchers have studied the problem of sewer corrosion to establish the mechanisms involved and factors having an effect on the rate of corrosion [2, 3]. Initially, in order to combat microbially induced concrete corrosion (MICC) of sewer pipes, authorities [4] imposed tighter regulations on the nature and toxicity of industrial wastewater that was discharged to sewers and this led to significantly lower levels of biologically toxic metals such as lead, chromium and mercury, and as a result, bacterial levels and MICC increased. This trend prompted further research which subsequently revealed the complexity and the environment of many species of bacteria as well as fungal species involved in MICC [5, 6]. Increase in MICC was also linked to increased sewage temperature, sulphate-containing detergents, and long sewer line lengths to service growing urban populations [7].

Fresh sewage entering a wastewater collection system contains organic sulphur compounds that are capable of being oxidized to sulphates (SO$_4^{2-}$). Initially, aerobic species flourish in a sewer but as oxygen used for catabolizing organic waste in the sewage becomes
depleted, anaerobic species occur, with two types of bacteria being involved in MICC. Firstly, 
there are sulphate reducing bacteria (SRB) in the liquid sewage which reduce $\text{SO}_4^{2-}$ to 
sulphide as an alternative source of oxygen; sulphide exists in the stale sewage as sulphide 
ions ($S^2-$), hydrogen sulphide ions ($\text{HS}^-$), and hydrogen sulphide molecules ($H_2S$) in both the 
aqueous and gaseous states, depending primarily on pH. At pH less than 7, $H_2S$ predominates 
in aqueous solutions, and is readily released into the sewer headspace especially under 
turbulent flow conditions. Secondly, there are sulphide oxidising bacteria (SOB), typically 
on the moist walls of the sewer pipe above the flowing sewage. It therefore follows that 
oxidation of $H_2S$ to $H_2SO_4$ occurs in two ways, through auto-oxidation by a spontaneous 
reaction of $H_2S$ with $O_2$ in an aqueous solution, or biologically due to SOB, namely 
*acidithiobacilli* bacteria, oxidising $H_2S$ to generate energy for assimilation of carbon for 
synthesis of cell materials. The latter process is generally referred to as biogenic acid 
formation. Figure 1 shows these significant sewer characteristics.

![Figure 1: Significant sewer characteristics.](image)

This paper reviews the performance of cementitious materials under conditions of 
biogenic corrosion of concrete sewer pipes. It draws on data from samples analysed in the 
laboratory and also installed in an experimental sewer in South Africa, as well as data from 
sewers in France, and work from simulation chambers in Germany. The data are placed in a 
design context by relating them to expected deterioration rates, and subsequently the 
implications for use of these materials in such aggressive environments are drawn. Further, 
the experimental scope of a related current research project is previewed, focusing on the 
expected outcomes and benefits.

## 2 FUNDAMENTALS OF ACID ATTACK ON CONCRETE SEWERS

### 2.1 Colonization of concrete sewer pipe surfaces by bacteria

Newly cast concrete pipes have a pH of about 12 to 13, which is too high for microbial 
activity to take place. Nonetheless, through the auto-oxidation of $H_2S$ to $H_2SO_4$, and also as 
$CO_2$ dissolves into the condensate film that forms on the walls of the sewer to form various 
forms of carbonic acid ($H_2CO_3$), these acids react with the alkali species in the concrete, 
and over time lower the pH of the concrete surface. In the presence of sufficient oxygen, 
nutrients and moisture, neutrophilic sulphur oxidising microorganisms (NSOM) such as 
*acidithiobacilli thioparus* can colonize the concrete surface once the pH falls to ~9. These
organisms produce H$_2$SO$_4$ through oxidation of the H$_2$S diffusing into the condensate film, which reacts with the concrete lowering the surface pH further, thus facilitating colonization by new bacterial strains adapted for lower pH conditions. When the pH of the concrete falls to ~4, acidophilic sulphur oxidising microorganisms (ASOM) such as acidithiobacilli thiooxidans can begin colonising the concrete surface and continue to oxidise H$_2$S to H$_2$SO$_4$, but can also oxidise thiourea and elemental sulphur that is deposited on the sewer walls after H$_2$S is directly oxidised by O$_2$ that is present in the headspace. These species lower the pH of the concrete surface to values of ~1 \[11\].

2.2 Characteristics of concrete subjected to H$_2$SO$_4$ attack

In Portland Cement (PC) concretes, H$_2$SO$_4$ initially converts the calcium hydroxide (Ca(OH)$_2$) to calcium sulphate (CaSO$_4$) (Equation 1).

\[
\text{Ca(OH)}_2 + \text{H}_2\text{SO}_4 \rightarrow \text{CaSO}_4 + 2\text{H}_2\text{O} \quad (1)
\]

This attack presents two somewhat opposing scenarios. Initially, H$_2$SO$_4$ destroys the polymeric nature of Ca(OH)$_2$ and substitutes a larger molecule into the matrix causing pressure and spalling of the adjacent concrete and aggregate particles, and in another instance, CaSO$_4$ precipitates as gypsum (CaSO$_4$.2H$_2$O), which may bind together the insoluble residue in the gel layer and create a barrier on the concrete surface thus slowing the rate of attack; this means that ultimately, the rate of attack will depend on the ionic diffusion coefficients and the thickness of the gypsum layer \[12\].

Most researchers agree that attack in sewers is mainly caused by H$_2$SO$_4$ produced by S-oxidising bacteria, and that large differences are found between tests involving purely chemical (mineral) H$_2$SO$_4$ and those involving microbially produced H$_2$SO$_4$ \[13\]. Bacteria play a distinctive role, especially their relationship with the concrete substrate which influences their metabolic activity \[14\]. The main products of corrosion when PC concrete is subjected to either mineral or biogenic H$_2$SO$_4$ attack are gypsum (Equation 1) and ettringite (3CaO.Al$_2$O$_3$.3CaSO$_4$.32H$_2$O - Aft) (Equation 2) which is formed by a secondary sulphate attack of aluminate phases by the gypsum.

\[
3\text{CaSO}_4.2\text{H}_2\text{O} + 3\text{CaO}.\text{Al}_2\text{O}_3 + 26\text{H}_2\text{O} \rightarrow 3\text{CaO}.\text{Al}_2\text{O}_3.3\text{CaSO}_4.32\text{H}_2\text{O} \quad (2)
\]

Subsequently, a soft and pulpy layer with an increased porosity forms on the corroded concrete surface. In the case involving mineral H$_2$SO$_4$ attack, this layer constitutes an extra barrier, while in the case of biogenic H$_2$SO$_4$ attack this layer creates excellent conditions for the growth of SOB \[13\].

In Calcium Aluminate Cement (CAC) concretes, the rate of H$_2$SO$_4$ attack is much slower than in PC concretes. The key to CAC’s better performance lies in the nature of the hydrates, particularly alumina hydrates, which are stable down to a pH of ~3. The dissolution of the calcium component of the other hydrates leads to the formation of additional quantities of this phase, which infill pores, thereby protecting the concrete from further attack and generally giving a smoother corroded surface with less aggregate loss (Equation 3).

\[
\text{C}_3\text{AH}_6 + 6\text{H}^+ \rightarrow 3\text{Ca}^{2+} + 2\text{Al(OH)}_3\downarrow + 6\text{H}_2\text{O} \quad (3)
\]

Below a pH of ~3.5, the alumina hydrate dissolves and neutralises more acid as shown in Equation 4; the overall neutralization reaction is shown in Equation 5.

\[
\text{AH}_3 + 6\text{H}^+ \rightarrow 2\text{Al}^{3+} + 6\text{H}_2\text{O} \quad (4)
\]

\[
\text{C}_3\text{AH}_6 + 2\text{AH}_3 + 24\text{H}^+ \rightarrow 3\text{Ca}^{2+} + 6\text{Al}^{3+} + 24\text{H}_2\text{O} \quad (5)
\]

1025
At these lower pH values, there still exists a zone of intermediate pH between that of the surface and of the unaffected core concrete, in which deposition of alumina hydrate provides a barrier to penetration of the acid \(^{[15]}\).

### 3 CEMENTITIOUS MATERIALS STUDIED

#### 3.1 Studies undertaken in South Africa

There was extensive research on sewer corrosion in South Africa by the National Building Research Institute (NBRI) of the Council for Scientific and Industrial Research (CSIR) that culminated in the publication of a book on the subject in 1959 \(^{[16]}\), in which several recommendations were made. The most significant of these recommendations was to pay attention to sewer hydraulics in order to avoid high velocities and turbulence so as to minimize H\(_2\)S release, and to use dolomitic (DOL) aggregate which provides more alkalinity to a concrete matrix thereby contributing to the neutralization of any acid attack. It was felt that facilities were required to allow the monitoring of actual performance of various materials that are used in the manufacture of concrete sewer pipes based on the CSIR recommendations.

For this reason, an experimental sewer section was installed alongside a bypass line in Virginia, the so-called Virginia Experimental Sewer (VES), in the Free State Province, South Africa. This location was proposed due to the nature of the effluent (high in sulphates), the flat terrain necessitating pumping, and the generally mild to warm climate (daily temperatures up to 35°C in summer, occasionally up to 27°C in winter) that results in conditions ideal for S\(^-\) generation and acid attack. Under such conditions, an extremely corrosive H\(_2\)SO\(_4\) environment (pH < 1.0) develops and H\(_2\)S levels in excess of 100 ppm are common \(^{[17]}\).

Three categories of sewer pipe material samples were installed in 1988 and the sewer was commissioned in March 1989. These samples included unprotected cementitious, protected cementitious and high density polyethylene (HDPE) pipes. The unprotected samples consisted of Portland Cement and siliceous aggregate (PC/SIL) concrete, Portland Cement and dolomitic aggregate (PC/DOL) concrete, Calcium Aluminate Cement and siliceous aggregate (CAC/SIL) concrete, and asbestos fibre reinforced cement (FC). The protected samples consisted of PC/SIL with a post-installed HDPE lining and FC coated with epoxy tar, polyurethane and epoxy \(^{[18]}\).

The corrosion rates estimated by taking in-situ measurements on the unprotected pipes after 5 and 12 years, and actual measurements taken on some pipe sections removed from the sewer after 14 years are given in Table 1.

<table>
<thead>
<tr>
<th>Material</th>
<th>Measured solubility*</th>
<th>5 year estimate (mm)</th>
<th>12 year estimate (mm)</th>
<th>14 year measured (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Total Ave./yr.</td>
<td>Total Ave./yr.</td>
<td>Total Ave./yr.</td>
</tr>
<tr>
<td>PC/SIL</td>
<td>0.20</td>
<td>&gt; 30.0  &gt; 6.0</td>
<td>&gt; 64.0  &gt; 6.0</td>
<td>&gt; 105.0  &gt; 7.5</td>
</tr>
<tr>
<td>PC/DOL</td>
<td>0.70</td>
<td>10 – 15  2 – 3</td>
<td>20 – 30  1.7 – 2.5</td>
<td>43  3.1</td>
</tr>
<tr>
<td>CAC/SIL</td>
<td>0.25</td>
<td>5 – 10  1 – 2</td>
<td>10 – 15  0.8 – 1.2</td>
<td>26  1.9</td>
</tr>
<tr>
<td>FC</td>
<td>0.65</td>
<td>10 – 12  2+</td>
<td>20 – 25  1.7 – 2.1</td>
<td>**  **</td>
</tr>
</tbody>
</table>

*Values based on insolubility tests by NBRI \(^{[20]}\)

**Measurements not taken on FC pipes as walls were swollen and soft due to products of corrosion
The corrosion rates estimated at 5 years varied slightly from the 12 year estimates and the 14 year measurements. The most significant finding was that the CAC based concrete performed better than other cementitious materials. From experimental work undertaken after 2000, CAC/DOL concrete was found to be about four times as effective in dealing with biogenic corrosion as the PC/DOL concrete and at least ten times as effective as PC/SIL concrete [21]. This was attributed to the bacteriostatic effect of CAC binders that stifle the growth of bacteria thus reducing acid generation, and the greater alkalinity provided by DOL to the cement matrix that contributes to the neutralization of any acid formed.

3.2 Studies undertaken in France

In situ experiments undertaken within Veolia Water sewers in Arcachon Bay showed better performance of CAC based mortar samples when compared to PC based ones [22]. Cylindrical mortar samples were exposed in two sewer networks; Site 1 had H$_2$S concentration of between 0 and 20 ppm and a temperature range of between 18 and 25°C, while Site 2 had H$_2$S concentration of between 100 and 200 ppm and a temperature range of between 25 and 30°C. Also, in order to measure the pH and detect Adenosine Triphosphate (ATP) as an indicator of microbiological activity in moisture on sample surfaces, a PVC tube was anchored to gather condensate from the samples.

After 4 months of exposure, the surface pH of PC based samples in Site 1 was ~5.5 and no mass loss was recorded, while the pH of PC based samples in Site 2 was ~2 and a mass loss of 1.59% was recorded. For CAC based samples, those installed in Site 1 had a surface pH ~6 with no mass loss, while those installed in Site 2 had a surface pH ~3 and a mass loss of 0.35% was recorded. Quantification of the total DNA extracted after 4 months from the biofilm on the sample surfaces showed that PC based samples were more bioreceptive (10 ng cm$^{-2}$ for Site 1 and 155 ng cm$^{-2}$ for Site 2) than CAC based samples (4 ng cm$^{-2}$ for Site 1 and 48 ng cm$^{-2}$ for Site 2). The analysis of condensed water in the PVC tube showed that the pH levels were ~1. Notably, ATP concentrations from PC based samples (1.1 x 10$^8$ RLU) were much higher than those from CAC based samples (3.8 x 10$^4$ RLU), indicating greater microbial activity on PC based samples.

3.3 Studies undertaken in Germany

Intensive research work on the corrosion of the Hamburg sewer system led to the construction of a totally controlled breeding chamber in which biogenic H$_2$SO$_4$ corrosion was simulated [23]. This test had the major advantage of allowing colonization of bacteria to occur on the surface of concrete samples in conditions as near to reality as possible. The only accelerating factors were the maintenance of an optimal air flow and temperature of 30°C for the bacteria, and the provision of ~ 20 ppm of H$_2$S gas and nutrients in the form of an aerosol spray. At set times between 3 months and 1 year, samples were removed and tested for surface pH and mass loss. The increase in temperature and optimal supply of H$_2$S and nutrients were estimated to accelerate the corrosion rate by at least 16 times. Results showed that the surface pH of PC based samples reduced to ~1 in 6 months, after which mass loss increased rapidly leading to complete destruction of the samples after ~350 days. On the other hand, CAC based samples showed a more rapid decrease in surface pH which tended to stagnate at pH ~3 after ~100 days, and the mass loss of these samples was considerably lower. This pH level coincides with that at which Al(OH)$_3$ increases in solubility and suggests that the entry of aluminium ions into solution inhibits the activity of SOB [13].

Another simulation system built by the Research, Development and Consulting Department of Heidelberger Zement, in which time spans of 3 to 5 months are sufficient to investigate the resistance of several concrete types against biogenic H$_2$SO$_4$ has been used.
The test system has two parts; a growth and a reaction part. In the growth part, a 25 L fermentor, monoculture of *acidithiobacilli thiooxidans* is cultivated at optimal conditions. The reaction part consists of a glass bio-reactor where test specimens are stored, and a warm and humid environment is sustained in this part. After 1 month of testing, it was possible to see the difference in deterioration between CAC and PC mortars. After 5 months of testing CAC based samples showed 3 – 4% mass loss, whereas PC based samples showed 18 – 31% mass loss.

4 DISCUSSION

Reviewed literature indicates that the composition of cementitious materials is the key factor to resistance against biogenic \( \text{H}_2\text{SO}_4 \) attack. This resistance is attributed to two fundamental mechanisms of defence – neutralization capacity of the cementitious material and its ability to stifle growth of SOB. The latter seems to be more critical when the measured solubility recorded in Table 1 is put into perspective. For example, the PC/DOL samples had a higher solubility value when measured in an acid digestion test than CAC/SIL samples, and yet the CAC based samples had a lower average measured corrosion rate of 1.9 mm \( \text{yr}^{-1} \) as compared to PC based samples with an average measured corrosion rate of 3.1 mm \( \text{yr}^{-1} \).

Higher mass loss is related to lower surface pH, particularly when the pH falls below \( \sim 4 \). Initially, the surface pH of CAC based samples reduce at a higher rate than that of PC based samples, but levelled off at \( \sim 3.5 \). Thus the surface pH on cementitious materials is significant as it indicates the rate of microbial activity.

5 SCOPE OF CURRENT EXPERIMENTAL STUDY

The Virginia Experimental Sewer is a ‘live’ laboratory that presents an aggressive \( \text{H}_2\text{SO}_4 \) environment for studying the performance of cementitious materials used in the manufacture of concrete sewer pipes. Since its inception, the experimental section has enabled researchers to better understand the performance of such materials, and the knowledge gained so far can effectively be used to correlate performances of cementitious materials in other ‘live’ environments with the view of upgrading the existing predictive approaches and better understanding the key parameters influencing sewer corrosion.

The main objectives of the current study are; (a) to critically review the existing empirical and numerical models used for sulphide and corrosion prediction in the design of concrete sewer pipes with the view of improving them, taking into account in-situ measurements of parameters in a range of sewer environments in South Africa, (b) to further characterise rates of deterioration of concrete sewer pipe materials and relate these to an understanding of their material properties, (c) to define the distinction between the neutralization capacity of a concrete mixture and its ability to stifle growth of acid-generating bacteria. Ultimately, the output is expected to yield a range of materials factors for a variety of cementitious materials that will be used in the existing models used for corrosion prediction of cementitious sewer pipes.

6 CONCLUSIONS

- The underlying mechanism of biogenic \( \text{H}_2\text{SO}_4 \) attack of cementitious materials is well understood.
- CAC based concretes perform better than PC based concretes when subjected to biogenic \( \text{H}_2\text{SO}_4 \) attack due to their bacteriostatic effect to SOB.
- Opportunities exist to characterise sewer environments with the view of upgrading models used in biogenic corrosion prediction of cementitious sewer pipes.
REFERENCES


