<u>HYDROGEN SULFIDE REMOVAL FROM BIOGAS</u> Part 2A: Microbial underpinnings of H₂S biological filtration

September 2016

BIOLOGICAL UTILIZATION OF H2S

Cornell University

Sulfur oxidizing bacteria (SOB) are lithoautotrophs; lithos meaning rock or mineral, for their ability to feed on elemental sulfur (S⁰); *autotroph* meaning self-feeding, for their ability to produce the complex compounds needed for cell growth [carbohydrates, proteins, fats, nucleic acids] from simple substances [energy from hydrogen sulfide (H_2S) and oxygen (O_2) , and carbon from carbon dioxide (CO_2)]. The biological breakdown of H₂S can be described by reactions $1 - 4^{[1]}$.

 $H_2S \leftrightarrow H^+ + HS^-$ (non-biological) (1)

 $HS^- + 0.5 O_2 \rightarrow S^0 + OH^-$ (biological) (2)

 $\mathrm{HS}^{-} + 2 \mathrm{O}_{2} \longrightarrow \mathrm{SO}_{4}^{2-} + \mathrm{H}^{+} \, (\mathrm{biological}) \tag{3}$

 $SO_4^{2-} + H_2O \rightarrow H_2SO_3 + O_2 \text{ (non-biological)}$ (4)

Using biotrickling filters (BTFs) as an example, when O_2 from air is limiting (reaction 2) S^0 is preferentially produced. When O_2 is not limiting (reaction 3) sulfate (SO₄) is preferentially produced. Elemental sulfur will accumulate in a BTFs. This is not ideal and is why the media needs to be removed and cleaned several times a year. Sulfate, however, will dissolve in water and form sulfuric acid (reaction 4), the acid that makes the pH inside a BTFs so low. The formation of the acid is preferred as the dissolved sulfur can be flushed from the BTFs and doesn't accumulate.

Anaerobic biofilters can be designed where SOBs use nitrate (NO₃) instead of O₂ (reactions 5 & 6). As O₂ in air, unlike NO₃-salts, is freely available, anaerobic H₂S removal from biogas is not typically used.

 $3H_2S + NO_3 \rightarrow 3S^0 + 0.5N_2 + 3H_2O \text{ (biological)}$ (5)

 $3H_2S + 4NO_3^- \rightarrow 3SO_4^{2-} + 2N_2 + 6H^+ (biological)$ (6)

OPTIMAL SOB GROWTH CONDITIONS

SOB belong to several different groups of bacteria known as genera. These include the Acidithiobacillus, Halothiobacillus, Paracoccuc, Sulfurimonas, Thiobacillus, and optimal Thiomonas. The growth temperatures for these genera are 82-95°F. Most SOB have optimal activities at pH 6-8. At neutral pH, species of Thiobacillus are typically dominate in BTFs. Some SOBs have optimal activities under more acidic conditions (pH 2-4). BTFs operated under acidic conditions are typically dominated by species in the genus Acidithiobacillus like Acidithiobacillus thiooxidans (Figure 1.)^[2].

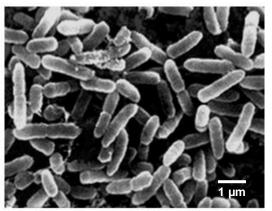


Figure 1. Scanning electron micrograph of *A*. *thiooxidans*^[3].

BIOFILMS

SOB bacteria typically grow as *biofilms*, or aggregations of cells, their metabolites and deposits of their wastes (S^0), attached to the surfaces of BTF media. These biofilms help protect SOB from acidic conditions while providing enhanced surface area for desulfurization. Excessive biofilm growth and the deposition of S^0 can clog BTFs (Figure 2.).



Figure 2. Simplified biofilm growth cycle. The rods represent the SOB, the green represents their metabolites and wastes. Note how the cells are embedded in the biofilm and how this growth form can increase surface area.

SOB INOCULATIONS & MICROBIAL COMMUNITY INTERACTIONS

Biotrickling filters are typically inoculated with SOB to reduce start-up time. Systems can be inoculated with manure and activated sludge, but typically specially developed bacterial cultures are used. As BTF are nonsterile and each has a unique environment, the SOB community will typically shift and deviate from the inoculum. This is dictated by both system operating conditions and microbial interactions. *It is advisable to collect a tote of the liquid trickling-phase from BTFs which is enriched in the system's unique SOB community prior to cleaning media, and use this to re-seed your BTF system after cleaning.*

In counter-flow BTFs where biogas and the trickling-phase are opposite, most H_2S elimination occurs in the lower portion of the

reactor where biogas and O₂ are loaded. SO₄ is also preferentially produced here due to high O_2 supply, while S^0 formation is more prevalent in the upper portions of the system. In BTFs where flow is co-current with the trickling-phase, most H₂S elimination occurs in the upper portion of the reactor with S^0 formation more prevalent in the lower portions of the system. SOB communities are recognized to partition in biogas desulfurization systems along these concentration gradients^[4].

Improved knowledge of the microbial interactions in BTFs and their responses to operational conditions could support the development of 1) inoculations that speed the establishment of an active microbial consortium, 2) selection methods for robust hydrogen sulfide reducing capacities, and 3) optimizations that limit the formation of S^0 and biofilm clogging. In the meantime, BTF are successfully managed to ensure H₂S reductions by using regular tower flushing, media backwashing, and re-seeding with collected trickling-phase after cleaning.

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References

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