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Hydrogen Sulfide (H_2S) Removal at a Northeastern Dairy Farm Digester using Iron Oxide: Case Study

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H_2S Removal with Iron Oxide

H_2S removal using iron oxide is one of the most common methods of biogas desulfurization. Iron oxides and hydroxides form insoluble iron sulfides when it reacts with H_2S. Iron oxide pellets or wood chips impregnated with iron oxide are packed into a scrubbing unit and the biogas is passed through it for desulfurization. The iron oxide reacts with the H_2S and is converted into iron sulfide. It is estimated that approximately 20 g of sulfur can be removed per 100 g of iron oxide media. Extending the life of the wood chip media after saturation is possible by aeration, which forms elemental sulfur and regenerated iron oxide. The primary drawback of the iron oxide media is the disposal of spent iron sponge, which may be classified as a hazardous waste material. Due to sulfur buildup and loss of reaction surface area, iron sponge activity is reduced by approximately 33% after each regeneration. Therefore, regeneration is only practical once or twice before new iron sponge is needed.

Hydrogen Sulfide Scrubber Overview

H_2S scrubber type	Iron oxide scrubber
Scrubber designer	Homemade
Year commissioned	2014
Herd Size	350
Vessel Size	55 gallons (0.208 m^3)
Media volume	5.5 ft^3 (0.156 m^3)
Media material	Iron filings
Vessel material	Plastic drum
Biogas utilization	110 kW engine generator

Farm Description

- The farm milks ~350 cows
- The digester was commissioned in 2010, with the iron oxide scrubber added in 2014.

Reason for Scrubber Installation

An iron oxide scrubber was added in 2014 to reduce the quantity of hydrogen sulfide (H_2S) reaching the generator. The farmer wanted a low-cost option to reduce H_2S concentrations and decided to construct a homemade iron oxide scrubber. Due to relatively low H_2S levels (603 ± 51 ppm for untreated biogas), a higher capital investment was avoided due to lower H_2S concentration reductions needed.

Scrubber system
The scrubber system was a simple system, built with the following components:

Vessel
The vessel for the scrubber was a 55-gallon blue plastic drum. PVC piping was used for the connection from the digester to the scrubber and then to the engine generator to prevent degradation of metal piping from the H_2S.

Media
Initially, the media consisted of scrap iron and steel filings. New media was added in September 2016 (without cleaning out used media). In November 2016, the media was changed again to fresh grade 000 steel wool to determine if the increased surface area of this material would affect scrubber performance.

Process Description
Biogas flow from the digester was measured before the biogas passed through the scrubber. There were not any condensation traps before the scrubber, as water vapor helps in the reaction of H_2S with the iron oxide media. The biogas from the digester entered the scrubber from the bottom and flowed through the barrel, passing through the scrubbing media before it exited from the top of the scrubber vessel. When the biogas generator was operating, a regenerative blower (Gast Regenair Model - R5325R-50) installed at the outlet of the scrubber was used to maintain a constant flow rate to the generator.

Within the scrubber reactor, iron oxide (Fe_2O_3) in the scrubbing media reacted with the H_2S in the biogas and formed an iron sulfide (FeS). Eventually, the media becomes saturated with iron sulfide and should be replaced with fresh media for continual H_2S removal. Once the iron oxide reacts with H_2S, the media will turn black, allowing for a visual gauge of media saturation.

Figure 1. Iron oxide scrubber

Scrubber Performance
Scrubber performance was monitored over the course of six months (August 2016 to January 2017).

A Siemens Ultramat 23 Biogas Analyzer was used to measure the H_2S concentrations before and after the oxide scrubber. The results are shown in Figure 2. During the monitoring period, the scrubbing media was changed twice to induce a treatment effect. The media replacement events are identified in Figure 2.

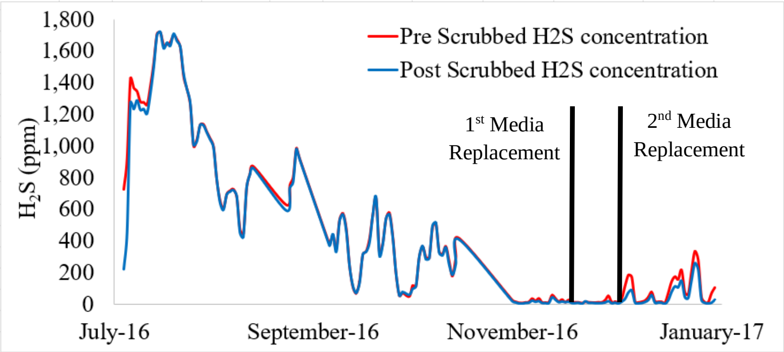

Figure 2. Biogas hydrogen sulfide (H_2S) concentrations before and after scrubber media replacement.

Performance Summary:

	Overall	After 2nd media replacement
Pre-Scrubber H_2S Concentration (ppm)	603 ± 51	66 ± 13
Post-Scrubber H_2S Concentration (ppm)	585 ± 50	41 ± 9
H_2S Removal Efficiency (%)	3.0%	37.9%
Daily H_2S removal (lbs/day)	0.056	0.0042
Engine-Generator Capacity Factor	0.2	0.0*

*The generator was not operated during this period, and the biogas was flared after passing through the scrubber

In the first three months of the study period, no major differences were seen between the hydrogen sulfide (H_2S) concentrations before and after passing through the scrubber. The average H_2S in the pre-scrubbed biogas was 740 ± 53 ppm, with a post-scrubbed average of 719 ± 52 ppm. In fact, certain data points in the pre-scrubbed H_2S concentration within the first 3 months were slightly lower than the post-scrubbed H_2S concentration in the biogas. This could be due to the measuring sensitivity of the instrument, but it is also possible that the saturated media was contributing to the higher post-scrubbed H_2S concentration due to volatilization of the H_2S from the saturated media.

The scrubbing media was changed twice in the following three months to induce a treatment effect. The first media change occurred in November 2016. This first media change showed a negligible treatment effect and therefore the media was changed again three weeks later. It was noticed that with the second media change, which consisted of fresh grade 000 steel wool and an increased surface area, a cleaner product after scrubbing was shown, with a scrubber outflow H_2S concentration of 41 ± 9 ppm compared to 66 ± 13 ppm before scrubbing (Figure 2). The second media replacement performed adequately for a period of five weeks (December 16, 2016 to January 25, 2017). The average H_2S removal efficiency for this period was 37.9%. It should be noted that flow rate of the biogas varied from 1769 scf/hr in the Summer (June – Oct 2016) to 74 scf/hr in the Winter (Jan – Feb 2017). The total volume of biogas passing through the scrubber before the media change (Aug – Nov 2016, 106 days) was 4.2 million ft^3 (119 million liters) with 8.39 lbs of H_2S removed from the biogas through the scrubber.

The biogas had a low average pre-scrubbing H_2S concentration of 66 ppm during the Winter period (December 16, 2016 to January 25, 2017), which could be due to lower digester temperatures, as the digester was unheated. After the 2nd media replacement, 64,353 ft^3 (1.8 million liters) of biogas flowed through the scrubber from December 20, 2016 to Jan 26, 2017 (36 days). The substantially lower biogas flow volume through the scrubber during the Winter period can be attributed to the unheated nature of the digester and the breakdown of the generator that caused the regenerative blower (used to maintain a constant gas flow rate) to be shut down. During the Winter period, the scrubbing media removed 0.15 lbs of H_2S.

The volume of the scrubbing unit was 7.4 ft^3 (without media addition) and the residence time of the biogas in the scrubber varied from 0.25 min (Summer) to 6 min (Winter). It is likely that the scrubber was undersized for the volume of biogas passing through it, especially during the Summer and thus, required more frequent media replacements for adequate desulfurization of the biogas. A larger scrubber volume that allowed for sufficient contact time with the media may have resulted in higher scrubbing efficiencies as well. Commercially available iron oxide media (require 1 – 15 min residence time) may also have been more efficient at removing H_2S, at lower residence times.

The generator produced 47,158 kWh in approximately four months of runtime (131 days). The generator capacity factor was difficult to estimate, as the generator was not run continuously every day. Typically, it was switched off during the night or had periods of downtime during the day. Assuming 12 hours of operation per day, the capacity factor was calculated as 0.27. The low capacity factor can be attributed to the variability in the generator runtime. On December 12, 2016, the generator stopped working due to an issue unrelated to H_2S. For the remainder of the study, the generator remained un-operational.

Economics

Capital Costs

The total capital cost of the scrubber system was approximately $525 based on the reactor vessel and piping: ($500) and initial scrubber media ($25).

Operation and Maintenance Costs

Labor

The scrubber required little maintenance due to its simplicity. All the maintenance was conducted by the farm owner, and the labor costs were considered negligible. Approximately one quart of oil was added to the generator every other day. Additionally, scrap iron was added by the farmer once during the study. The media replacement to grade 000 steel wool was done by the researcher and took approximately 2-3 hours to remove the used media and replace with the new media. With this system, labor may be more significant to the farmer, depending on maintenance time devoted to changing media. The frequency of changing the media is dependent on the size of the scrubber compared to the volume of biogas moving through the scrubber and the concentration of H_2S in the produced biogas.

<u>Replacement Parts/Supplies</u>

Parts and supplies for use in maintaining the equipment:

- 55 gallon drum oil (220 quarts):
    - ~$450/year: One quart of oil added to the generator every other day (183 quarts/year)
- Replacement media:
    - $650/year with original iron filings based on 26 changings per year
    - $960/year with grade 000 steel wool based on 12 changings per year

Total annual cost to own and operate the scrubber:

- With iron filings: $1,100
- With grade 000 steel wool: $1,410

Lessons Learned

The original media used in the scrubber was rusted scrap metal and was not a commercially available iron oxide media for H_2S scrubbing. In the first three months of monitoring, minimal treatment effect was observed, and a decision was made to change the media to a commercially available grade 000 steel wool. Once the scrubber material was changed, a treatment effect was observed after the second media replacement. It was shown that scrap metal is not an ideal media for H_2S removal because it did not significantly decrease H_2S concentrations in the biogas. When media was changed to steel wool, a treatment effect was observed. Further tests using commercially available iron oxide pellets could not be conducted due to the generator failure and subsequent intermittent flow of biogas through the scrubber.

Due to the digester being unheated, low concentrations of H_2S during the Winter prevented us from obtaining a treatment effect for higher H_2S concentrations (740 ± 53 ppm) seen in the Summer. More frequent media changes may be necessary when H_2S concentrations are higher, and the biogas production value is higher, as the frequency of scrubbing media changes depends on the total concentration of H_2S passing through the scrubber. Biogas flow and H_2S concentrations vary widely in the system throughout the year, as the digester is unheated and fluctuates with ambient temperature throughout the year.

Furthermore, the low scrubber volume (7.4 ft^3, media volume - 5.5 ft^3) in comparison to the large volume of biogas (4.3 million ft^3) passing through the scrubber resulted in low residence times. Inefficient scrubbing media coupled with the low residence times substantially affected scrubber performance. Even though the scrap iron media was able to remove 8.39 lbs of H_2S during the Summer period, the change in the H_2S concentration (ppm) in the biogas after treatment was negligible. Iron oxide media specially prepared for biogas desulfurization and an adequately sized scrubber that allowed for >1 min residence time would have substantially improved the scrubber performance.

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