ACID RESISTANT CONCRETE SEWER PIPES

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Abstract

Acid resistant concrete sewer pipes are required in areas where sufficiently large quantities of hydrogen sulphide are released into the sewer atmosphere, leading to the generation of severely corrosive sulphuric acid (pH < 1 typically) on the sewer walls. Conventional methods to ensure service life in such conditions are to use acid-soluble dolomite aggregate but this may be inadequate in many such areas. A more effective strategy under particularly corrosive conditions is calcium aluminate-based materials (binders and/or aggregates) to neutralise and stifle the growth of the bacteria.

Two plausible solutions are discussed in this paper: 1) use of a concrete consisting entirely of calcium aluminate-based materials, and 2. development of an acid-resisting but partly insoluble concrete using an interlocking siliceous aggregate network. This minimises attack on the binder by isolating it from direct acid attack, and may provide acceptable integrity in an acid environment. Other possible solutions are discussed to attain an acid resistant binder. A truly acid resistant concrete however requires both a robust acid resistant aggregate network and cementing binder.

1. INTRODUCTION

Concrete sewer pipes in warm areas of flat topography are prone to sulphuric acid attack. Anaerobic conditions in the slimes layers beneath the slow flowing sewage and in sewage retained in rising mains allow growth of sulphur reducing bacteria whereby sulphate is reduced to sulphide which escapes into the sewer atmosphere as hydrogen sulphide (H$_2$S). Auto-oxidation of the hydrogen sulphide into sulphuric acid occurs with absorption into the moist layer on surfaces above the sewage. The resulting deterioration of concrete due to the decrease in pH provides sites for the growth of acid-loving thiobacillus bacteria. Sulphide utilised by these bacteria is oxidised to sulphuric acid further lowering the pH, leading to severe attack on the concrete.

Severely corrosive environments with pH < 1 are common in sewers in South Africa. Conventional concrete pipes perform poorly in these environments. Sites for growth of the thiobacillus develop on OPC cement binders within 3 months [1] due to the high concentrations of hydrogen sulphide in the sewer atmosphere throughout the year. Acid-insoluble siliceous aggregates are exposed and fall out. Conversely, acid-soluble dolomite
aggregates dissolve and slow the rate of attack but cannot effectively neutralise all the acid generated. Although attack is spread over the entire surface, preferential dissolution of the OPC binder still occurs [2]. Acid resistance of the binder is improved by replacing OPC with CAC, which proves toxic towards the thiobacillus bacteria [3]. However, CAC and OPC binders dissolve at similar rates in a mineral acid solution [1] and sites favouring the growth of thiobacillus eventually form due to the auto-oxidation of the hydrogen sulphide into sulphuric acid.

A robust sewer pipe for use in such areas requires a concrete capable of a) resisting the sulphuric acid formed (as described above), and b) one that contains elements which are toxic towards the thiobacillus colony. Two solutions are discussed in this paper. The one is a concrete consisting entirely of calcium aluminate materials and contains CAC and Alag™ aggregates. The other is a concrete containing a robust interlocking siliceous aggregate network that traps the corrosion debris and shields the cement binder from the acid environment. An acid resistant concrete ideally is one containing compounds that are toxic towards the thiobacillus bacteria, and also reacts with sulphuric acid to form a barrier against further attack.

The paper documents testing done on the two different types of concrete in a hydrochloric acid solution at a pH of 1,00, as well as preliminary testing in a manhole where conditions were such that the sulphuric acid environment decreased to a pH of below 1,00. Acid attack mechanisms are discussed and compared to conventional sewer pipe concrete containing OPC and dolomite aggregates, and similar concrete using a CAC binder.

2. EXPERIMENTAL METHODOLOGY

2.1 Specimen preparation

Cylindrical concrete specimens (80 mm diameter × 150 mm) were prepared in a manner similar to that of pipe manufacture, so as to ensure a representative concrete by simulating the roller suspension method.

2.2 Concrete mixtures

Acid resistances of twelve concrete mixtures are discussed here. (Table 1). A CAC dolomite aggregate mixture, an OPC dolomite aggregate mixture and a CAC synthetic alag™ aggregate mixture (2 – 4) were assessed in a hydrochloric acid solution and in a live sewer in which an OPC siliceous aggregate mixture (1) was also tested. A total of eight siliceous aggregate mixtures (5 – 12) were designed each containing the same granite stone but differing with respect to the type of binder or siliceous fine aggregate; for these mixtures, binders were either OPC, or 10% silica fume and OPC, the latter mixtures containing a superplasticiser (approximately 1% by mass of binder).

Siliceous fine aggregates were either filler or crusher sands, or versions of the filler or crusher sands modified to give coarser gradings. The modified sands were both of similar particle sizes differing only in shape (Figure 1) and were designed to assess the impact of siliceous fine aggregate particle size and shape on acid resistance. Coarser particles are exposed at a slower rate and take longer to fall out. Angular particles interlock and as a result are less likely to fall out than the rounder particles. Slower exposure and fall-out of the fine aggregate particles results in a slower attack on the binder and entraps corrosion debris, more effectively slowing attack on the binder.
Table 1: Mixture proportions based on ratio to total binder content

<table>
<thead>
<tr>
<th>Mixture</th>
<th>Stone</th>
<th>Sand</th>
<th>Cement</th>
<th>Additive</th>
<th>w/b</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. OPC siliceous</td>
<td>3.25</td>
<td>2.89</td>
<td>1.00</td>
<td>-</td>
<td>0.30</td>
</tr>
<tr>
<td>2. CAC dolomite*</td>
<td>1.67</td>
<td>1.67</td>
<td>1.0</td>
<td>-</td>
<td>0.28</td>
</tr>
<tr>
<td>3. CAC Alag™*</td>
<td>1.67</td>
<td>1.67</td>
<td>1.0</td>
<td>-</td>
<td>0.28</td>
</tr>
<tr>
<td>4. OPC dolomite*</td>
<td>1.67</td>
<td>1.67</td>
<td>1.0</td>
<td>-</td>
<td>0.28</td>
</tr>
<tr>
<td>5. OPC siliceous std/filler</td>
<td>2.28</td>
<td>2.28</td>
<td>1.00</td>
<td>-</td>
<td>0.36</td>
</tr>
<tr>
<td>6. SF siliceous std/filler</td>
<td>2.28</td>
<td>2.28</td>
<td>0.90</td>
<td>0.10</td>
<td>0.32</td>
</tr>
<tr>
<td>7. OPC siliceous std/crusher</td>
<td>2.28</td>
<td>2.28</td>
<td>1.00</td>
<td>-</td>
<td>0.36</td>
</tr>
<tr>
<td>8. SF siliceous std/crusher</td>
<td>2.28</td>
<td>2.28</td>
<td>0.90</td>
<td>0.10</td>
<td>0.32</td>
</tr>
<tr>
<td>9. OPC siliceous mod/filler</td>
<td>2.28</td>
<td>2.28</td>
<td>1.00</td>
<td>-</td>
<td>0.36</td>
</tr>
<tr>
<td>10. SF siliceous mod/filler</td>
<td>2.28</td>
<td>2.28</td>
<td>0.90</td>
<td>0.10</td>
<td>0.32</td>
</tr>
<tr>
<td>11. OPC siliceous mod/crusher</td>
<td>2.28</td>
<td>2.28</td>
<td>1.00</td>
<td>-</td>
<td>0.36</td>
</tr>
<tr>
<td>12. SF siliceous mod/crusher</td>
<td>2.28</td>
<td>2.28</td>
<td>0.90</td>
<td>0.10</td>
<td>0.32</td>
</tr>
</tbody>
</table>

*These mixtures represent those used for thin (e.g. 20 mm) linings of concrete sewers, and are richer at about 23% binder content.

2.3 Hydrochloric acid solution test

Specimens were tested in a rig consisting of one or more compartments made of PVC sheeting. The full-capacity of a compartment is approximately 72 ℓ. Each compartment contains two rubberised rollers, a PVC brush and a PVC drain valve (Figure 2).

![Filler sand](image1.png)  ![Crusher sand](image2.png)

Figure 1: Schematic showing the different shapes of the filler and crusher sand particles

A compartment is filled with approximately 50 ℓ of a hydrochloric acid solution (pH=1). (HCl is used since it produces readily-soluble salts (e.g. CaCl₂) that do not mask the surface of the concrete. This simulates the condition in a flowing sewer at the water line where corroded material is constantly removed by the sewage, continually exposing the concrete to fresh attack). A cylindrical concrete specimen pre-saturated with tap water (approximately 2 kg in mass), is immersed in the solution and rotated at approximately 16 revs, per minute. A brush on the surface of the specimen dislodges corrosion debris. Measurements of mass and specimen dimensions, and hydrogen ion concentration of the solution, are recorded with time. A pH of between 1.00 and 1.05 is maintained for the duration of the test. Solutions are
renewed every 24 hours of running time to ensure accurate control of the hydrogen ion concentration.

![Figure 2: Schematic arrangement of test rig illustrating cross-section of a single compartment, showing rotation and brushing of a concrete specimen on rubberised rollers (not to scale)](image)

Attack is estimated from the measurements of mass loss and hydrogen ion consumption with time. A test is run for a period sufficient to ensure the physical and chemical factors influencing the attack are reflected in these measurements. A recommended test period for dolomite aggregate concrete is approximately 96 hours of running time, although 48 hours will often suffice to establish clear trends. A modification of the test procedure is required for siliceous aggregate concrete. Specimen mass losses and hydrogen ion consumptions are determined using the standard dolomite aggregate concrete procedure for the initial 48 hours of testing. Specimens are then removed once every 24 hours and sprayed with a high-pressure jet of water to remove the corrosion debris entrapped by the fine aggregate particles from between the stone particles to accelerate the attack on the binder portion and fall-out of stone particles. Specimen mass losses alone are determined and recorded to the point of stone particle fall-out.

### 2.4 Sewer test

Cylindrical specimens (80 mm diameter × 150 mm) were sliced lengthwise to yield two half cylinders (40 mm radius × 150 mm length) one of which was inserted into a PVC holder mounted onto a manhole wall directly above the average daily sewage level region in an area
where turbulent flow conditions occurred (Figure 3). Specimens were visually inspected after 5 months and 17 months and surface pH of the specimens was measured. Specimens were removed after 17 months and cleaned (under running water using a stiff nylon bristle brush) to remove the loose corrosion debris. Specimen percentage mass losses were calculated.

![Figure 3: Specimens located in positions 1 to 5 on manhole wall directly above the daily sewage level mark](image)

Hydrogen sulphide concentrations of the sewer atmosphere and pH on the concrete wall in the manhole were measured. A pH-probe was inserted into the slimy moisture layer along the concrete wall directly above the sewage level.

3. RESULTS AND DISCUSSION

3.1 Hydrochloric acid solution testing

*Siliceous aggregate specimens*

Specimen mass loss rates (average of four determinations) decreased with time over the initial 72 hours of testing after which the rates remained constant with time, but sharply increased at the point of stone particle fall-out (Figure 4). OPC standard filler sand specimen mass losses at any given time were significantly higher than those of the remaining OPC and silica fume specimens.

The use of silica fume and the size of the fine aggregate particles influences the acid resistance of the siliceous aggregate concrete (Figure 4. A substantial decrease in mass loss occurs with the addition of silica fume to the mixtures, probably due to improved integrity of the material, particularly improvements in the interfacial zone between the cement binder and siliceous aggregate particles and pore refinement [4].

Substantial increase in the time to stone particle fall-out (approximately 100 hours) supports the speculation that silica fume improves binding of the aggregate particles. Cleaning the surfaces of the specimens revealed that siliceous aggregate particles standing proud were easier to dislodge from the standard OPC binders than the silica fume binders.
Coarser siliceous sand particles reduce the attack on the cement binder portion, thus prolonging the stone particle fall-out. Coarse standard crusher and modified crusher and filler sands more than halved the mass loss of the OPC concrete after 48 hours and substantially increased stone fall-out time of the OPC concrete (standard crusher sand from 216 to 312 hours, modified filler sand to 336 hours and the modified crusher sand to 384 hours). Coarser sand particles decreased the mass loss of the silica fume concrete to a lesser extent. After 48 hours, mass losses of the specimens containing the coarser sands were lower by a third, and stone particle fall-out time increased from 384 to 432 hours.

![Figure 4: Mass losses with time of siliceous aggregate concrete specimens (mixtures 5 – 12) measured using the hydrochloric acid solution test](image)

Shape of the sand particles influenced mass loss and stone particle fall-out time less than size. Specimens containing the rounded modified filler sand particles lost similar amounts of mass and reflected similar stone particle fall-out times as the specimens containing the angular standard and modified crusher sand particles, which was due to the coarseness of the particles in comparison to that of the standard filler sand particles.

**Dolomite aggregate specimens**

CAC/alag™ aggregate specimens reflected substantially lower mass loss rates with time than the OPC and CAC dolomite aggregate specimens in the hydrochloric acid solutions (Figure 5). After 96 hours, the mass loss of the CAC/dolomite aggregate specimens (50.9 %) was significantly higher than that of the OPC/dolomite aggregate specimens (43.2 %) and substantially higher than that of the CAC/alag™ aggregate specimens (15.2 %).

Hydrogen ion consumption rates of the CAC/alag™ aggregate specimens remained constant with time and were substantially lower than those of the specimens containing the dolomite aggregates, which increased with time (Figure 6). Acid solubility of the CAC binder
and alag™ aggregates are similar and after exposure of the alag™ aggregate particles hydrogen ion consumption remains the same. Acid solubility of the dolomite aggregate is significantly higher than the OPC and CAC binders and after exposure hydrogen ion consumption increases. After 96 hours, hydrogen ion consumptions of the CAC/alag™ (7.79 mg/cm²) were substantially lower than those of the OPC/dolomite aggregate (46.53 mg/cm²) and CAC/dolomite aggregate (47.03 mg/cm²) specimens.

![Graph showing mass loss vs time for OPC, CAC, and Alag aggregates](image)

Figure 5: Mass losses with time of OPC dolomite aggregate, CAC dolomite aggregate and CAC alag™ aggregate specimens in a hydrochloric acid solution at a pH of 1.00

The substantially lower mass losses and hydrogen ion consumptions of the CAC/alag™ aggregate specimens compared to the OPC and CAC dolomite aggregate specimens are considered to be due to a combination of the following factors:

- absence of an interfacial zone between the CAC binder and alag™ aggregate particles
- slower dissolution of the alag™ aggregate particles compared with the dolomite aggregate particles
- entrapment of corrosion debris between the slower dissolving alag™ aggregate particles

A strong bond forms on reaction between the CAC paste and alag™ aggregate particles due to their similar compositions and the reactivity of the alag™ particles. A weaker bond with an interfacial zone forms between the cement pastes (CAC and OPC) and the dolomite aggregate particles due to their different compositions and the inert aggregate. Such a weak bond permits more rapid penetration of acid and increases the dissolution rates of both the binder and dolomite particles thereby contributing to the faster dissolution of dolomite aggregate specimens.

An investigation into the solubility of the different types of aggregate particles in a hydrochloric acid solution revealed that the alag™ aggregate particles dissolved at a
significantly slower rate than the dolomite aggregate particles. Approximately 300 g of alag™ coarse aggregate particles retained on a 6.70 mm sieve and a similar amount and size of dolomite stone particles were exposed to separate hydrochloric acid solutions maintained at a pH of 1.00. After 96 hours, the mass loss of the alag™ coarse aggregate particles was approximately half that of the dolomite stone particles.

![Graph showing hydrogen ion consumption with time of 23% lining dolomite aggregate and alag™ aggregate specimens in a hydrochloric acid solution at a pH of 1.00](image)

**Figure 6:** Hydrogen ion consumption with time of 23% lining dolomite aggregate and alag™ aggregate specimens in a hydrochloric acid solution at a pH of 1.00

Attack on the binder in the CAC/alag™ specimens is reduced due to the entrapment of corrosion debris between the tightly packed network of alag™ particles standing proud of the attacked surfaces, due to the slow dissolution and fineness of the alag™ aggregate particles. Attack on the CAC binder is masked in a manner similar to that on the OPC binder in the siliceous aggregate specimens. Static conditions result in a localised drop in the pH between the exposed aggregate particles allowing the precipitation of salts mainly alumina, which isolates the binder from the hydrochloric acid. This masking effect is not as effective in the alag™ aggregate specimens as in the siliceous aggregate specimens. Alag™ particles dissolve to re-expose the CAC binders.

### 3.2 Sewer testing

A substantial amount of hydrogen sulphide was liberated from the sewage flowing through the manhole throughout the year (Figure 7). Average daily hydrogen sulphide concentration during the summer months was 55 ppm whereas that during the winter months was 27 ppm.

Hydrogen sulphide concentrations were substantially higher than the concentration (10 ppm) to sustain a sulphuric acid environment capable of severely attacking concrete sewers [5]. Surface pH on the manhole walls directly relates to the hydrogen sulphide concentrations. During the summer months the pH was less than 1.00 and during the winter months between
1.00 and 2.00. Such low pHs throughout the year provide an ideal environment for growth of the thio-oxidans and explains the severe attack on the concrete walls above the sewage level in the manhole.

![Hydrogen sulphide profiles](image)

Figure 7: Typical maximum, minimum and average daytime hydrogen sulphide profiles for summer (S) and winter (W) months in the manhole

Signs of attack were evident on the specimens 5 months after insertion in the form of a moist slimy layer of corrosion debris (Figure 8). The OPC siliceous aggregate surface was attacked relatively severely and appeared frothy in the binder area. A milky liquid with a pH of 1.20 to 2.00, significantly lower than that on the remaining surface area (pH of 6.00 to 6.50) was released on piercing with the pH probe. Attack was negligible on the CAC/alag™ aggregate, CAC/dolomite aggregate and OPC/dolomite aggregate specimens with only a slight dissolution of the cement skin evident on the surfaces; surface pH (6.00–6.50) was significantly higher than the adjacent manhole walls (pH < 2.00) implying that substantially less sulphuric acid was generated.

Table 2: Comparison of attack on the 4 specimens after 5 months and 17 months of exposure in the manhole

<table>
<thead>
<tr>
<th>Position/Mixture</th>
<th>After 5 months</th>
<th>After 17 months</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Attack*</td>
<td>pH</td>
</tr>
<tr>
<td>1. OPC siliceous</td>
<td>aggressive</td>
<td>0,40 – 1,20</td>
</tr>
<tr>
<td>2. CAC dolomite</td>
<td>negligible</td>
<td>6,00</td>
</tr>
<tr>
<td>3. CAC Alag™</td>
<td>negligible</td>
<td>6,50</td>
</tr>
<tr>
<td>4) OPC dolomite</td>
<td>negligible</td>
<td>6,00</td>
</tr>
</tbody>
</table>

*aggressive – frothy surface due to dissolution of cement skin, negligible – slight dissolution of cement skin

**aggressive – aggregate standing proud of attacked surface, moderate – exposure of aggregate, negligible – dissolution of cement skin
After 17 months, CAC/alag™ aggregate specimen experienced no mass loss and mass loss of the CAC dolomite aggregate specimen (0.35 %) was slight. Mass loss of the OPC dolomite aggregate specimen (2.46 %) was significantly higher but substantially lower than the mass loss of the OPC siliceous aggregate specimen (4.14 %). Surface pH of the OPC siliceous aggregate specimen CAC and OPC dolomite aggregate specimens (6.70) was significantly lower than that of the CAC/alag™ aggregate specimen (7.14).

Attack on the siliceous aggregate specimen was noticeably higher than that on the dolomite and alag™ aggregate specimens. Siliceous stone particles were fully exposed in areas and particle fall-out was evident (Figure 8). Attack on the CAC specimens was the lowest mainly due to the influence of the calcium aluminate materials and to a lesser extent the dolomite aggregate on the activity of the thiobacillus bacterial colony. Calcium aluminate materials stifle the growth of the bacteria lowering the generation of sulphuric acid and prolonging the growth of the acid-loving thiobacillus thiooxidans responsible for the severe corrosion. On visual inspection, the negligible signs of attack on the CAC/alag™ and CAC/dolomite aggregate specimens are clear (Figure 8). Only a small area of exposed dolomite aggregate was visible on the CAC/dolomite aggregate specimen due to dissolution of the surrounding cement layer. Attack on the OPC/dolomite aggregate specimen was substantially higher (Figure 8). The cement skin was entirely removed and areas were noticeable in which severe attack was starting.

4 CLOSURE

Absence of acid-soluble aggregates in certain areas and areas where large amounts of sulphuric acid are generated throughout the year presents a serious problem for concrete sewer pipe manufacturers. Alternative means of extending the service life of concrete pipes in these areas is to either modify a siliceous aggregate mixture to resist the acid attack or use a special acid resistant concrete mixture to line the insides of sewer pipes.

A siliceous aggregate mixture not only requires modification of the cement binder to resist attack from acids but also a siliceous aggregate network to minimise fine and coarse particle fall-out thereby further slowing attack on the cement binder. A completely insoluble hydraulic cement binder is improbable due to the acid-soluble components occurring in hydrated cements. Acid resistance of cement binders is however improved with the use of calcium aluminate cement, which presents a degree of toxicity towards bacteria and prevents attack on the binder. Acid resistance of the cement binders is further improved with the inclusion of additional compounds, for example silica fume, which improves integrity of the cement binder in the acidic sewer environments. A robust siliceous aggregate network is achieved by varying the shape and size of siliceous crusher and filler sands.

A special concrete lining mixture that is acid resistant is easily cast into conventional concrete sewer pipes and therefore ideal to protect the dolomite aggregate pipes from severely aggressive sewer environments or siliceous aggregate pipes from sulphuric acid attack if no acid soluble dolomite aggregate is available. An effective lining material must dissolve at an extremely slow rate and also severely retard the activity of the thiobacillus bacteria. A promising material is CAC/alag™ aggregate mixture, which is currently being tested in a live sewer. A concern is the acid resistance of the CAC binder. It is speculated that the binder needs further modification as with the siliceous aggregate mixtures so as to prove more
resilient towards the sulphuric acid generated by auto-oxidation and toxic towards the acid-loving micro-organisms occurring in the sewers.

Figure 8: Attacked surfaces of a) OPC siliceous b) CAC alag™ aggregate c) CAC dolomite aggregate and d) OPC dolomite aggregate specimens exposed to a severely corrosive sulphuric acid sewer environment for 17 months

REFERENCES