

Biogenic Sulfuric Acid Attack and Case Studies

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Biogenic sulfuric acid attack (BSA) is probably the most common and most severe biodegradation mechanism affecting concrete. BSA causes widespread global infrastructure deterioration, and it is reported to be responsible for damages totaling about 10 billion dollars per year in the United States alone.^{1,2} Several different names have been attributed to the distress, including microbially or microbiologically induced deterioration (MID), microbially induced corrosion (MIC), biogenic sulfide corrosion, and hydrogen sulfide corrosion. Identifying the characteristics of BSA distress can raise awareness of the distress and its impact. Improved understanding of the mechanisms and rate controlling factors is crucial in designing new, durable concrete structures and mitigating existing concrete against the deterioration.

BSA involves cycling different sulfur species (of various valence) and eventually concentrating sulfuric acid on the concrete surface of sewer systems, waste digesters, chimneys, or similar structures, under the influence of various bacteria (Fig. 1). Normal sewage effluents have a pH of 5 to 8, which is not low enough to severely degrade concrete in contact.³ However, anaerobic bacteria (for example, *Desulfovibrio* species) in the sewer system can decompose inorganic and organic sulfur compounds (for example, sulfate), releasing hydrogen sulfide (H_2S) gas to the headspace above the effluent/sludge waste. The hydrogen sulfide is absorbed into a surficial moisture film on inner walls of concrete pipes, which contain aerobic bacteria such as thiobacilli. Hydrogen sulfide is oxidized into sulfur and eventually into sulfuric acid by bacterial metabolism. The sulfuric acid reacts with the cementitious paste of concrete (as well as steel and carbonate aggregate, if present) and causes deterioration.

Research has been devoted to designing and developing new durable concrete with good resistance to BSA.⁴ Calcium aluminate cement, calcium sulfoaluminate cement, and geopolymers are reported to exhibit better performance in resisting BSA than portland cement.⁵ Concrete mixtures with carbonate aggregates also perform better relative to mixtures with siliceous aggregates,⁶ due likely to the sacrificial role or greater acid-neutralizing effect of carbonate aggregates. Coatings, polymer linings, surface treatments, antimicrobial and mineral admixtures, running the pipes at full capacity, or decreasing the effluent residence time are all measures that reportedly reduce the detrimental effects of BSA.

BSA deterioration is generally manifested as exfoliated surface loss with aggregate exposed, discoloration, and progressively altered zones with varying composition and texture in the existing concrete. This article discusses two case studies:

- A relatively new waste digester; and
- A decades-old sewer tunnel structure.⁷

The focus of the discussions is on distinct compositional

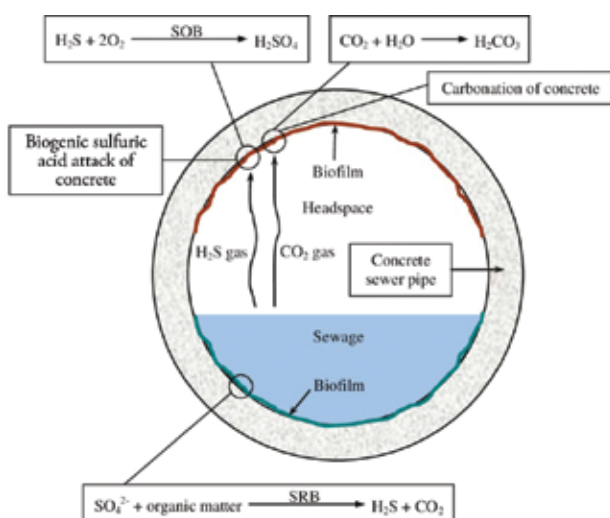


Fig. 1: Schematic representation of biogenic sulfuric acid attack (BSA) mechanism in a concrete sewer pipe (after Reference 2), where SOB is sulfur-oxidizing bacteria and SRB is sulfur-reducing bacteria. Elemental sulfur can be formed via chemical reaction: $2 H_2S$ (gas) + O_2 (gas) \rightarrow $2 S$ (solid) + $2 H_2O$ (liquid)



Fig. 2: Fractured concrete roof panel. BSA-caused deterioration manifested as paste color lightening and weakening along the cell perimeter (arrows) as well as corroded and broken prestressing strands

and textural characteristics and variations from the exposed surface to sound concrete in these BSA-affected structures.

Case Study I: Manure Digester

The concrete roof of a methane production facility failed prematurely because of BSA-caused corrosion. The roof consisted of a topping slab supported on hollow-core precast prestressed concrete planks. The concrete planks were apparently manufactured using an extrusion fabrication method, resulting in large amounts of irregular, interconnected, entrapped air voids in the concrete. Field investigation revealed that the plank concrete suffered severe deterioration throughout the roof area, with up to 5 in. (127 mm) of localized spalling from the underside and with broken or corroded prestressing strands (Fig. 2).

Concrete cores extracted from the top surface to the mid-depth of the planks (that is, the upper half of the planks) were studied using petrographic methods. The plank concrete exhibited distinct deterioration along the perimeter of the empty cells (cores) to a maximum depth of about 20 mm (0.8 in.), shown in Fig. 2 to 6. The deterioration appeared to be progressive, starting from the cell surface and propagating to the interior web and flange concrete to the side and above each cell. No deterioration or alteration of the concrete matrix was observed in the topping concrete.

Material layers or alteration zones from the cell surface to the interior concrete included:

- An elemental sulfur (S) layer, approximately 1 mm (0.04 in. or 40 mils) thick, at the perimeter of the cell (Fig. 3 and 4). The layer comprised many thin sublayers and exhibited an overall banded or lamination texture. Acicular sulfur crystals occurred and aligned perpendicular to the banding or the cell surface. Generally, no cement paste or aggregate particles were present in the sulfur layer. The layer did not appear to have been derived or altered from concrete or exhibit evidence of concrete constituents. The

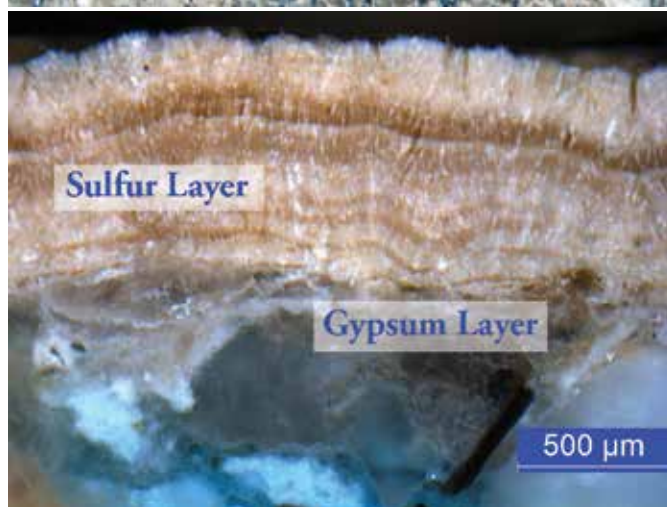
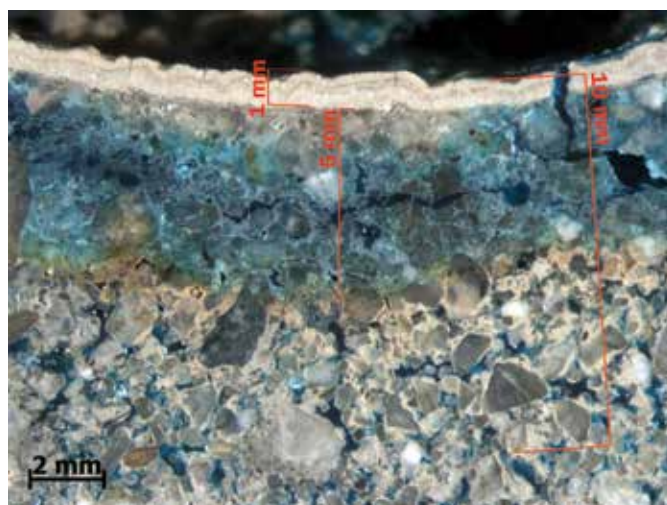


Fig. 3: Close-up views of near-surface concrete subjected to BSA with a banded sulfur layer (buff or pale white); a porous, weak, heavily paste-depleted zone; a brown carbonated front; and sound concrete. Blue epoxy applied in sample preparation readily soaked into the porous altered paste but not much into the dense, unaffected concrete except for large voids (Note: Different lighting condition and greater magnification for the bottom photo)

surface of the sulfur layer was smooth and did not appear to have ever been in direct contact with the effluent or waste sludge;

- Large, frequently tabular euhedral gypsum crystals behind the sulfur layer. The thickness of the large gypsum zone was approximately 0.2 mm (8 mils), shown in Fig. 3 and 4. Only a few aggregate particles were present in the gypsum layer. Large euhedral gypsum crystals are presumed to have recrystallized from solution, and the presence of the large crystals (as well as the sulfur layer described previously) would indicate a long period of a stagnant, nonturbulent environment;
- A zone behind the large gypsum layer of intimately mixed microcrystalline gypsum and amorphous silica-alumina gel that encased aggregate particles. The thickness of this

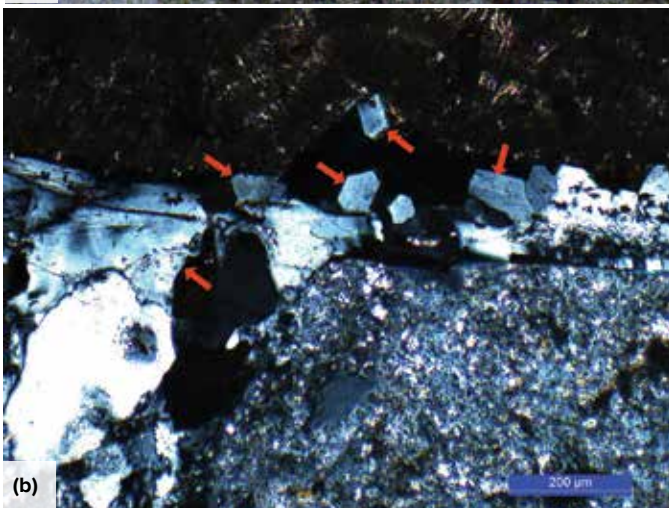
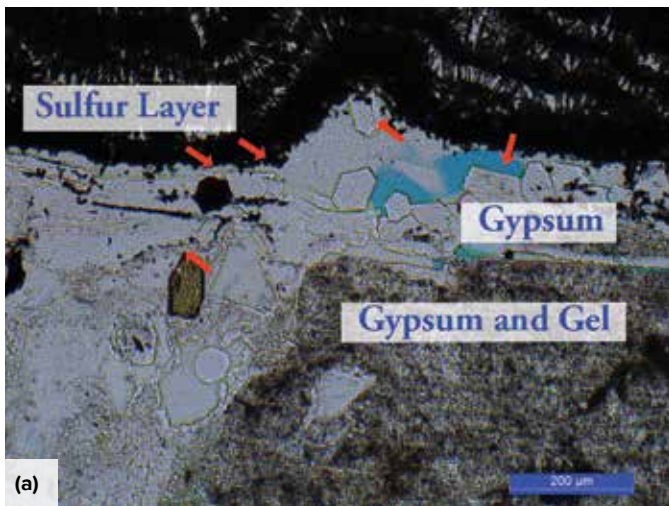


Fig. 4: Thin-section photographs show a sulfur layer (black) backed by large euhedral tabular gypsum (red arrows), and a microcrystalline gypsum and silica gel zone: (a) plane-polarized light; and (b) cross-polarized light

zone ranged from less than 0.1 to 0.6 in. Gypsum and gel materials had almost fully replaced portland cement paste in the zone. No residual cement particles, calcium hydroxide, or normal calcium silicate hydrate (CSH) paste were observed in the zone. Abundant surface-parallel cracks and microcracks were present. Also, sand particles frequently exhibited cracks that were filled with gypsum. Peripheral/rim cracks surrounding aggregate particles were also frequently lined with gypsum. Materials in this zone were pale white and overall porous, soft, and friable. No carbonation or carbonated products were observed. The alteration in this zone was considered complete or near complete;

- A thin brown-orange discolored layer or line less than 0.05 in. thick, which likely represents the reaction front and signifies the bottom of the severely deteriorated concrete. The discoloration or staining appeared to be mainly related to ferrite in the cement paste that perhaps

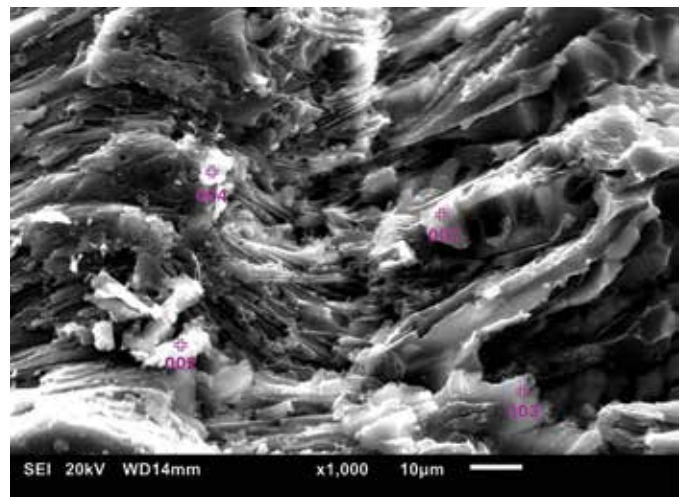


Fig. 5: Secondary electron image (SEI) of sulfur deposit on BSA-affected plank concrete. The composition of the deposit was confirmed using energy dispersive X-ray spectroscopy

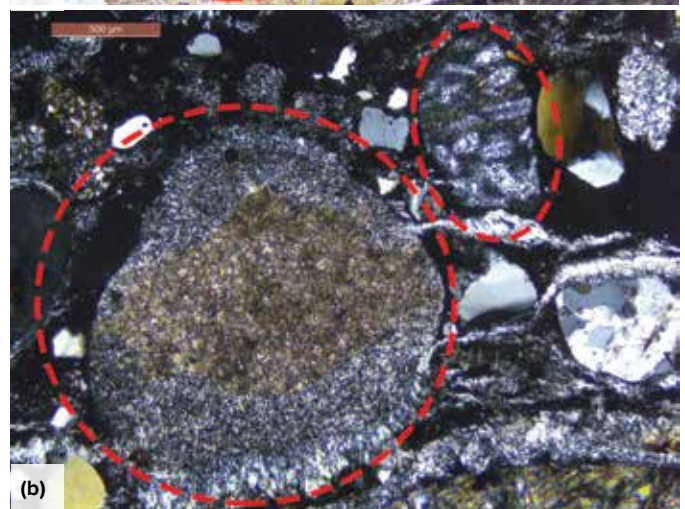
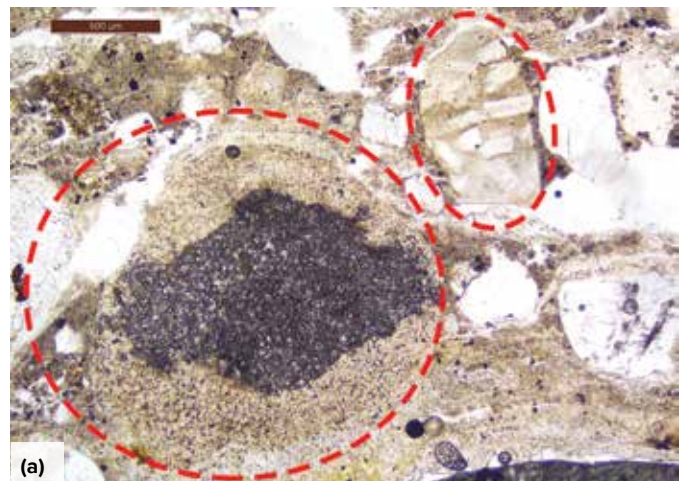


Fig. 6: Thin-section photo shows two carbonate sand particles (circled) partially replaced by gypsum: (a) plane-polarized light; and (b) cross-polarized light. Quartz/quartzite and other siliceous particles were not chemically affected by the acid attack but could frequently exhibit cracks lined with gypsum



Fig. 7: Sewer tunnel with exposed second mat of steel reinforcement. Top concrete and the first mat of steel reinforcement were reportedly lost to the existing surface (from Reference 7)

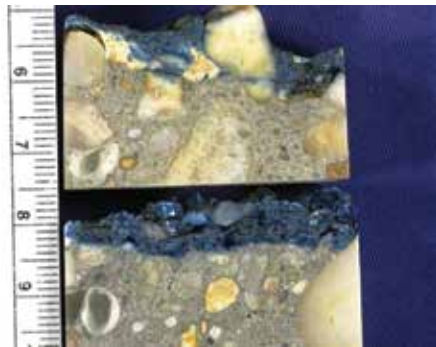


Fig. 8: Close-up views of the near-surface region of the tunnel concrete. The depth of affected paste is well defined by the visible change in color and appearance of the degraded cement paste. Blue epoxy readily soaked into the porous off-white or pale-yellow altered paste but not into the dense, unaffected body concrete. Scale is in millimeters

was affected by the acidic pore solution;

- An intensely carbonated zone, up to 0.5 in. thick, behind the brown-orange line. Cement paste was severely carbonated. Gypsum was occasionally observed in voids or cracks. However, no significant reduction in paste hardness was observed; and
- Sound, partially carbonated bulk concrete at a depth of up to 0.8 in. from the exterior surface of the sulfur layer. There was no apparent depletion of calcium hydroxide associated with the carbonation, probably due to an overall low calcium hydroxide content

that would be associated with a low water-cement ratio (w/c) concrete mixture.

The described characteristics are generally consistent with widespread distress caused by BSA. BSA deterioration is generally more severe for concrete exposed to closed gas/air headspace (that is, the “crown” of a sewer pipe or, in this case, the roof soffit of the subject digester, which was not submerged) compared to concrete that remains submerged in the effluent/waste, due to accumulation of H_2S gas in the atmosphere. This differential deterioration can be used to distinguish general acid attack from BSA-caused acid attack.

A third concrete core from the project exhibited no deterioration to a minimal deterioration layer that was typically less than 2 mm (0.08 in.) thick in the cell concrete, based on the visual examination. The exposure condition for this concrete core is not known. Localized variations in depths of deterioration around a specific cell were noted and were mainly related to localized variations in microporosity, void content and connectivity, and paste volume. No soffit portions of the planks were provided for comparison.

Case Study II: 100-Year-Old Tunnel

Concrete from a 100-year-old buried tunnel structure exhibited severe discoloration, spalling, and steel reinforcement corrosion. The interior surface of the tunnel showed a severely corroded reinforcement mat, reportedly the second layer of reinforcement (Fig. 7). Cored concrete studied in the laboratory exhibited overall compositional and textural characteristics similar to those discussed in Case Study I (Fig. 11 and 12 from Reference 7), except that the elemental sulfur layer was not observed. The BSA-affected layers were thin, typically about 0.2 in. in total thickness. Concrete in the exterior of the structure appeared to be in good condition and did not exhibit BSA-related or other distress. The tunnel concrete appeared to have been

batched with a low w/c that resulted in hard and dense paste (Fig. 8).

BSA: Conventional Sulfate Attack or Not?

The two case studies and other publications indicate that BSA deterioration rates may vary substantially. The rate of deterioration in the waste digester was high, while that in the tunnel was quite low. Major contributing factors for the rapid deterioration noted in Case I may include the frequently interconnected voids associated with the extrusion production process, failed or defected protective coating layers, relatively high average temperatures within the digester, possible high sulfur content in the waste, or long residence time of the waste in the facility.

In describing BSA, De Belie⁸ and others¹ state that sulfuric acid reacts first with calcium hydroxide in concrete to form gypsum. The gypsum then reacts with monosulfate to form ettringite, resulting in a large volume expansion that causes internal pressure and deterioration of the concrete matrix.^{1,8}

Formation of ettringite through the reaction between gypsum and calcium aluminate hydrate (monosulfate) is also a major reaction of “conventional” or “classical” sulfate attack.^{3,9,10} However, ettringite or thaumasite, observed in other forms of sulfate attacks,^{11,12} were not detected in the deteriorated zones in our BSA case studies. These phases are considered unstable at pH levels below 10.^{9,10,13} Values of pH lower than 4 were confirmed in the BSA-affected zones using litmus tests. Measured pH values were approximately 2 after concrete coupons were exposed to sewer environments for 100 days and longer.¹⁴ Concrete suffering from BSA often did not exhibit evidence of expansion.

BSA appears to be mainly an acid attack with involvement of microbiological activities, resulting in a progressive sectional loss and severe reinforcement corrosion. Superimposition with the conventional sulfate attack due to formation of ettringite did not appear to have taken place based on observations

from the two case studies and other similar projects. Gypsum appears to be a stable end product resulting from BSA, instead of a reactant or an intermediate material to produce ettringite as in classical sulfate attack, based on the case studies reported here and many of our other similar projects. Gypsum and silica gel layers formed on the exterior surface of concrete are anticipated to slow down the deterioration.

Summary

BSA is an acid attack caused or promoted by involvement of microbiological metabolism. BSA can cause significant physical, chemical, and mechanical changes that may result in huge maintenance and rehabilitation costs, compromise serviceability, and reduce the service life of affected structures. The distress is manifested as paste discoloration,

softening, and progressive sectional loss and accelerated corrosion of embedded steel reinforcement. Affected concrete exhibits altered zones with distinct compositional and textural characteristics. These altered zones can be effectively assessed by petrographic studies in accordance with ASTM C856, “Standard Practice for Petrographic Examination of Hardened Concrete.”

Laboratory studies can reveal or confirm the distress mechanism and determine the maximum depth of affected concrete. Furthermore, field and laboratory studies may also help assess deterioration rates and test the resistance of materials to the distress.

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Note: Additional information on the ASTM standard discussed in this article can be found at www.astm.org.

Selected for reader interest by the editors.



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