Waste water applications: corrosion due to biogenic sulphides and other aggressive waters

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Abstract

Corrosion in sewer systems is a main cause of damage and shortening of the effective life-time of pipes. Several materials are vulnerable to biogenic sulphides. This damage can happen on various places within a sewer system. These places can easily be identified and in most cases the damage can be rehabilitated with application of plastic pipe materials.
The chemical resistance of plastic pipes has been tested for most chemical substances. Test methods are standardized in ISO 4433 (Thermoplastics pipes – Resistance to chemicals – classification). Test results are given in ISO/TR 10358 (Plastics pipe and fittings – Combined chemical-resistance classification table).
The phenomena of biogenic sulphide corrosion is explained. The risks are determined and the places where this will occur identified. The rehabilitation of this damage is often done by the use of plastic materials.

A lot of investigations has been done, but most of them not from the perspective of asset management. One can ask the question if, with the knowledge we already have now, investment in more research is cost effective in relation to a good design, adequate preventive actions and rehabilitation with good materials.

Key Words

Corrosion, biogenic sulphides, sewers, asset management, corrosion investigation, corrosion control, concrete corrosion, plastics, sewer rehabilitation

Introduction

The phenomena of biogenic sulphides in concrete sewer systems from septic sewage and the effect on materials is since the description of the mechanism by Parker (1945, 1951) extensively investigated. Since that time a lot of research has been done on the basis of a stochastic approach resulting in empirical quantitative models (Pomeroy, Boon & Lister, Thisthlewayte, Bielecki & Schremmer, etc.). Some more recent research has resulted in modelling partly on the basis of a more detailed numerical description of the underlying microbiological processes and partly by using empirical investigation results of detailed research on aspects of these processes (Vollertsen et al., Hvitveld & Jacobsen, Vincke, Wells et al,).The basic mechanism of the corrosion process is fairly well understood. However some basic key factor

related to in-sewer processes needs more understanding (Vincke, 2006; Wells, et al; 2012).
This article focuses on sewer systems, mainly operation under gravity. Clay-pipe materials and plastic pipes systems are not effected by biogenic sulphides. Cast iron, steel (Mohebbi, 2011) and concrete materials in sewers systems are effected by this type of corrosion, in all cases resulting in deterioration and at the end loss of structural stability. The focus lies in this article on concrete materials because of the vulnerability of this material for this type of corrosion.

Situations with corrosion can easily be localized. Knowing this it is possible to prevent corrosion in the design stage of a sewer system. Measurements in the design stage consists out of lay-out of the systems and the choice of alternative materials. In cases of rehabilitation mostly renovation techniques with plastic materials are used.

The first part of this article describes the process of microbiological sulphide corrosion and the state of the art of the research. It gives an overview of the locations where this type of corrosion can be localized and data to recognize and analyze the process in practise. The second part deals with corrosion prevention and rehabilitation of corroded sewers.

Corrosion process

Sources of sulphide can be autogenic, allogeneic, or exogenous. In the first case the sulphides are generated within the pipe itself, in the second case the initial source is external but the process is continued in the pipe e.g. generation of H_2S in a pressure pipe and emission and corrosion in a gravity sewer. In the third case there is an external input e.g. discharge of industrial wastewater in a sewer directly causing corrosion. In general H_2S is not only causing corrosion but can lead to severe odor problems. There is a direct causality between odor and corrosion.
Corrosion due to biogenic sulphides is a process in 3 steps.

Step 1: Conversion of sulfate SO_4^{2-} to hydrogen sulfide H_2S.
In this step sulphides are formed under anaerobic circumstances form reduction of sulphates by bacteria in bio films in the slime layer on the pipe wall, deposits on the bottom of the pipe or directly in the bulk water. The formation of bio films on the slime layers depends on the composition of the sewage (BOD), the hydraulic conditions in the flow mainly the shear stress.
On the basis of existing literature it is suggested that sulphide build-up could not occur with dissolved oxygen levels greater than 0.1 - 0.5 $mg.l^{-1}$ (Hvitveld-Jacobsen). The processes in the sewage includes cycles of carbon, nitrogen and sulphur.

Dissolved oxygen is depleted as bacteria begin the catabolism of organic material:

$$SO_4^{2-} + organic\ carbon \rightarrow HCO_3^- + H_2S$$

In the absence of dissolved oxygen and nitrates, sulfates are reduced by sulfate reducing bacteria (SRB) to hydrogen sulfide as an alternative source of oxygen for catabolizing organic waste. The bacteria are identified primarily from the obligate anaerobic species *Desulfovibrio.* The bacteria that reduces the sulphates (anaerobic circumstances are characterised by low redox potentials where sulphate functions as electron acceptor) are of the type *Desulfovibrio desulfuricans.* The sulphate reducing

process can start after 0,5 – 1,0 hour of detention time of the water in the full pipe (Wells et al, 2012).
Depending on the pH, the sulphides are dissociated in the form of the ion HS^- , S^{2-} or as the gas H_2S. At a pH of 7.0 50% of the sulphides is in the form of the gas H_2S. If the sewers or pressure mains are running full, the gas will not be emitted and stay in the bulk of the water.

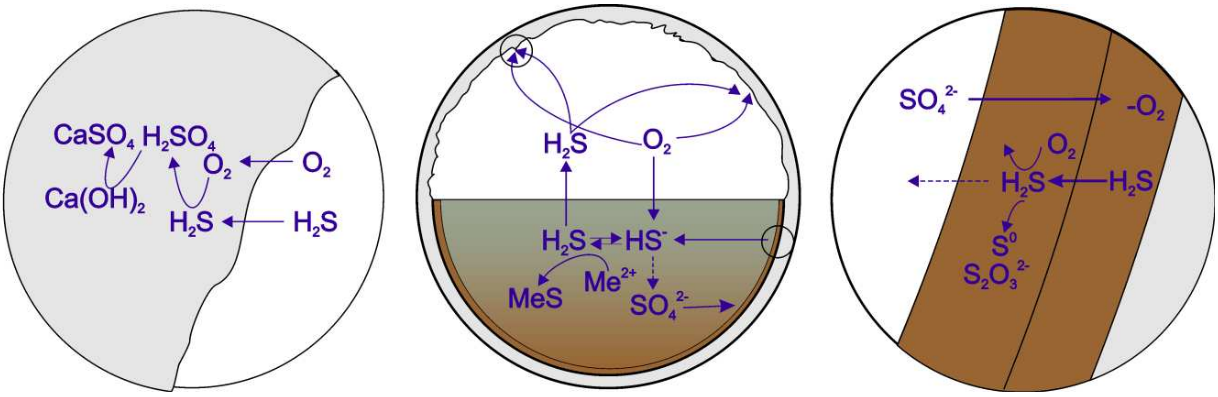

Figure: Reaction pathways for sulphur in sewers (from: H. Jensen 2009).

The sources of the sulphate in the sewage is drinking water (groundwater), industrial waste water or proteins. Normally the amount of sulphate is not a limiting factor in the production of sulphides. In drinking water a maximum value of 250 mg/l sulphate is allowed (see EC Directive 1998/83/EC), what can lead to ca. 85 mg/l sulphides. About 5 mg/l comes from proteins.
In stagnant water production of sulphides will also take place in the bulk of the water. The production rate varies and will stop within a few days because of running out of sulphates.

Step 2: Transfer of hydrogen sulphide (H_2S) to the sewer air
In the second step the H_2S gas diffuses into the air above the level of the wastewater. The flux to the air depends on the equilibrium with the partial pressure of the gas above the liquid according to Henry's Law. This is influenced by temperature and the (limited) solubility of H_2S in water. In a parallel reverse process the water is re-aerated with oxygen from the sewer atmosphere. This reduces the emission: in practise only 2 – 10 % of the equilibrium concentration will enter the air above the water. The flux also depends on the turbulence of the water. Turbulence increases the surface contact between water and air.
Hvitved-Jacobsen (2002) suggests that sulphide concentrations in sewage of 0.5, 0.5-2 en > 2 mg H_2S./l are an indication for respectively low, average and substantially risks of problems related to H_2S. Bielecki (1987) gives related to corrosion problems for gravity sewers a critical value at 1.0 mg/l (total S).

Step 3:. Conversion of hydrogen sulphide to sulphuric acid H_2SO_4
In the third step moisture evaporated from the sewage may condense on unsubmerged walls of sewers, and is likely to hang in partially formed droplets from the crown of the sewer. As a portion of the hydrogen sulphide gas and oxygen gas from the air above the sewage dissolves into these stationary droplets, they become a habitat for sulphur oxidizing bacteria, of the genus *Acidithiobacillus*. Colonies of

these aerobic bacteria metabolize the hydrogen sulphide gas to sulphuric acid (see box) On the pipe wall in the presence of oxygen, aerobic bacteria like *Acidithiobacillus thiooxidans*, *Thiobacillus thioparus*, and *Thiobacillus concretivorus*, all three widely present in the environment, are the common corrosion-causing the factors resulting in biogenic sulphide corrosion.

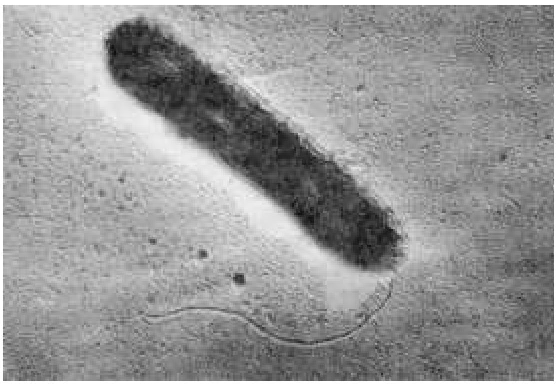

Figure: Thiobacillus concretivorus; size 1.10^{-3} mm

Fresh concrete may have a pH of 11 – 13. This high alkalinity is neutralised without involvement of bacteria by weak acids from CO_2 present in the sewer atmosphere, entering in condensed moisture on the pipe wall and intruding in pores of the structure causing carbonation and a decrease of the pH (Wells, 2012) :

$$Ca(OH)_2 + CO_2 \rightarrow CaCO_3 + H_2O$$

$$2CO_2 + Ca(OH)_2 \rightarrow Ca(HCO_3)_2$$

At a pH of 9 neutrophillic bacteria and fungi begin to grow on the pipe wall causing weak acids further lowering the pH. At a pH of 4 acid loving bacteria begin to grow producing sulphuric acid. From fresh concrete to this stage may last for more than 3 – 6 months (Wells, 2012).
The sulphuric acid converts the calcium in the concrete to calcium sulphate (eq. 1, 2, 3). This is subsequently hydrated to form gypsum ($CaSO_4 \cdot 2H_2O$). This the appears on the surface of concrete pipes in the form of a white, mushy substance with no cohesive properties. In the continuing attack, the gypsum reacts with the calcium aluminate hydrate in the cement to form ettringite (eq. 4), an expansive molecule causing pressure and spalling of the adjacent concrete and aggregate particles.

$$H_2SO_4 + CaOSiO_2.2H_2O \rightarrow CaSO_4 + Si(OH)_4 + H_2O \quad (1)$$

$$H_2SO_4 + CaCO_3 \rightarrow CaSO_4 + H_2CO_3 \quad (2)$$

$$H_2SO_4 + Ca(OH)_2 \rightarrow CaSO_4 + 2H_2O \quad (3)$$

$$3CaSO_4 + 3CaO.Al_2O_3.6H_2O + 2H_2O \rightarrow 3CaO.Al_2O_3.3CaSO_4.31H_2O \quad (4)$$

The effect of the corrosion is a decrease of the wall thickness. The corroded surface enlarges the surface for stimulation of the biological and chemical activities

(Yamanaka *et al.*, 2002; Zhang *et al.*, 2007 in Meersseman, 2012). Due to the flow of the water these corrosion products will be easily washed away and a fresh front for continuous acid attack is available. The maximum erosion is near the waterline and in the crown of the pipe, both the locations with the highest structural bending forces (moments). The weakened pipe becomes unstable and may collapse under heavy overburden loads.

Corrosion increases with increasing temperature, H_2S concentration and humidity. Typical corrosion rates are reported in various case studies and range from 12 mm/year at particularly aggressive locations (50 ppm H2S in air, T=27℃) down to ~1 mm/year at benign sites (1 ppm H2S, T=20℃) (Wells, et. al, 2012). Bielecki (1998) reports strong corrosion at a rate of 3 - 6 mm/year.

Figure: Corroded concrete pipe

Figure: Corroded reinforced concrete pipe

Models
Physicists and chemists have considered the mechanisms of cement hydration, microstructures, chemical resistance, etc. Mechanical researchers have modelled the behaviour of concrete structures under certain (laboratory) conditions or in conditioned field experiments. A third group in the research on the influence of environmental impacts on concrete structures are the biologists. Surfaces of concrete structures, when exposed to non sterile environments, become the site of number of aerobic and anaerobic biological activities, many of which cause deterioration to the surface.(Vincke at al; 2006).The more recent models tries to describe and model the microbiological processes.

There are a lot of models available to try to predict sulphides build up in pressure- and rising mains and the emission of this produced sulphides in gravity sewers. The models gives indications about:

- sulphide production
- (yearly) rate of corrosion: average or maximum
- sensitivity for anaerobic circumstances
- biological activities
- biomass production
- critical length of corroded pipes
- critical design parameters
- effects of prevention measurements

In most cases:

- every model is a more or less simplified reproduction of a very complex reality and has to be assessed depending on the conditions where the model is going to be applied;
- the variety of input parameters that determine the processes is enormous, is widely dispersed and the more complex the model, the more difficult to measure the parameters in practise;
- the uncertainty in the parameters and their deviations is hardly known;
- existing empirical models are based on limited statistical and mostly not representative data. Samples are valid for a few local situations;
- empirical models needs estimation of empirical key parameters; numerical models are to complex and need very detail (lab-scale) information, besides validation is often very limited;
- the validity of the models based on lab-scale experiments under conditioned circumstances in practice can be discussed because of the way of making the samples and the modelling;
- every situation and every environment with corrosion processes is different, has local circumstances and almost needs a tailor-made approach;
- a lot of empirical research has been done in countries with high temperature and by consequence with more problems and the need for a more risked based safe and conservative way of approach;
- because the wide spread of the results of the various models used in the same situation, it is almost impossible to predict reliable corrosion-rates;
- most of the research and modelling focuses on the biological and material aspects only and not on the functional requirements and design parameters of the system. In a lot of cases the input parameters e.g. influent quality, pump

pauses, diurnal patterns in inflow and temperature are supposed to be constant.

Figure: research and field samples (Sydney; Wells et al, 2012)

More recent modelling is dealing with two-phase flow simulating water and gas conveyance in sewers as well as biological transformation processes (Hvitveld-Jacobsen, 2002). The flow simulation is fully dynamic and process simulation takes carbon, sulphur and nitrogen into account. The corrosion itself is simulated by a conceptual approach, accounting for the sulphide and sulphur oxidizing biomass and for kinetics and stoichiometry of the involved processes (Vollertsen et al; 2011).

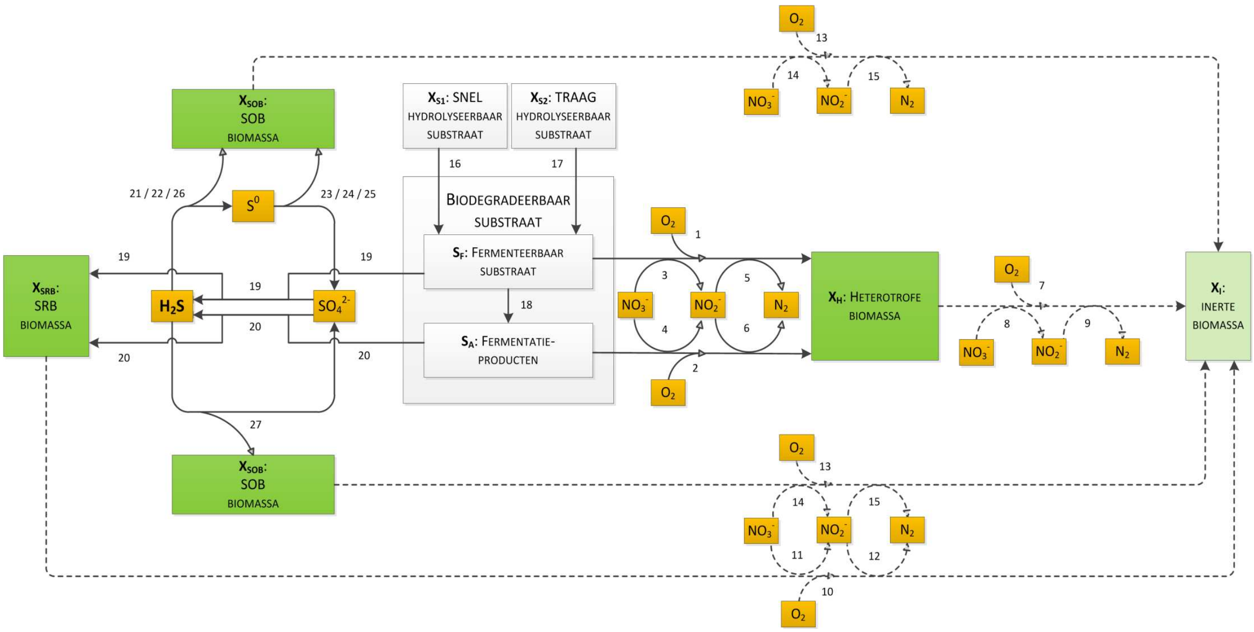

Figure: Example of a schematic for a model for kinetics and stoichimetry of processes (in Meersseman, 2012)

Corrosion: locations in sewer systems and developments

Corrosion will occur after the formation of H_2S under anaerobic circumstances and after release of the gas from the bulk water. Corrosion prevention starts with identifying locations with:

- anaerobic circumstances: preventing autogenic production of sulphides
- gas release and odour: prevention of discharge of autogenic produced sulphides;
- extraneous input of flows containing sulphides.

Experienced sewer management can recognize on the basis of good knowledge of his system where problems may arise and can take preventive action in time.

It is almost impossible to prevent autogenic production of sulphides in pipes running full. Anaerobic circumstances are inevitable in:

- rising mains
- pressure and vacuum systems
- surcharged gravity sewers (trunk sewers)
- syphons

Risks of anaerobic circumstances also arise in:

- wet wells of pumping stations
- places with risks of stagnant water (storage mains)
- not underpiled gravity sewers in settlement areas
- partly filled large transport sewers with dry-weather flow, low flow velocity and minimal slopes
- dry-weather systems in areas with high temperatures
- unventilated sewers

Points to control and (yearly) to inspect are:

- pumping stations
- possible air pockets in pressure mains near ventilation points (Lubbers, 2007);
- discharge points of pressure systems
- inflow from higher connecting pipes and lateral connections in an almost anaerobic flow in transport sewers (turbulence)
- manhole drops and falls causing turbulence in anaerobic flow in transport sewers

Anaerobic conditions are characterised by an oxygen rate less than 1.0 mg/l. The oxygen rate can easily be measured.

Sewer systems develop. Some of the developments tends to higher risks for biogenic acid attack.

- Increase of the application of pressure systems and centralisation of wastewater treatment causing longer transportation distances of wastewater
- Increase of the pollution of the wastewater with a higher biological oxygen demand, more frequent application of separate sewer systems and leakage prevention

- Infiltration of rainwater leaving the combined sewer system with oversized pipe diameters and more and longer unfavourable flow conditions during dry weather flow
- Increase of wastewater temperature and climate change (combined sewer systems with larger diameters).

Corrosion due to other aggressive waters

Corrosion of concrete due to other aggressive waters is in general below the waterline. The concrete pipes are not designed to the exposure of these waters. A classification of exposure classes is given in EN 206-1 (2000); Concrete part 1: Specification, performance, production and conformity, Table 4. The table makes distinction between corrosion induced by carbonation, corrosion induced by chlorides from sea water, free/thaw attack with or without de-icing salts and chemical attack. Examples of chemical attack are given in the figures

Figure: Examples of corrosion induced by the chemical quality of the wastewater

Design aspects

The design aspects are related to the locations with anaerobic conditions as mentioned before. For new sewer system construction adequate guidelines and design parameters can be found in literature (USEPA, Pomeroy, Bielecki, etc.). Planning of measurements for long transport sewers are given in Lohse (2013). Guidelines are available for:

System layout and discharge points

Discharge points on gravity sewers should be avoided. Discharge points of pressure systems are often found in the up-stream parts of gravity sewers with little or no flow of fresh wastewater. In these cases the anaerobic flow can make damage in a large part of the up-stream system. It is advised to discharge anaerobic water in places where it is immediately diluted by fresh sewage. Fresh sewage has in general a pH of 7.0 and a rate of Dissolved Oxygen of 6.5 – 7.0 $mg.l^{-1}$.

Minimum velocity, minimum slope and degree of filling

Minimum velocity is advised at a minimum of 0.6 $m.s^{1}$ in pressure mains (see EN 1671). For gravity sewers the velocity depends on the flow, slope, diameter and filling degree (hydraulic radius), diurnal daily flow, rate of pollution and temperature. Pomeroy advises a minimum flow velocity depending on the Effective BOD.
A fast assessment of risk of corrosion can be obtained from the so-called Z-formula of Pomeroy (USEPA, 1985; Pomeroy, 1977).

Shear stress

Shear stress is important in preventing growth of the slime layer and the deposits of sludge on the bottom of the pipe. To prevent deposits shear stress should have a minimum value of > 2 - 4 $N.m^{-2}$ in gravity sewers.

Turbulence

Turbulence can be used to strip the gas at the discharge point for treatment or has to be avoided. Pressure systems must be preferable discharge under water level. Manhole drops and falls in the systems if the sewage is almost anaerobic, must be avoided. Places with high turbulence can be protected by choice of plastic materials.

Self cleaning

Frequent cleaning prevents deposits on the bottom and removes slime layers on the pipe wall. Self cleaning conditions are almost impossible in flat areas.

Detention time

Detention time in wet wells of pumping stations and in detention tanks should be as short as possible to prevent the development anaerobic conditions. Adequate ventilation is a prerequisite.
Detention time in pressure mains can only be influenced by lay-out of the system, optimizing pumping regime and diameter.

Stagnant water

Stagnant water can occur in wet wells, detention tanks and settlements in de sewer systems. Good ventilation is necessary to keep enough oxygen in the sewer air.

Choice of materials
Clay pipes and plastics are resistant to sulphuric acid and can be used at discharge points. The necessary pipeline length depends on the discharge volume, the possible dilution with fresh sewage and the way the sewer is ventilated. Concrete can made more resistant by the use of polymers, or reducing the Portlandcement fraction by adding blast furnace granulate.

Rehabilitation
For existing systems, corrosion problems can resolved with increased ventilation, chemical treatment and the application of protective coatings, vinyl and epoxy resins, plasticized PVC sheets, cement and polyethylene linings, and others.
Strategies for design and rehabilitation are described in EN 752: Drains and sewers outside buildings; management (2008) and in EN 13508-1: Drains and sewers outside buildings; part 1 investigation and assessment (2013).

Before taking measures it is always necessary to do further investigations necessary for a adequate assessment of the failure risks (see EN 13508-1; 2013). These investigations comply:
- visual inspection of the corroded pipe lengths;
- core drilling and determining the properties of the concrete (carbonation, intrusion of acid, remaining wall thickness, etc.);
- structural calculation to determine risks of failure;
- the function of the pipe within the system and the need for replacement;

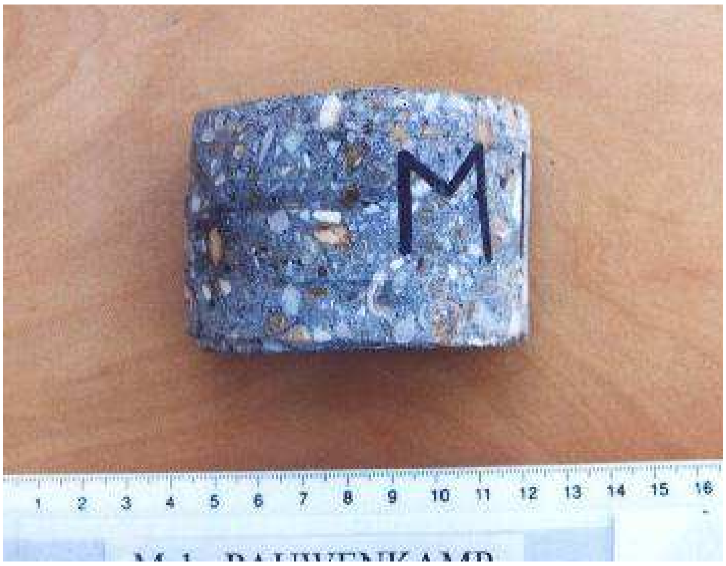

Figure: The need for further investigation: core drilling

Rehabilitation techniques are listed and classified in EN 15885 Classification and performance characteristics of techniques for renovation and repair of drains and sewers (2013). Most of the described techniques are with application of plastic materials.
According to ISO/TR 10358:plastic materials (e.g. PVC) are satisfactory resistant to sulphuric acid.

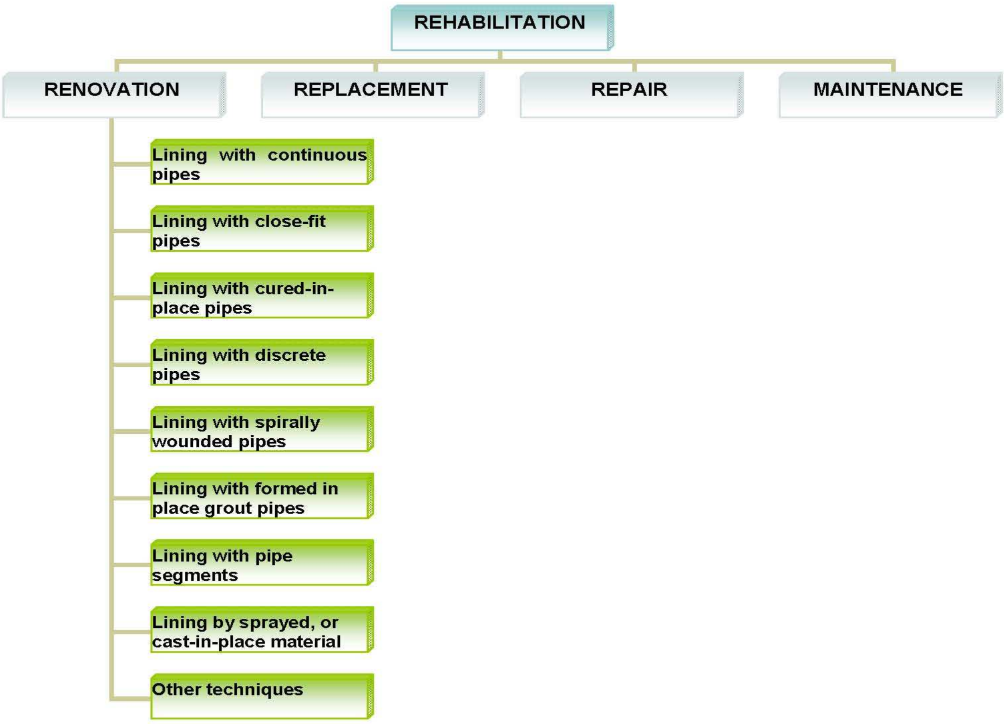

Figure: Renovation techniques (EN 15885)

Conclusion

A lot of modelling has been done to get knowledge on the phenomena of Biological Sulphuric Acid Attack (BSA) in concrete sewers. Though some key factors are missing, the phenomena is well know and intensively modelled. The modelling is mainly empirical and not reliable enough for exact predictions in all situations. A lot of investigations has been carried out, but most of it lacks the perspective of asset management.

Experienced sewer management can identify on the basis of good knowledge of his system where problems may arise and can take preventive action in time. One can easily determine where in a concrete sewer system corrosion can occur. Building up of autogenic sulphides can not in all circumstances be prevented. But a good design and the use of adequate resistant materials (e.g. plastics and clay-pipe) can take care for a long and durable system life. In all situations with BSA plastics can be used for repair and rehabilitation.

One can ask the question if with the knowledge of today, investment in more research is cost effective to obtain a good designed, well rehabilitated, based on adequate preventive actions and the choice of good materials.

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