Sewer concrete subjected to biogenic acid corrosion: analysis of concrete deterioration phases using QEMSCAN

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Abstract. QEMSCAN (Quantitative Evaluation of Minerals by Scanning Electron Microscopy) was used to analyse the evolution of cementitious phases of sewer concrete after biogenic acid attack. Two concrete mixes; a blend of Sulphate Resisting Portland Cement and Fly Ash (SRPC+FA) and Calcium Sulpho-Aluminate (CSA) cement, with calcite and siliceous aggregates, were subjected to a field sewer environment, with a maximum H2S gas concentration of 100 ppm, for about two years. After exposure, both concretes experienced thickness losses, with CSA indicating mass gain and SRPC+FA mass loss. QEMSCAN analysis results indicated that SRPC+FA was rich in calcium silicate hydrates in the intact zone, Mg-silicate in the transition zone, and Al-silicate, gypsum, and quartz in the deterioration layer. CSA contained ettringite and portlandite in the intact zone, gypsum and aluminate phases in the deterioration zone, while the transition zone was challenging to observe due to the superimposition of ettringite before and after the attack. It was concluded that, despite CSA showing a lower corrosion rate than SRPC+FA, it exhibited severe deterioration under QEMSCAN. Therefore, QEMSCAN is a potential tool for preliminary analysing of concrete microstructural phases under biogenic acid attack. However, it should be incorporated with other microstructural analysis tools.

1 Introduction

Biogenic corrosion - also known as microbiologically induced corrosion (MIC) – results from biological activities of Sulphur Oxidising Bacteria (SOB) on concrete sewer surfaces that produce sulphuric acid, thus corroding the concrete matrix and underlying steel reinforcement. Sewer environments provide favourable conditions for these bacteria to grow, such as ambient temperature, relative humidity, and energy. With wastewater consisting of biodegradable organic matter with sulphate compounds, and due to the depletion of dissolved oxygen, anaerobic reactions take place in the wastewater under the influence of Sulphate Reducing Bacteria (SRB) to produce Hydrogen sulphide (H2S) gas [1,2]. Turbulent flow conditions and high velocity facilitate the release of these gases to the sewer headspace. With the moisture absorbed by concrete sewer walls, H2S is adsorbed and subsequently oxidised to sulphuric acid by SOBs.

Consequently, this lowers the concrete pH, facilitating further SOB growth and producing sulphuric acid with a very low pH. Sulphuric acid reacts with the various hydration phases of the cementitious matrix to form deterioration phases such as ettringite and gypsum. Gypsum and ettringite are expansive products that lead to internal cracking and spalling of concrete, which provide sites for further acid penetration. Thus, concrete loses its structural integrity, increases porosity, and exposes the underlying steel reinforcement to corrosion [1,3,4].

Biogenic corrosion of the sewer structure causes both economic and environmental effects. Over time, cracks, erosion, spalling of sewer structures, and rebar corrosion can cause sewage leakage, leading to air, water, soil, and visual pollution and the eruption of waterborne diseases. These result in a significant increase in the direct cost of sewer system repair and rehabilitation and indirect costs linked to the loss of productivity of other functionaries and lost wages (social service interruption) due to the non-operating systems [5–7].

Before undertaking repair or rehabilitation of deteriorated sewer concrete structures, it is crucial to assess the sewer condition [8], analyse the nature of deterioration, and, most importantly, confirm that biogenic acid corrosion is the leading cause of the attack. Analysis of sewer conditions is accompanied by visual inspections using passive/semiautonomous robots controlled by a human inspector or fully autonomous robots requiring no human intervention [8]. Concrete samples are usually cored for microstructural analysis depending on the degradation severity. The

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microstructural analysis involves assessing the deteriorated concrete samples by studying concrete morphology and mineral composition of concrete before and after corrosion. With such information, the leading cause and the concrete compositions influencing the deterioration can be identified, thus aiding in understanding the overall attack mechanism. The analyses typically include X-Ray Diffraction Analysis (XRD), Scanning Electron Microscope (SEM) paired with Energy Dispersive Spectroscopy (EDS), and, sometimes, Thermo-Gravimetric Analysis (TGA).

XRD analysis is one of the most prominent analytical techniques for qualitative and quantitative analysis of crystalline phases in cementitious materials. It provides information such as the types and nature of crystalline phases, structural make-up of phases, degree of crystallinity, amorphous content, and orientation of crystallites[9]. In most cases, samples used for analysis are in the form of finely ground powders or flat surfaces [10]. However, applying this technique to concrete under biogenic acid corrosion might be challenging, especially when the corrosion products are insufficient or ineffectively collected for analysis or when the concrete contains a significant amount of aggregates. The analysis is possible if the corrosion products are carefully scraped from the corroded concrete, dried, ground, stored carefully to avoid carbonation, and then analysed [10].

The flat surface of the corroded concrete must be selected and cut to fit the XRD mould, then analysed in layers from the exposed surface into the concrete depth. The analysis provides information on minerals or phase composition of the deteriorated concrete without explicitly indicating how they evolve, migrate, or dissociate in the concrete zones (i.e., an intact zone, a transition zone, and a deteriorated zone). Additionally, the method is more effective on cement paste or mortar-based samples than on concrete-based samples containing abundant aggregate phases.

On the other hand, SEM analysis is performed chiefly with Energy-Dispersive X-ray spectroscopy (EDS), where images are generated by raster-scanning in a vacuum chamber [11]. A primary electron beam is focused on a sample. Depending on the electron detector mounted in the chamber, the sample can reflect three signals, i.e., secondary electrons (SE), backscattered electrons (BSE), and X-rays [11]. These signals assist in imaging and X-ray microanalysis, thereby examining and determining sample properties such as surface morphology, elemental composition, and spatial distribution of components. On concrete under biogenic acid corrosion, concrete morphology evolution before and after corrosion, concrete zonation and corrosion front can be identified and distinguished, and most importantly, elemental distributions of the concrete before and after corrosion can be observed [12–14]. However, the morphology and elemental distribution interpretation depend on the image analyser's knowledge and experience. Accompanying EDS provides only elemental distribution, which unfortunately requires expertise to identify the mineral phases associated with those elements [2,15].

With these challenges and limitations associated with XRD and SEM-EDS analysis, QEMSCAN (Quantitative Evaluation of Minerals by Scanning Electron Microscopy) is a viable tool that can provide combined information of XRD and SEM-EDS analysis on the concrete specimen under biogenic acid attack. QEMSCAN analysis uses a field emission gun-scanning electron microscope combined with high-resolution BSE and an automated SEM-EDS Spectral Analysis Engine (SAE) to collect the EDX spectrum of all elements contained in a sample at different analysed points [16]. With the aid of the elemental concentration method embedded in the iDiscover™ v.5.0 software, the identification and quantification of mineral phases with similar chemical compositions as the spectra can be achieved. The elemental concentration method is based on a database of 72 essential reference spectra collected from Species Identification Protocol (SPI) reference standards on several commercial SEM-EDS detector combinations [17]. Therefore, this study aimed to apply QEMSCAN analysis to analyse the evolution of cementitious phases of concrete when subjected to biogenic acid corrosion in sewers.

2 Methodology

2.1 Materials and concrete casting

Two types of binder systems supplied by LafargeHolcim (LH), France, were used in this study; a blend of 80% CEM I 52.5 N – SR3 (SRPC) and 20% Fly ash (FA) (i.e., SRPC+FA), and Calcium Sulpho-Aluminate (CSA) cement. The chemical compositions are shown in Table 1. According to EN 197-1[18], SRPC is a sulphate-resisting Portland cement with a C3A content of less than 3 % (SR3). FA substituted 20% of SRPC to produce a binder system which, according to [19], performed better than plain concrete in sewers. CSA cement used was Calumex® Quick, which improves resistance to sulphate attack and other aggressive environments. Crushed calcite (CaCO3) coarse and fine aggregates and siliceous sand were used as aggregates.

Table 2 shows the concrete mixes designed and cast by LH in France and then delivered as concrete cubes of 150 mm to the University of Cape Town civil engineering laboratory in South Africa for field sewer exposure.

After delivery, the cubes were plastic-wrapped and stored in the environmental room at 21±2°C and 60% relative humidity. At 28 days of age, three concrete cubes per mix were taken for saturated density and compressive strength testing (SANS 5863 [20]). The concrete had an average compressive strength of 44.8 ± 11.0 MPa and 40.3 ± 3.9 MPa, and an average saturated density of 2379 kg/m³ and 2320 kg/m³ for SRPC+FA and CSA concrete, respectively.

2.2 Concrete specimens for sewer exposure
Other concrete cubes were cored, epoxy-coated on their cylindrical surfaces, and then cut to obtain concrete discs of 70 mm diameter and 50 mm thickness. The concrete disc’s initial masses and dimensions were measured before exposure. After that, the specimens were fixed in a plastic basket for sewer exposure for two years.

The sewer site had an average H₂S gas concentration of 23.6 ± 9.3 ppm in autumn, 6.4 ± 2.0 ppm in winter, 6.8 ± 3.2 ppm in spring and 13.6 ± 8.5 ppm in summer. The maximum H₂S concentration was about 100 ppm. The sewer headspace temperature ranged between 15°C and 30°C, with the lowest values in winter and the highest in summer. Relative humidity was between 70% and 100%, with the highest readings in winter and the lowest in summer.

After two years of exposure, the specimens were retrieved from the site and taken to the laboratory for mass and thickness bulk measurements, and then a piece of corroded concrete from each mix was cut for SEM and QEMSCAN microstructural analysis.

### Table 1: Oxide composition of cementitious materials

<table>
<thead>
<tr>
<th>Binders</th>
<th>Oxide and composition, wt %</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>CaO</td>
</tr>
<tr>
<td>SRPC</td>
<td>67.95</td>
</tr>
<tr>
<td>CSA</td>
<td>41.75</td>
</tr>
<tr>
<td>FA</td>
<td>4.32</td>
</tr>
</tbody>
</table>

### Table 2: Concrete mix proportions – kg/m³

<table>
<thead>
<tr>
<th>Mix designation</th>
<th>SRPC+FA</th>
<th>CSA</th>
</tr>
</thead>
<tbody>
<tr>
<td>Binder systems</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Constituents</td>
<td>kg/m³</td>
<td>kg/m³</td>
</tr>
<tr>
<td>Binder</td>
<td>280</td>
<td>350</td>
</tr>
<tr>
<td>Fly Ash (FA)</td>
<td>70</td>
<td>0</td>
</tr>
<tr>
<td>Water</td>
<td>133</td>
<td>133</td>
</tr>
<tr>
<td>Fine aggregates</td>
<td>0/1 mm Siliceous</td>
<td>520</td>
</tr>
<tr>
<td></td>
<td>1.6/3 mm Calcite</td>
<td>520</td>
</tr>
<tr>
<td></td>
<td>3/6 mm Calcite</td>
<td>343</td>
</tr>
<tr>
<td>Coarse aggregates</td>
<td>6/11 mm Calcite</td>
<td>516</td>
</tr>
<tr>
<td>BASF-Glenium 7700 (% by mass, binder)</td>
<td>0.64</td>
<td>1.08</td>
</tr>
<tr>
<td>% Total binder</td>
<td>16</td>
<td>16</td>
</tr>
<tr>
<td>Theoretical density of concrete</td>
<td>2383</td>
<td>2383</td>
</tr>
</tbody>
</table>

### 2.3 Sample preparation for microstructural analysis

SEM and QEMSCAN analyses were conducted on a single sample extracted from a corroded concrete specimen. The sample for analysis was prepared following the standard sample preparation indicated in [10]; see Fig.1. Without disturbing the corroded surface, the concrete specimen from the site was immersed in isopropanol for about seven days to remove free water as the analysis was performed under a high vacuum. Before cutting and sectioning the specimen along its depth to obtain a small sample of about 20 x 20 x 5 mm, the specimen was dried under vacuum, followed by epoxy impregnation to support the microstructure and to avoid cracking during saw cutting. After impregnation, the specimen was cut and mounted in a mould with the studied surface, i.e., 20 x 20 mm cross-section, facing down. The sample in the mould was again epoxy impregnated, followed by surface polishing as recommended by [10] and [21]. Before setting the polished sample for analysis, its polished surface was coated with a thin carbon coat to avoid surface charging.

### 2.4 SEM and QEMSCAN analysis

SEM analysis to obtain BSE images was conducted using an FEI Nova NanoSEM 230 at the UCT Centre for Imaging and Analysis. BSE images were collected by a BSE detector in low vacuum mode with an accelerating voltage of 20 kV and beam intensity of 10 nA, and the areas of interest were selected for QEMSCAN analysis.

QEMSCAN analysis uses a combination of EDS and BSE brightness to identify the minerals present within the sample. The analysis was conducted using the QEMSCAN 650F machine, equipped with EDS, at an accelerating voltage of 25kV and a beam current of 10 nA. Mineral identification and distribution across the concrete microstructure were analysed using Species Identification.
Protocol (SIP) built in the iDiscover™ v.5.0 software, according to [16,17].

![Concrete sample from the sewer exposure](image1)

**Fig. 1:** A schematic indicating sample preparation for SEM and QEMSCAN analysis from the concrete specimens exposed in the sewer under biogenic acid corrosion for two years.

![Location where a sample for SEM & QEMSCAN analysis was cut](image2)

![SEM & QEMSCAN analysis sample to be epoxy impregnated and polished](image3)

![Epoxy impregnated and surface polished sample](image4)

**Table 3:** Summary of mass and thickness measurement of concrete exposed to the sewer site for two years

<table>
<thead>
<tr>
<th>Concrete Mix</th>
<th>Mass, in g</th>
<th>% Change</th>
<th>Thickness, in mm</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Initial</td>
<td>Final</td>
<td>Change</td>
</tr>
<tr>
<td>SRPC+FA</td>
<td>459.0 ±</td>
<td>444.6 ± 4.0</td>
<td>-3.22 ± 0.90</td>
</tr>
<tr>
<td></td>
<td>3.3</td>
<td></td>
<td>51.78 ± 0.54</td>
</tr>
<tr>
<td></td>
<td>45.08 ±</td>
<td>4.0</td>
<td>5.56 ± 1.05</td>
</tr>
<tr>
<td>CSA</td>
<td>459.4 ±</td>
<td>460.0 ±</td>
<td>+1.22 ±</td>
</tr>
<tr>
<td></td>
<td>2.3</td>
<td></td>
<td>50.92 ± 3.60</td>
</tr>
<tr>
<td></td>
<td>48.95 ±</td>
<td>3.6</td>
<td>1.97 ± 0.59</td>
</tr>
</tbody>
</table>

3 Results and Analysis

3.1 Mass and thickness loss

Table 3 summarises the mass and thickness measurements of concrete specimens after being exposed to the sewer site for two years. The mass change was -3.22 ± 0.90% for SRPC+FA and +1.22 ± 1.23% for CSA of the original mass of the concrete specimen. These results indicate that SRPC+FA concrete experienced mass loss, while CSA concrete experienced mass gain while also showing a continuous build-up of corrosion products on its surface.

The mass loss for SRPC+FA was associated with substantial biogenic acid corrosion. The mass gain for CSA concrete was associated with moisture absorption and corrosion products accumulated within the concrete voids and at the concrete-epoxy coating interface. The acid penetration through the surface and at the concrete-epoxy coating interface influenced the formation of corrosion products that appeared as blisters on the epoxy coating surface.

Thickness loss was 5.56 ± 1.05 mm for SRPC+FA and 1.97 ± 0.59 mm for CSA after two years of exposure. Therefore, despite CSA showing a mass gain, it experienced thickness loss at a lower rate than SRPC+FA concrete. These thickness losses were equivalent to initial corrosion rates of 2.78 ± 0.74 mm/yr and 0.99 ± 0.42 mm/yr, respectively.

3.2 SEM analysis results

SEM-BSE images aim to study concrete morphology evolution after corrosion, to identify and distinguish the affected zones, i.e., concrete zonation and corrosion front, and to evaluate concrete altered depth that could not be measured under thickness measurements.

In both concretes, two distinct zones were observed, i.e., an intact zone and an altered zone; the latter is further subdivided into a deteriorated zone and a transition zone.
The transition zone is a thin layer between the intact and deteriorated zone.

### 3.2.1 SRPC+FA concrete

Fig. 2 shows the SEM-BSE image for SRPC+FA concrete after two years of exposure to the sewer site. In Fig. 2 (A), the altered zone is about 1.0 mm in width and consists of loose fine aggregate particles and a fragmented cement matrix with high porosity. However, the altered depth differs between the cement matrix and coarse aggregate particles. The altered depth of the coarse aggregate particle is approximately 0.2 mm, which is less than in the cement matrix. Along with the aggregate particle, i.e., calcite, the acid reacts uniformly with the exposed aggregate surface without leaving any residue [22]. However, the attack progresses differently with the aggregate surface in contact with the altered cement matrix, in this instance, on the top side of the particle. The aggregate particle dissolves on the front face, loses cohesion as the altered matrix loses its integrity, and dislodges from the cement matrix. On the other hand, quartz fine aggregate particles do not react with the acid but detach from the cement matrix in the altered zone. This behaviour of aggregate is to be confirmed by QEMSCAN analysis results.

Fig. 2 (B) shows cracks in the altered zone through calcite aggregate particles and the cement matrix. The cracks indicate further acid penetration into the concrete, leading to loss of cement matrix cohesion and aggregate detachment. Fig. 2 (C) shows two fly ash particles in the altered zone: bright and dark grey particles. The dark particle contains microcracking as a sign of disintegration, and the bright one seems intact [23]. Since the fly ash particles used in this study consisted of silica and alumina [24], the dark particle may be alumina-rich, while the bright may be silica-rich, which explains the dark microcracking particle.

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Fig. 2. SEM-BSE image for SRPC+FA concrete after two years of exposure to the sewer site

### 3.2.2 CSA concrete

CSA concrete, by contrast, has a different concrete microstructure because it contains a higher amount of...
ettringite than other cementitious hydrates[25]. Fig. 3 (A) shows an altered zone about 1.26 mm in width with increased porosity and loss of cohesion. In the altered zone, the cementitious particles are disaggregated, while in the intact concrete, they remain compact. The brightness of both zones is similar, making it difficult to demarcate between the altered and intact zones, especially in the cement matrix. However, the two zones can easily be distinguished in the aggregate. As in the previous concretes, calcite aggregates dissolve and crack at the surface, while quartz remains unaltered.

It was observed in section 3.1 that CSA concrete experienced thickness loss and mass gain. The reason was related to the increasing formation of ettringite phases in the pore and void spaces as the hydration of CSA cement continued due to absorbed moisture and organic matter penetration the concrete microstructure [26]. In this concrete, anhydrous CSA cement remained in the system after initial hydration, which could be activated for further hydration under a sufficient supply of moisture from the sewer. The presence of excess voids compensated for the increased volume by providing more space for the formation of ettringite without causing substantial expansion of the concrete matrix. Fig.3 (B) shows ettringite deposits in the CSA concrete voids.

Fig.3 (C) shows black organic material, which appears as strands on the cross-section, rich in carbon and oxygen. This indicates that these organic materials penetrated the concrete microstructure, possibly due to the high porosity in the concrete.

3.3 QEMSCAN analysis results

The QEMSCAN analysis gave concrete mineralogical phase distribution and evolution from the altered zone to the intact zone. The analysis assisted in understanding the role of the cementitious phase under biogenic acid attack. The phases of interest were calcite and quartz for the aggregates, and for the cement matrix, were calcium silicate (Ca-silicate), silica (donated as fine quartz particles), calcium aluminate (Ca-aluminate), portlandite, gypsum, ettringite, gibbsite and on some occasions, magnesium silicate (Mg-silicate), and aluminium silicate (Al-silicate) depending on the type of binder system. Therefore, the following discussions indicate the findings in each binder system.

3.3.1 SRPC+FA concrete

Fig.4 shows a QEMSCAN analysis of SRPC+FA concrete after deterioration. The first image in the first row indicates a general distribution of mineralogical
phases in the concrete microstructure based on the SEM-BSE image, with the legend indicating each phase's colour, percentage weight, and volume. Other images depict the distribution of selected phases in the microstructure.

In terms of phase composition, calcite and quartz (45.27% and 29.31%, respectively) were the main observed phases, which were associated with about 80% of the concrete composite being the aggregate component. In the cement matrix, the percentage weights of mineralogical phases from the highest to the lowest were 9.06% Ca-silicate, 4.83% Mg-silicate, 4.21% Al-silicate, 1.95% Fe-phases, 1.81% gypsum, 1.56% portlandite, 0.96% gibbsite, and 0.58% ettringite.

As discussed in section 3.2.1, the intact and altered (i.e. transition and deteriorated) zones were easily distinguished in this analysis based on the mineralogical distribution. It was evident that the intact zone was dense, mainly containing calcium silicate in the cement matrix. Unlike the SEM analysis, in this analysis, the transition zone was observed between the intact zone and the deteriorated zone, mainly consisting of a continuous and consistent layer of Mg-silicate and some gypsum deposits.

This indicated a possibility of migration of magnesium ions, which react with silicate after calcium silicate decalcification by the acid penetration. With that, Mg-silicate may offer some sort of inhibiting action to the acid-producing bacteria due to its ability to maintain a higher surface pH [27]. On the other hand, the deteriorated zone was very porous, consisting of disintegrated cementitious phase particles of Al-silicate, gibbsite, gypsum, and fine silica particles (observed as fine quartz particles).

Calcite seemed to disintegrate immediately after the concrete composite started to lose its integrity, that is, at the interface of the transition zone and deteriorated zone to produce more gypsum [28]. It is possible that at the interface, the pH of the concrete was lower than 8.0 as calcite dissolves at a pH of less than 8 [29]. On the contrary, quartz aggregates detached from the transition zone, while finer disintegrated quartz was observed at the limit of the deteriorated zone [28]. The finer quartz particles were associated with a silica-rich layer [30] after the disintegration of Ca-, Al- and Mg-silicate since it was challenging to map them separately.

Therefore, it can be concluded that the main cementitious phase before the attack is calcium silicate (expected), which may contain some aluminium, iron, and magnesium oxides. Once sulphuric acid is generated on the exposed concrete surface, it leads to decalcifying calcium silicate [31]. As a result, magnesium ions migrate into the transition zone to react with silicate, then aluminium ions in the deteriorated zone form Al-silicate, while some ions form gibbsite. On the other hand, gypsum is observed in the transition zone along with Mg-silicate and the deteriorated zone along with gibbsite and Al-silicate. Gypsum precipitates from the reaction between...
calcium ions (from the decalcification of calcium-rich phases) and sulphate ions (from the attacking acid) [32].

3.3.2 CSA concrete

Fig. 5 shows a QEMSCAN analysis of CSA concrete after deterioration. The first image in the first row indicates a general distribution of mineralogical phases on the concrete microstructure based on the SEM-BSE image, with the legend indicating each phase's colour, percentage weight, and volume. Other images depict the distribution of selected phases on the microstructure.

Besides a high composition of calcite and quartz from the aggregate (44.31% and 32.93%, respectively), the cementitious matrix consisted of a higher percentage of ettringite phases of about 6.17%, followed by 6.00% portlandite, 4.18% Al-silicate, 3.89% CaAl-silicate, 1.18% Fe-phases, 0.74% gypsum, and 0.57% gibbsite. This shows that the main hydration phase of this concrete is ettringite, as discussed earlier, with portlandite and some aluminate phases.

The preparation of CSA concrete had been challenging during compaction, which resulted in significant entrapped air voids. Significant amounts of black organic materials also appeared as strands observed throughout the cross-section, as shown in Fig. 3 (C). Since they are rich in carbon and oxygen, QEMSCAN analysis is limited in analysing these elements; thus, they were considered as background. However, the images easily identified concrete zonation based on the mineralogical phase distribution. The area which appeared dense was considered an intact zone, and the porous zone was considered an altered zone. The transition zone was not easily distinguished from the deteriorated zone, possibly due to the superimposition of new ettringite formation (as a result of acid penetration and subsequent reaction of gypsum and calcium aluminate bearing phase [33]) in the transition zone, which is similar to ettringite in the intact zone.

Ettringite and portlandite were only observed in the intact zone, while calcium aluminium silicate and gibbsite were observed in both intact and altered zones. On the contrary, gypsum was mainly observed in the altered zone. Calcite and quartz behaved similarly regardless of the binder system, while the Mg-silicate layer was not observed in this concrete. As mentioned in section 3.2.2, the voids near the exposed surface were filled with ettringite, then gibbsite and gypsum, while those in the intact zone were filled with only ettringite. This indicates that once the acid penetrates and the concrete pH is lower than 10.7 [34,35], no ettringite was found within the deteriorated zone due to the rapid thermodynamics of gypsum formation [36]; as a substitute, gypsum and gibbsite were observed. Due to minimal gibbsite and gypsum, it was challenging to observe in the figure.

Therefore, it can be concluded that CSA performance was associated with ettringite transformation to gibbsite, which contributes to the biogenic acid resistance, as demonstrated in the Calcium Aluminate Cement (CAC) [37–39]. Gibbsite can offer some mechanical or physical integrity to the deteriorated layer, thereby providing a barrier for further attack until the concrete surface pH is less than 3 [19,26].

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Fig. 5: QEMSCAN analysis of CSA specimens subjected to the sewer site for two years. The first image indicates a general distribution of concrete mineralogical phases on the concrete cross-section based on the SEM-BSE image, with the legend indicating the colour.
3.4 General discussion and summary

The evolution of concrete cementitious phases under biogenic acid corrosion in sewers was studied using QEMSCAN analysis. Two concrete mixes with SRPC+FA and CSA were exposed in the sewer site with the maximum H₂S gas of 100 ppm, temperature between 15°C and 30°C, and relative humidity between 70% and 100%.

After two years of exposure, SRPC +FA concrete experienced a mass loss of 3.22 ± 0.90% (of its original mass). CSA concrete experienced a mass gain of 1.22 ± 1.23%. SRPC+FA mass loss was associated with substantial concrete loss due to sewer corrosion. In contrast, CSA mass gain was linked to moisture absorption and corrosion products accumulated within the concrete voids and at the concrete-epoxy coating interface. On the other hand, both concretes experienced thickness losses equivalent to the corrosion rates of 2.78 ± 0.74 mm/yr and 0.99 ± 0.42 mm/yr for SRPC+FA and CSA concrete, respectively. Mass and thickness bulk measurements indicated that CSA performed better than SRPC+FA concrete.

Under SEM analysis, both concretes showed two distinct zones, i.e., an intact zone and an altered zone. SRPC+FA altered zone was further observed as two zones, the transition zone and the deteriorated zone, while identifying a CSA transition zone was challenging because it had similar phases (i.e., ettringite) as the intact zone. Altered zone depths of about 1.06 mm and 1.26 mm were observed for SRPC + FA and CSA concrete, respectively.

In cementitious phase evolution, QEMSCAN analysis indicated that the concretes consisted of a significant amount of calcite and quartz, with 80% of the concrete composite aggregates. SRPC+FA concrete was rich in calcium silicate hydrates in the intact zone, Mg-silicate in the transition zone, and Al-silicate, gypsum and quartz fines in the deterioration zone. On the other hand, CSA concrete contained ettringite and portlandite in the intact zone, while gibbsite, gypsum and other aluminate phases were observed in the deteriorated zone. The poorer performance of SRPC+FA was associated with the decalcification of Ca-silicate because of its susceptibility to biogenic acid attack [40]; however, the formation of Mg-silicate in the transition zone possibly decelerated its attack [27]. CSA's better performance was associated with ettringite disintegration to gibbsite, which contributes to biogenic acid resistance, as demonstrated in CAC cement. Therefore, despite the CSA concrete showing better performance in mass and thickness bulk measurements, an altered zone is still observed, implying that it was experiencing deterioration, although at a slower rate than SRPC+FA concrete. Finally, it was concluded that QEMSCAN analysis was a very appropriate tool for analysing the cementitious phase evolution of concrete under sewer biogenic acid attack, although it should be used along with other microstructural analysis tools for the best results.

4 Conclusion

Based on observations given in this paper, and subject to the experimental details such as 2 years of exposure in the sewer environment, the following was concluded:

- Mass and thickness bulk measurements indicated that CSA performed better than SRPC+FA concrete, with an average corrosion rate of 2.78 ± 0.74 mm/yr and 0.99 ± 0.42 mm/yr for SRPC+FA and CSA concrete, respectively.
- Under SEM and QEMSCAN analysis, SRPC+FA concrete showed three distinct zones, i.e., the intact zone, the transition zone, and the deteriorated zone, while CSA concrete showed the intact zone and deteriorated zone only: the transition zone was challenging to observe due to similar ettringite phases as in the intact zone.
- SRPC+FA concrete was rich in calcium silicate hydrates in the intact zone, Mg-silicate in the transition layer, and Al-silicate, gypsum and quartz fines in the deterioration layer.
- CSA concrete contained ettringite and portlandite in the intact zone, while gibbsite, gypsum and other aluminate phases were observed in the deteriorated zone.
- SRPC+FA's poorer performance was associated with the decalcification of Ca-silicate because of its susceptibility to biogenic acid attack; however, the formation of Mg-silicate in the transition zone possibly decelerated its attack.
- CSA's better performance was associated with ettringite transformation to gibbsite, which contributes to the biogenic acid resistance.
- Despite the CSA concrete showing better performance in mass and thickness bulk measurements, microstructure analysis showed that it was experiencing deterioration, although at a slower rate than SRPC+FA concrete.
- Finally, QEMSCAN analysis is an appropriate tool for analysing the cementitious phase evolution of concrete under sewer biogenic acid attack.

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