Abstract

The expense of repair and maintenance of private and public sewage systems in Germany runs to about 100 billion US$. This primarily affects concrete pipes and brickwork sewers. Approximately 40 per cent of the damage can be attributed to corrosion by biogenous sulfuric acid attack as a result of long flow periods and insufficient ventilation of waste water. The report deals with investigations into the prediction of concrete corrosion by biogenous sulfuric acid.

For testing of service life in cases of dissolute and expansive chemical attack a very simple easily reproducible comparative simulation method has been developed. The specimens are stored in diluted sulfuric acid for 35 days. After 6 days the specimens are removed from the solution, stored under running water for 24 hours and all loose parts removed in an ultrasonic vessel. This procedure corresponds to the practical conditions of cyclic flooding in combined sewers. After the exposure time the undamaged cross-section, the residual weight, the residual compressive strength and the acid penetration depth are determined.

The ageing progress of the specimens stored in acid is compared with the observed corrosion of concrete pipes in real sewer systems. The result is a very good correlation between the calculation of corrosion by Pomeroy’s equation and the time-accelerated laboratory test involving storage in diluted sulfuric acid. The predicted corrosion after laboratory tests in sulfuric acid at pH value 2 corresponds to the average observed corrosion in a 20-years-old combined sewer.

Keywords: Concrete sewer pipe, time-accelerated test, biogenous sulfuric acid attack, durability, prediction of chemical corrosion
1 Introduction

The historical development of the German sewerage network shows that the majority of sewers are more than 70 years old and have reached the end of their service life. Of the pipe materials used, concrete and stoneware predominate for pipe dimensions of 200 to 1200 mm. Most damage is caused by cracks, defective pipe connections, joint displacements and corrosion. The restoration of the damaged sewerage network, indispensable for ecological as well as economic reasons, is estimated to cost about 100 billion US$. Figure 1 shows some technical data on the German sewerage network (Kaempfer 1998).

Fig. 1: Technical data on the sewer network in Germany
Fig. 1, cont’d: Technical data on the sewer network in Germany

Many sewers show pipe damage on account of
• improper construction
• improper sewage engineering and
• high traffic loads.

In a large number of cases, damage in sewer pipes will actually result in exfiltrations into ground water. It estimated that, due to this damage, 500 million cubic meters of contaminated liquids per year can leak into soil and ground water. This quantity of waste water represents an overall risk for the environment and public health. Damaged sewer systems are one of the main sources of underground contamination with sulfate, chloride and nitrogen compounds.

Approximately 40 per cent of the damage in concrete and brickwork sewers can be attributed to biogenous sulfuric acid attack. The resistance of conventional mortar and concrete using standard mix composition is not sufficient to prevent chemical corrosion in the long flow of waste water (Kaempfer 1998).

2 Sulfide generation and corrosion

Under certain conditions hydrogen sulfide, which occurs particularly in sewerage, is converted into sulfuric acid by the action of sulfur bacteria. As a result, a sulfuric acid concentration of several percent may be reached in a matter of weeks. With regard to the intensity of the acid formation, the temperature and the flow period of waste water are very important factors in the formation of sulfuric acid. As the bacteria which produce sulfuric acid can grow only in the 0.5 to 6.0 pH range, a reduction in surface pH value is essential when cementitious material is attacked. This is facilitated by the presence of CO\(_2\) in the atmosphere of sewerage canals (Meyer 1980).

The term biogenous sulfuric attack is used for processes in sewerage systems where microorganisms form sulfuric acid and cause the cement paste matrix to be attacked until it dissolves. Damage due to biogenous sulfuric acid leads to a scrubbed
concrete surface above the effluent line in part-flow sewer pipes, especially dirty waste water sewers. The typical appearance of a chemically-damaged pipe wall surface is shown in Figure 2.

![Image of chemically-damaged pipe wall](image)

**Fig. 2: Damage by biogenous sulfuric acid attack in sewer pipe atmosphere**

The formation of harmful biogenous sulfuric acid depends on the presence of components in the sewer that contain sulfur. Insufficient ventilation of sewer pipes leads to the accumulation of hydrogen sulfide in the atmosphere on the pipe walls. This is then oxidized into elemental sulfur by the oxygen. The biochemical activities of differing microorganisms of the species *Thiobacillus* lead to the formation of sulfuric acid (Schmidt 1997).

The reduction of sulfate (SO$_4^{2-}$) in the presence of waste organic matter proceeds as follows:

\[
2C + 2H_2O + SO_4^{2-} \xrightarrow{\text{Desulfovibrio}} H_2S + 2HCO_3^-.
\]

Sulfate-reducing bacteria thrive in the slime layer that coats the inner wet pipe wall. Oxygen cannot normally penetrate this layer, leading to the formation of an inert anaerobic zone next to the pipe wall where the sulfides are formed. Hydrogen sulfide in the atmosphere can be oxidized on moist surfaces by bacteria, producing sulfuric acid according to the following reaction (Meyer 1980):

\[
H_2S + O_2 \xrightarrow{\text{Thiobacillus thiooxidans}} H_2SO_4.
\]

This can lower the pH value on the surface to 1.0 or even lower and can cause a very strong acid attack. The corrosion rate of the sewer pipe wall is determined by the rate of sulfuric acid generation and the properties of the cementitious materials.
Fig. 3: Sulfide generation and corrosion in domestic and industrial waste water systems

The rate of corrosion of concrete pipes depends on the strength and density of concrete, the degree of acid penetration, the acid value and the circulation of hydrogen sulfide in the atmosphere. An important influence on the rate of corrosion is exerted by the geometry of the pipes and the filling capacity. The theoretical corrosion prediction equation - CR corrosion rate - by Pomeroy (1977) is given by

$$CR = 11.4 \cdot k \cdot \varnothing_{sw} \cdot (1/a)$$

where

11.4 = empirical factor

C = average rate of corrosion of concrete by acid (mm per year)

k = coefficient for acid reaction, accounting for estimated fraction of acid remaining on wall

0.8 for $S$ (increase of sulfide concentration) $\leq$ 1.0

0.7 for $1.0 \leq S \leq 5.0$
0.6 for \( S > 5.0 \)
\( \varnothing_{sw} = \) flux of hydrogen sulfide to pipe wall (g/m² * h)
\( a = \) coefficient for alkalinity of concrete, normally 0.16.

The CR corrosion rate can be simplified and formulated as:

\[
CR = 0.4 * S_1 \quad \text{for part-flow pipes with capacity < 10 \% and} \tag{2}
\]
\[
CR = 1.0 * S_1 \quad \text{for part-flow pipes with capacity 10\ldots50 \%.} \tag{3}
\]

Corrosion is a function of exposed perimeter, surface width of stream, velocity, and dissolved sulfide. From the corrosion rate the so-called critical sewer length \( L_c \) can be calculated as follows, from Pomeroy (1977)

\[
L_c = 3.6 * v * t_c \tag{4}
\]

where
\( L_c = \) critical sewer length (m)
3.6 = empirical factor
\( v = \) velocity of waste water (m/s)
\( t_c = \) flow period (s).

The rate of corrosion of concrete pipes has been expressed by Thistlethwayte (1972) using the theoretical equation

\[
CR = 19.9 * 10^6 \frac{K_{sa} * p_{H_2S} * A_{sa}}{z * \rho * A_{aw}} \tag{5}
\]

where
\( K_{sa} = \) rate of absorption of H₂S on pipe wall (kg/m² * h)
\( p_{H_2S} = \) partial pressure of H₂S (ppm)
\( A_{sa} = \) ratio of surface width of waste stream to exposed perimeter of pipe wall above water surface (m²/m)
\( z = \) of cement content of concrete (kg/m³)
\( \rho = \) density of concrete (kg/m³)
\( A_{aw} = \) exposed perimeter of pipe wall above water surface (m²/m).

Using the equations 1 and 4, the hydraulic and sulfide data of a number of examples were used to calculate the predicted corrosion and the critical sewer length in Table 1.
Table 1: Calculation of predicted corrosion rates for different sewer conditions

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Sewer Condition</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rate of flow (l/s)</td>
<td>I</td>
</tr>
<tr>
<td>Part-flow capacity (%)</td>
<td>≤ 10</td>
</tr>
<tr>
<td>Velocity of waste water (m/s)</td>
<td>0.50</td>
</tr>
<tr>
<td>Rate of corrosion (mm/year)</td>
<td>0.72</td>
</tr>
<tr>
<td>Critical sewer length (km)</td>
<td>1.5</td>
</tr>
</tbody>
</table>

The calculation based on the values established by Pomeroy (1977) allow an exact prediction to be made for the expected level of biogenous sulfuric acid attack in sewers. The examples clearly shows that concrete pipes do not only need to be protected against acid corrosion when exposed to extreme conditions.

3 Time-accelerated laboratory tests

To simulate resistance to biogenous sulfuric acid attack, a very simple test procedure has been developed that provides an authentic demonstration of how sulfuric acid attacks in dirty and combined waste water systems. In these tests waterlogged specimens are weighed and stored in plastic containers. Each container is filled with diluted sulfuric acid (pH value 1, 2 or 4.5). The pH value of the acid bath is kept constant over 35 days. This test procedure is suitable for a decision on service life under various working conditions. Figure 4 illustrates the test equipment for the acid storage of concrete specimens.

After 6, 13, 20, 27 and 34 days the specimens are removed from the solution, then stored under running water, vigorously brushed off and all loose parts removed. After this the specimens are weighed and stored, following the same procedure. This operation corresponds to practical conditions of cyclic flooding in combined waste water sewers after downpours. The acid is circulated permanently. In order to keep the pH value constant, concentrated acid is added. The acid bath is restored after each storage cycle.
4 Correlation between predicted and observed corrosion

It is a well-known fact that corrosion in the crown of pipes may be up to 80 %
greater than the average in exposed pipe wall areas. Use of the Pomeroy equations for
the prediction of generating corrosion proves a helpful tool in the design of sewers. 
The predicted corrosion using Pomeroy’s equations and carrying out time-accelerated
tests in diluted sulfuric acid is compared with the observed corrosion in real concrete
sewers. This is illustrated in Table 2.

Table 2: Comparison of predicted corrosion with observed corrosion

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Type of corrosion</th>
<th>I</th>
<th>II</th>
<th>III</th>
<th>IV</th>
</tr>
</thead>
<tbody>
<tr>
<td>Residual weight (%)</td>
<td></td>
<td>-</td>
<td>94</td>
<td>84</td>
<td>95</td>
</tr>
<tr>
<td>Undamaged cross-section (%)</td>
<td></td>
<td>86</td>
<td>85</td>
<td>74</td>
<td>88</td>
</tr>
<tr>
<td>Residual compressive strength (%)</td>
<td></td>
<td>86</td>
<td>84</td>
<td>72</td>
<td>81</td>
</tr>
<tr>
<td>Acid penetration depth (%)</td>
<td></td>
<td>14</td>
<td>12</td>
<td>19</td>
<td>10</td>
</tr>
</tbody>
</table>

I - Calculation of predicted corrosion using Pomeroy’s equation
II - Corrosion after 35 days storage in diluted sulfuric acid pH 2
III - Corrosion after 35 days storage in diluted sulfuric acid pH 1
IV - Observed corrosion in sewer

For laboratory tests, different concrete samples taken from the whole perimeter
of the wall were removed by coring and then measured. After removal of the soft surface layer, some of them were stored in diluted sulfuric acid to determine the corrosion in time-accelerated laboratory tests. All specimens were tested for residual weight, undamaged cross-section, residual compressive strength and acid penetration depth.

The sewer under investigation is located in the central part of Germany. The sewer conveys both domestic and industrial waste water. The trunk is 8.8 km long. Of this, 2.8 km is unreinforced concrete pipe, 1.200 mm in diameter. The original wall thickness was 120 mm. The trunk was put into operation in 1976. Visible corrosion occurs in the upstream sections of pipe, especially at the springline. However, the measurable corrosion at the crown is usually greater than the average corrosion of the pipe.

The trunk was designed and constructed with a compressive concrete strength of 35 N/mm², and made of ordinary Portland cement type CEM I 32.5R. The cement content was 340 kg/m³ and the water-cement ratio 0.40. In order to reduce the cement content, fly ash was added.

The total flow period of waste water through the trunk amounts to 10.5 hours. The part-flow capacity alternates between 10% and 30%. After downpours the sewer is full-flow. The concentration of hydrogen sulfide in the atmosphere was measured at 1.6...2.8 ppm. The pH value of the thin wet film on the pipe wall surface averaged 3.5.

5 Conclusions

Biogenous sulfuric acid corrosion is one type of corrosion in sewerage systems. Chemical attack on the pipe wall surface takes place above the effluent line. The corrosion in the crown of pipes may be greater than the average for exposed areas. Values of more than 1.0 mg/l for total sulfide content in waste water and of more than 0.5 ppm for hydrogen sulfide concentration in the sewer atmosphere point to the possibility of high-level chemical attack. The generation of biogenous sulfuric acid depends on pipe diameter, sewer length, pipe gradient, pipe ventilation, turbulence and other aspects of construction.

Due to the fact that sewers worldwide are increasing in size and that flow distances and periods are getting longer, the necessity of monitoring biogenous sulfuric acid corrosion is becoming more urgent. Sewers are large-scale investments with a planned service life of at least 80 years. Special consideration must be given to problems of sulfuric acid corrosion.

Investigations by Parker (1951), Pomeroy (1977), Thwistlethwayte (1972), Bielecki (1987) and others have led to the establishment of equations for predicting corrosion of sewers and critical sewer length. Although the general rate of corrosion can vary considerably, it is possible to predict corrosion by using both theoretical equations and time-accelerated laboratory tests. For an exact prediction of service life, the main parameters of waste water quality, pipe atmosphere and concrete specifications must be available.

The observed corrosion of a 22-years-old unreinforced concrete pipe was simi-
lar to the average predicted corrosion using Pomeroy’s equation. The laboratory simulation tests provide a useful tool for determining the service life of mortar and concrete in sewer atmospheres. The designers can provide a protective concrete cover over the reinforcement steel.

The very simple time-accelerated laboratory tests of storage in diluted sulfuric acid give results which can easily reproduced. Extensive laboratory tests showed that storage in diluted sulfuric acid for 35 days with 5 cycles corresponds to real-time stresses in ordinary combined sewers of about 20 years.

6 References


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