Hydrogen Sulfide Removal Alternatives for Renewable Natural Gas

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Biogas Hydrogen Sulfide Content is Variable

- As low as 10 ppmv (dry landfills) to over 5,000 ppmv (wet landfills with high C&D fractions). A range of 100 to 500 ppmv is most typical.
- Municipal WWTP DG 50 ppmv to 5,000 ppmv (depending on whether the WWTP adds iron). A range of 100 to 2,500 ppmv is most typical.
- Dairy DG 500 ppmv (seasonal low with air injection) to 5,000 ppmv (without air injection).

Speciation of Sulfur Compounds Varies by Biogas Type

- About 5% of the total reduced sulfur (TRS) compounds in LFG are compounds other than H_2S.
- Municipal WWTP DG is similar to LFG.
- Based on limited SCS data, dairy DG is generally 100% H_2S.
- Important to know because some removal processes only remove H_2S, but not TRS.

Biogas Has Variable Oxygen Content

- LFG wellfields supplying RNG plants without nitrogen removal equipment have very low oxygen contents (typically less than 0.1%). With nitrogen removal the oxygen can be 2.0% or more.
- Municipal WWTP DG has very low oxygen contents (typically less than 0.05%).
- Dairy DG varies from very low oxygen content (less than 0.05%) to 1.5% (if air injection is employed). If air injection is employed, it is usually suspended to avoid the addition of oxygen and/or nitrogen removal equipment to the RNG plant process chain.
- Almost all H2S removal technologies like, or must have, some oxygen.
- The LFG RNG industry's shift toward the addition of nitrogen removal equipment is helpful in H_2S removal, since there is more oxygen available in the LFG.

Biogas Has Variable Trace Constituents

- LFG has a wide variety and relatively high concentration of VOCs
- Municipal WWTP DG has a much lower concentration of VOCs
- Dairy DG has few VOCs and no siloxane – you don't put lipstick on a pig
- The presence of VOCs and hydrocarbons will affect the performance and operation of some H_2S removal technologies

Hydrogen Sulfide Removal Alternatives

- Non-regenerative technologies
  - Activated carbon based
  - Iron – inert based media (SulfaTreat, SulfaRite, etc.)
  - Iron – wood based media (iron sponge)
- Regenerative technologies
  - Caustic regenerative (DMT, Thiopaq, etc.)
  - Iron-redox (LO-CAT, Ecotec, etc.)

Non-Regenerative Technologies – Activated Carbon

- An example is Darco BG-1. Adsorbs about 0.32 lbs H_2S/lb of media. Cost is about $1.65/lb. Density about 26 lbs/ft^3.
- SCS typically inserts into the process chain with fiberglass vessels at 5 to 10 psig. 6 to 12 month changeout target.
- Removes TRS, not just H_2S.
- SCS has switched its operating SulfaTreat sites to Darco BG-1 or Darco H2S based on cost-effectiveness, and on ease of media removal during changeout.

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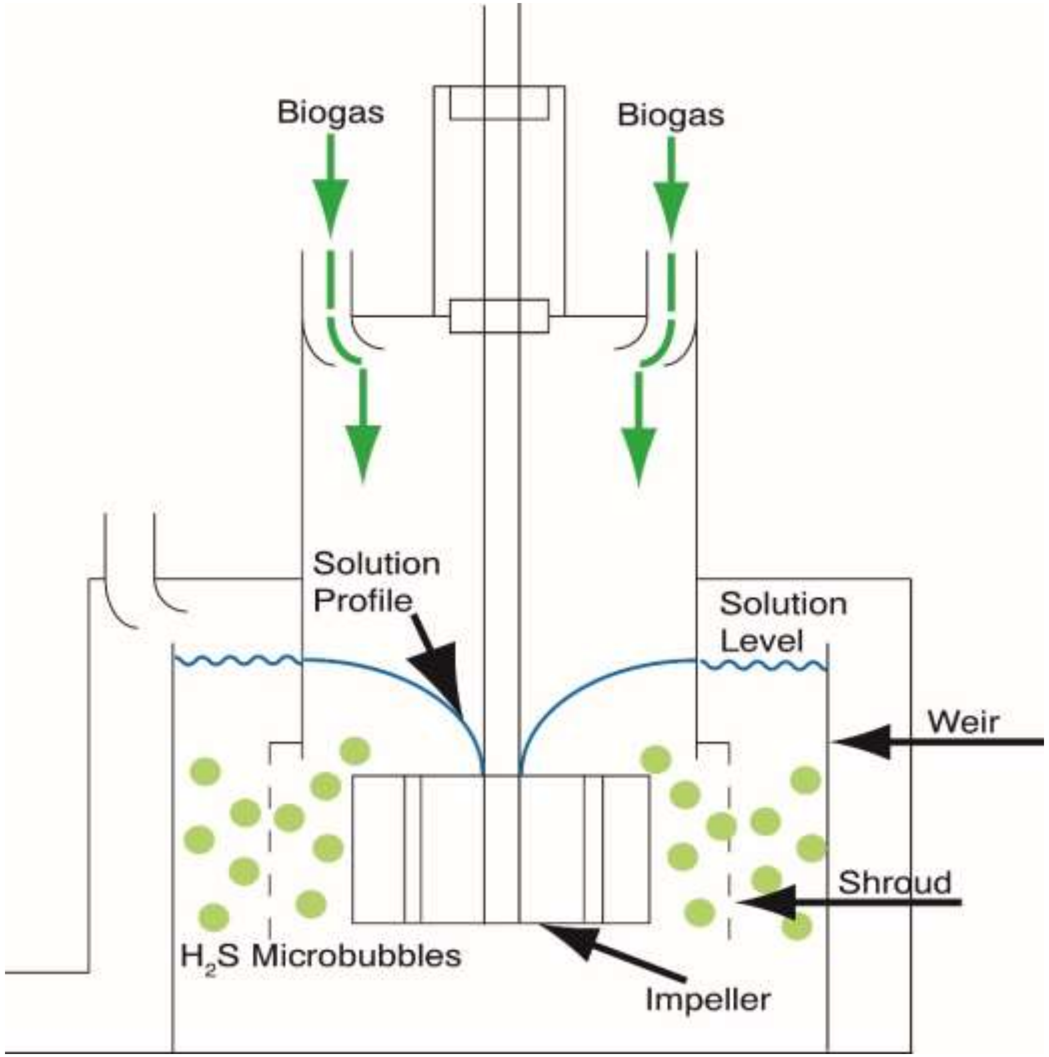
Non-Regenerative Technologies – Inert Media-Based – Iron

- The "classic" media in this category is SulfaTreat. Adsorbs about 0.1 lbs H_2S/lb of media (with proper environmental conditions – oxygen, temperature and moisture). Cost is about \$0.70/lb. Density is about 65 lbs/ft^3.
- SCS typically inserted in the process chain with fiberglass vessels at 5 to 10 psig, but sometimes at 100 psig to 200 psig in stainless steel vessels.
  6 month changeout was a typical target.
- Removes TRS, not just H_2S.
- SulfaTreat is difficult to remove, particularly if "overrun" to maximize media utilization.


BgPur
eco-tec


Biogas
Biogas
Solution Profile
Solution Level
Weir
Shroud
H_2S Microbubbles
Impeller

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Non-Regenerative Technologies – Wood Based Media-Iron

- Adsorbs about 0.12 lbs H_2S to 0.26 lbs H_2S per lb of media depending on environmental conditions. Cost is about $0.40/lb. Density is about 50 lbs/ft^3.
- Fiberglass vessels with removable vessel top dishes are mandatory, in SCS's opinion, because of the difficulty of media removal. Liquids management is a small concern – not 100% set it, and forget it. Ignitability is a very minor concern.
- SCS has installed MV Technologies systems at one power plant, and SCS will be considering iron sponge as an alternative on future RNG projects where:
  - A reasonable amount of oxygen is available; and
  - Cases where pressure can be limited to 6 psig or less (to support easy top dish resealing).

Regenerative Technologies – Caustic Regenerative

- H_2S is scrubbed from the biogas in a packed tower with a caustic solution (pH 8-9)
- The solution is circulated through an external oxidization vessel in which bacteria regenerates the caustic and produces elemental sulfur
- Elemental sulfur is separated in a gravity settler to produce a 5% solids slurry
- The slurry is then dewatered to a sulfur cake using a centrifuge of plate-and-frame press
- The process requires make-up caustic, proprietary nutrients, and make-up water. The process produces a blowdown
- The vendors seem comfortable with quoting 50 ppmv, on as high as 5,000 ppmv inlet, although there are often caveats in their proposals that the ppmv will reach 100 ppmv with somewhat undefined variations in inlet conditions.

Regenerative Technologies – Caustic Regenerative (continued)

- SCS has designed two caustic regeneration systems for dairy DG projects (one is in startup) and has provided operations consulting for two LFG projects.
- The LFG projects have performed poorly. Extended periods of operation at H_2S at well over 200 ppmv on inlets of 1,000 to 1,500 ppmv are common. It is believed that this is due to the nature of LFG.
- Only H_2S is being removed by a caustic scrubber. At 1,500 ppmv vs. 200 ppmv, the 5% to 10% “other” TRS compounds represent a material sulfur load to the downstream process.
- Being biological, these systems do have turndown limitations ,and rapidity of response limitations.
- One of the LFG sites is now being retrofitted with post-scrubber Darco BG-1 “polishing” vessels. A retrofit is under consideration at the second site.
- SCS observed satisfactory operation of a Thiopaq scrubber at a municipal WWTP in Chile, during construction of our RNG plant at that site, which gives SCS comfort that performance is better on “less complex” biogas.
- Nevertheless, SCS is providing Darco BG-1 “polishing” even on its dairy DG projects.
- The water make-up problem can be partially resolved by artful construction of the process flow sheet.
- The need for redundant chilling on cluster dairy DG projects, or medium-Btu LFG transmission projects, is an undesirable feature of scrubbing.

Regenerative Technologies – Iron-Redox

- SCS provides ongoing operations consulting and has provided upgrade engineering for a large iron-redox system. SCS is now designing an Eco-Tec system, and has designed a LO-CAT system many years ago. All are on LFG.
- H_2S is scrubbed from the biogas in a tower or other type of vessel through contact with a solution containing iron (2,000 to 4,000 ppm) at a pH of 8 to 8.3.
- The iron is reduced to Fe^2 in the scrubber during H_2S removal. It is oxidized back to Fe^3 in an external oxidizing vessel before being returned to the scrubber; however, if sufficient oxygen is available in the LFG, in some systems the external oxidizer can be eliminated.
- Elemental sulfur is usually removed in a gravity settler and then dewatered into a cake. The typical dewatering device is plate-and-frame press.
- The process requires an iron make-up solution, a chelating agent solution, caustic (or other agent for pH adjustment), and an anti-foam agent.
- Some vendors quote as low as 10 ppmv H_2S, but it seems as if 50 ppmv is more readily attainable. Like the caustic systems, the iron-redox systems are subject to upset, but being 100% physical-chemical much less so than biological systems.
- These systems do not have turndown limitations and respond well to rapid variations in inlet H_2S concentration.

Conclusions

- A broad range of alternatives are available for H2S removal. Important factors in a making a project specific selection are:
- Mass load of H2S (flow times H2S concentration);
- Current inlet H2S load and expected future H2S load trend;
- Desired outlet H2S concentration;
- Desire for unattended, simple operation; and
- Water availability, wastewater disposal availability, solids disposal cost, and power cost.