Corrosion resistance of cementitious based materials in wastewater applications

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ABSTRACT

Microbial induced corrosion, by means of biogenic sulfuric acid attack, appears as the dominant corrosion encountered in the field of sewage treatment and wastewater networks. As a result of intense research during the past few decades by scientists and engineers, the general mechanism of the biogenic corrosion of cementitious based materials has now become well understood. Biogenic corrosion is not a simple chemical attack of acid sulfuric; behavior of cement in sewers is complicated by interactions between bacteria development which produce sulfuric acid as a metabolic by-product and chemical composition of the cement and aggregate.
In this paper, the mechanisms of biogenic sulfuric acid corrosion of cementitious-based materials are reviewed, as well as some illustrations of very different behaviors of various concrete mix in wastewater applications.
As the corrosion potential will vary from sewer to sewer depending upon the operation conditions and the composition of the effluent, appropriate cementitious materials should be chosen according to the environment. Some examples of cement-based materials available and suitable for aggressive wastewater environment applications are also given.

1. INTRODUCTION

Concrete is widely used in all wastewater structures such as holding tanks, manholes and sewer pipes. It performs well and offers many benefits such as ease of installation, cost effectiveness and is environmentally friendly. However, in some cases, ordinary concrete pipes, i.e. Portland concrete pipes, could suffer from biogenic sulfuric acid corrosion; the combination of some factors such as temperature, network design,…, favours the sulfuric acid corrosion. Different solutions are known to reinforce the service life in such aggressive environments.

2. SULFURIC ACID GENERATION PROCESS

The general process is widely agreed on by researchers and engineers and can be summarized as follow (cf. Figure 1)[Parker (45), Guilchrist (53), Sand and Bock (84), Scrivener et al. (99), American Concrete Pipe Association (01)]:

- The sulfates contained in the wastewater are reduced to hydrogen sulfide H_2S by anaerobic micro-organisms living in the slime layer, which builds up on the pipe walls below the effluent, by following reaction :

$$SO_4^{2-} + 2H^+ \overset{anaerobic\ \ micro-organisms}{\Rightarrow} H_2S + 2O_2 \qquad \text{(Eq. 1)}$$

Sulfur compounds, such as sulfate, sulfite or other inorganic or organic sulfur, must be present in the wastewater to provide the raw material for conversion to sulfide. Most domestic sewage naturally contains sufficient sulfates for this to occur.

Cementitious notation: C = CaO, A = Al_2O_3, F = Fe_2O_3, H = H_2O, S = SiO_2, $ or $\overline{S}$ = SO_3, T = TiO_2

- At sufficient concentration, the additional H_2S is no more soluble and is then ejected into the sewer atmosphere as gas. Turbulence in the effluent flow increases the ejection rate. The ejection of H_2S depends also on the effluent pH and temperature.

- H_2S is carried to the pipe wall by convection currents and is oxidized to elemental sulfur by the oxygen or dissolves in moisture on the pipe walls to form sulfurous acid, both of which are used by various types of sulfur oxidizers bacteria as nutrients. The reactions are as follow :

$$2H_2S + O_2 \Rightarrow 2S + 2H_2O \qquad \text{(Eq. 2)}$$

$$H_2S \overset{H_2O}{\Rightarrow} H^+ + HS^- \qquad \text{(Eq. 3)}$$

$$HS^- \overset{H_2O}{\Rightarrow} H^+ + S^{2-} \qquad \text{(Eq. 4)}$$

- The sulfur oxidizers bacteria found in the corroded concrete in wastewater applications belong to the species of Thiobacillus, which include T. tioparus, novellus, neapolitanus, intermedius, and thiooxidans. Their metabolic end product is sulfuric acid by following reaction :

$$2S + 3O_2 + 2H_2O \overset{metabolism\ of\ bacteria}{\Rightarrow} 2H_2SO_4 \qquad \text{(Eq. 5)}$$

- Each strain of Thiobacillus can only exist within a particular pH range (cf. Figure 2). Many thiobacilli are acidophiles. However, some of them, such as T. tioparus, T. novellus, and T. neapolitanus, are able to tolerate a slightly alkaline environment. They are the first to settle on the concrete surface as the pH of the concrete drops through carbonation or the formation of sulfurous acid. The pH of the concrete surface is thus further reduced by acid produced by these species, so that suitable growth conditions for other species of bacteria such as T. thiooxidans are created.

The Thiobacillus bacteria are the driving force of sulfuric acid production.

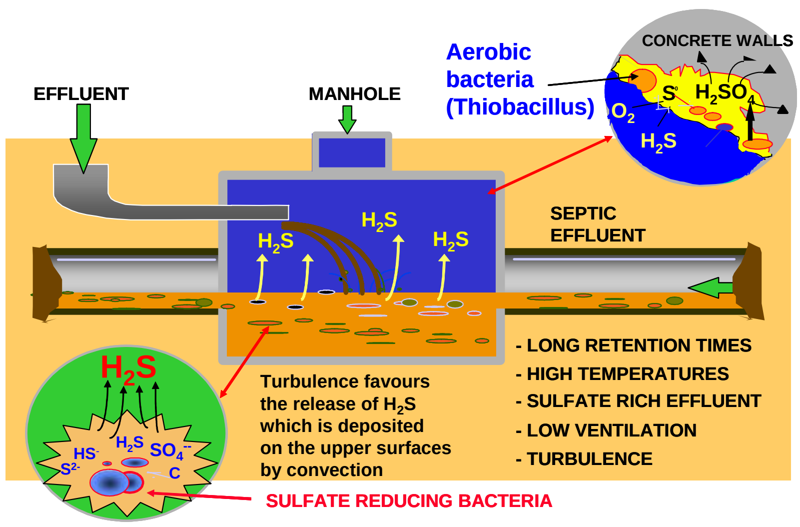


Figure 1: The process of acid generation by bacteria in sewage networks

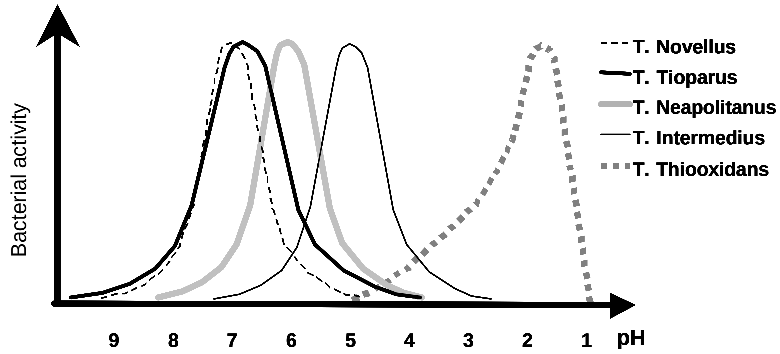


Figure 2: Suitable pH ranges for activity of bacteria in the genus Thiobacilli- Successive colonization: for example, the most aggressive type, T. Thiooxidans, can only colonise the surface once the pH has been brought down by other types.

3. BEHAVIOUR OF PORTLAND CEMENT IN SULFURIC ACID MEDIA

The degradation of concrete in wastewater networks is a biogenic sulfuric acid attack which is a process of dissolution - precipitation of some minerals.

The hydrates of Portland cement consist mainly of calcium silicate hydrate (C-S-H) and calcium hydroxide (portlandite CH).

The reactions which lead to its degradation may be summarized as follows:

- Attack of the most vulnerable part of the binder, portlandite:

$$Ca(OH)_2 + 2H^+ \rightarrow Ca^{2+} + 2H_2O \qquad \text{(Eq. 6)}$$

- Decalcification of the C-S-H which leaves a structureless silica gel:

$$C_x - S - H_y + 2xH^+ \rightarrow xCa^{2+} + SiO_2 + (2y+1)H_2O \qquad \text{(Eq. 7)}$$

Attack by sulfuric acid leads to gypsum formation $CaSO_4.2H_2O$, which is a white colored, soft paste- like product. Ca^{2+} ions generated in (Eq. 6) and (Eq. 7) will react with SO_4^{2-} ions from sulfuric acid.

4. HAZARDOUS ZONE

Corrosion in pipes is concentrated above the flow line.

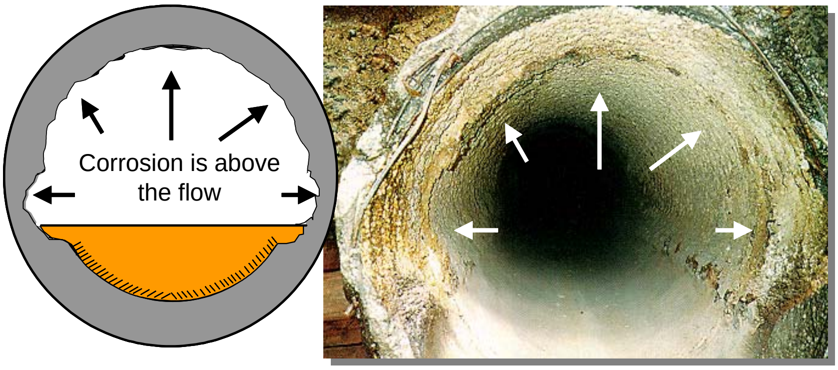
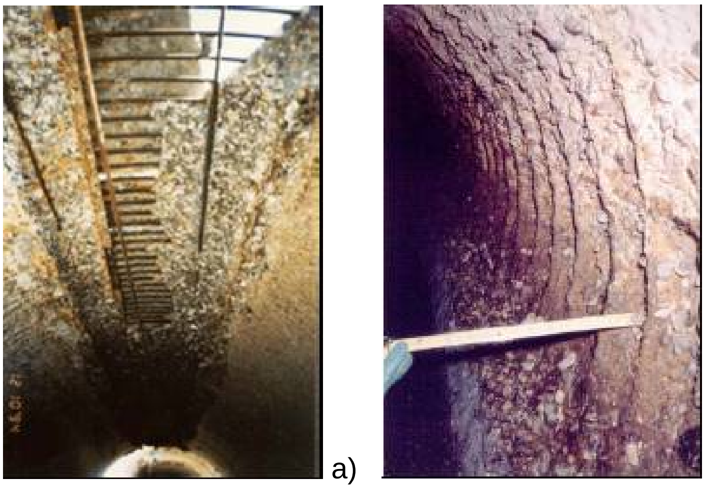


Figure 3: Areas of corrosion in concrete pipes



a) b)

Figure 4: a) Corrosion by H_2SO_4 of the crown composed of ordinary Portland concrete b) Uncovered reinforcements after less than 10 years of service of ordinary Portland cement pipes

a) b)

Figure 5: a) Corrosion of ordinary Portland concrete in a lift station. b) Ordinary Portland concrete corroded structure

5. KINETIC OF BIOGENIC SULFURIC ACID ATTACK

It is well-known that the rate of corrosion could be affected by several parameters which are mainly centralised around H2S released and H_2SO_4 generation. Based on this understanding, solutions have been proposed to enhance the long term performance in aggressive environments.

5.1. Wastewater network operating conditions

Main factors relative to the sewer service conditions are reviewed below.

- Wastewater quality
  - pH : the released of H_2S is favoured by a low pH
  - Dissolved $O_{2:}$ as the lack of oxygen in the effluent is the condition of reduction of sulphate by the anaerobic microorganisms, lower dissolved oxygen content in the effluent favours the production of H_2S, thus potentially more H_2SO_4 generation at the end of the process.
  - Sulfates content
  - Temperature (the anaerobic bacterial proliferation is favoured by a high temperature as well as the released of H_2S).

- Flow conditions
  Lower the slope of the pipeline, lower the stream velocity, in particular for pipe without external pressure. This lead to a longer retention time of effluent. The presence of turbulences has two effects: increase of oxygen dissolution into effluent and increase of H_2S released into atmosphere. Globally, the presence of turbulence is rather a very unfavourable condition.

- Climate: temperature and humidity of atmosphere

- Abrasion: flow conditions, abrasive contents in effluent

Thus, the designer would avoid the turbulence areas and long retention time of effluent. A ventilated network will reduce the H_2S released. This paper is not to describe the different strategies used by designers and operators to avoid potential corrosion problems but it highlights potential critical points which could affect the service life.

5.2. Materials properties

Another key parameter is the choice of the material. Different levers could be considered. In locations where an increase of the sacrificial layer does not fill up the target service life, protective linings are a suitable option. Thus, with the use of Calcium Aluminates Cements, the applications field of the traditional concrete is enlarged. The following reviews briefly the reasons of the good performance of Calcium Aluminates Cements in aggressive environments.

The hydrates of calcium aluminate cement consist of calcium aluminate hydrates (metastable hydrates CAH_{10} and C_2AH_8, and stable hydrate C_3AH_6) and hydrous alumina gel (AH_3).

The reaction equations in acidic media are as follows :

$$CaO \cdot Al_2O_3 \cdot 10H_2O + 2H^+ \Rightarrow Ca^{2+} + 2Al(OH)_3 + 8H_2O \quad \text{(Eq. 8)}$$

$$2CaO \cdot Al_2O_3 \cdot 8H_2O + 4H^+ \Rightarrow 2Ca^{2+} + 2\,Al(OH)_3 + 7\,H_2O \qquad \text{(Eq. 9)}$$

$$3CaO \cdot Al_2O_3 \cdot 6H_2O + 6H^+ \Rightarrow 3Ca^{2+} + 2\,Al(OH)_3 + 6\,H_2O \qquad \text{(Eq. 10)}$$

The precipitation of $Al(OH)_3$ whose solubility threshold is about pH=4, creates locally a barrier layer which reduces further acid ingress. As in the case of Portland cement, the released Ca^{2+} will precipitate as gypsum.
At pH levels lower than 4, $Al(OH)_3$ dissolves but in doing so neutralises more acid, as seen in (Eq. 11).

$$2\,Al(OH)_3 + 6H^+ \Rightarrow Al^{3+} + 6\,H_2O \qquad \text{(Eq. 11)}$$

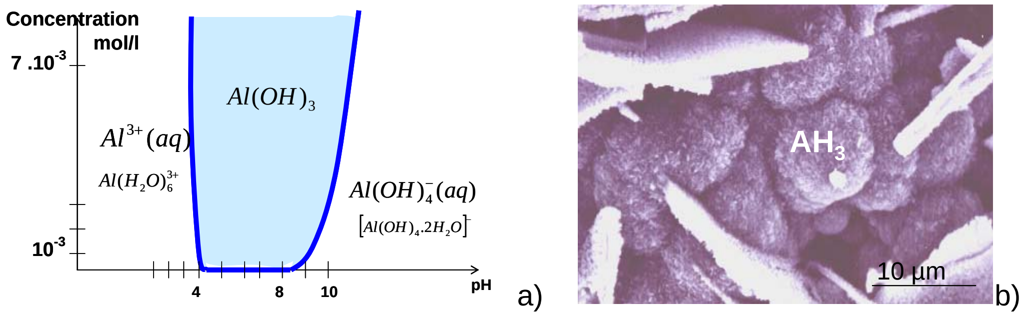


Figure 6: a) Aluminium diagram. b) Microstructure of $Al(OH)_3$ gel, blocking porosity

Calcium Aluminate Cement owes its stability against many aggressive agents not only to the nature of the hydrates but also to its greater neutralization capacity and to a bacteriostatic effect on Thiobacillus bacteria. The consequence of the latter is a limited H_2SO_4 production. Thus the pH is imposed by the materials, see Figure 7: for the CAC, the pH is stabilized to 3 versus 1 for Portland cement (i.e. 100 times more acid produced on Portland cement mortars compared to CAC mortars).

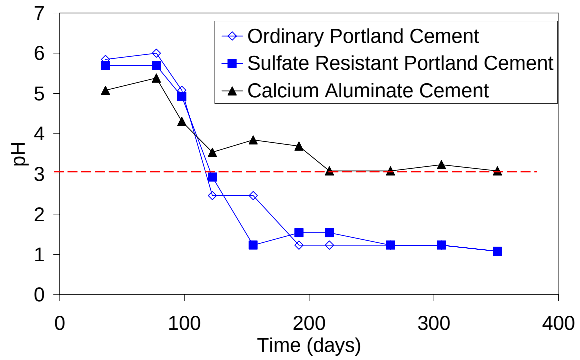


Figure 7: Decrease of the superficial pH of mortars in microbial corrosion tests [Ehrich (98)]

The production process the CAC have the same simplicity of production process as the traditional concretes.

CAC concretes whose the application process is similar to traditional concretes have a long history of successful use as linings and coatings for concrete and ductile iron sewage pipes and in associated wastewater applications. A thermal curing in confined atmosphere is recommended to fully take advantage of CAC potential and optimize the quality and the durability of the pipes.
Several examples of long-term performance exist. Solid calcium aluminates sewage pipes were installed in Australia in the 1950's [Baker (96)]. When last inspected in 1991 these were found to be in good conditions. Also in the 1950's centrifuged Portland concrete pipes lined with calcium aluminates mortar were laid in Kuala Lumpur [Dumas (90); these are still in use today. In the 1960's, many kilometres of Portland concrete pipes lined with calcium aluminates mortar were used in Durban, South Africa, and in the 1980's similar pipes were laid in Cairo, Egypt [Dumas (90)].

6. CONCLUSIONS

Concrete corrosion in wastewater applications should not be restricted to a simple sulfuric acid attack; other parameters such as interactions bacteria – substrate or abrasion resistance should be included. Pipe dimensions, design and sewer operating conditions should be fully integrated in the building of wastewater network for a long term performance.
In aggressive environments where ordinary Portland concrete does not fully satisfy the service life, the use of calcium aluminates cement is a durable solution.

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