Cornell CALS
College of Agriculture and Life Sciences

Dairy Environmental Systems Program
425 Riley-Robb Hall, Ithaca, NY 14853
cag26@cornell.edu | (607) 255-2088
www.manuremanagement.cornell.edu

PRO-DAIRY Education & Applied Research

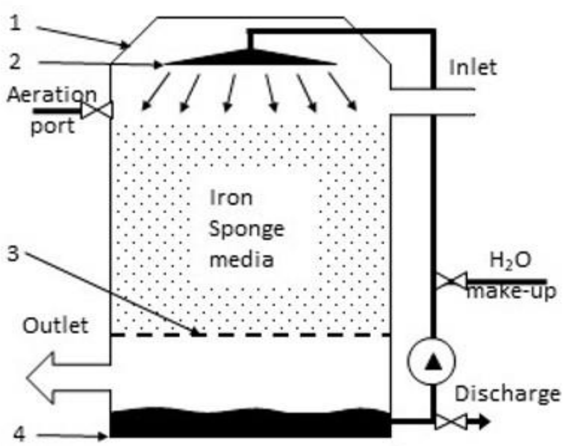
HYDROGEN SULFIDE REMOVAL FROM BIOGAS
Part 3A: Iron Sponge Basics

November 2017

One of the oldest technologies for the removal of hydrogen sulfide (H_2S) from gas is the use of "Iron Sponge". A chemical-physical process, originally developed to remove H_2S from natural and coal gas streams, iron sponge has been in use for over 140 years and more recently to remove H_2S from biogas.

SYSTEM DESCRIPTION

An iron sponge system consists of: 1) a reaction vessel containing bark impregnated with ferric oxide (Fe_2O_3), 2) a misting system to maintain moisture levels, 3) support for the impregnated bark, and 4) a reservoir of surplus recirculated water.



Biogas is typically introduced at the top of the vessel (down-flow) and as it makes its way down the column, H_2S reacts with the Fe_2O_3 to form ferric sulfide (Fe_2S_3) in the following reaction:

$$2Fe_2O_3H_2O + 6H_2S \rightarrow 2Fe_2S_3H_2O + 6H_2O$$

Water is produced during this reaction, and typically biogas is saturated with water vapor, which reduces the need to add additional water to maintain moisture in the media. Water is trickled from the top as needed to keep the wood chips damp.

The pH of the trickle water is typically maintained at approximately 8, with a requirement to add sodium bicarbonate or other base if the pH drops below 7.

Temperatures are usually kept between 50 and 130ºF, as above 130ºF the water of crystallization (the water in complex with the ferric oxide) can be driven off, reducing the ability of the iron sponge to react with H_2S until temperature is dropped.

REQUIREMENTS

Reactor vessels are relatively simple designs that seek to maximize the contact time between the biogas and media, while preventing short-circuiting. Typically at the bottom of the vessel there is a gas collection system to improve the uniformity of gas collection, and a sump to collect condensed biogas moisture and possible excess trickled water. Typically reactor vessels are a minimum of 5 feet tall with the media evenly packed throughout. (See **Hydrogen Sulfide Removal from Biogas Part 3B: Iron Sponge Design Considerations** for more information on sizing reactor vessels.)

If the biogas flow rate and concentration of inlet H_2S remain constant, the time between media change-outs will also be consistent. However, this is rarely the case with manure-derived biogas and so both the H_2S concentration at the outlet, and the pressure increase across the media bed need to be monitored. Increasing outlet concentration indicates that there is less ferric oxide available to react. Pressure increases signal that the media may be becoming fouled with solid ferric sulfide.

Spent Media

It is necessary to change the iron sponge as the ferric oxide becomes replaced with ferric sulfide. It is possible to "regenerate" or "revivify" the media by aerating the vessel; however, regeneration is not complete and typically 30% of the reaction capacity is lost each time. Alternatively, oxygen can be added to the biogas stream (2 to 3% air injection) to continuously regenerate the media. This process is not 100% efficient either, but can lengthen the lifespan of the media by 2 to 3 times.

The regeneration reaction:

$$2Fe_2S_3H_2O + 3O_2 \rightarrow 2Fe_2O_3H_2O + 6S$$

is an exothermic reaction, meaning it gives off heat. Sufficient heat can be produced to cause spontaneous combustion thus the need to keep the media moist.

To maintain biogas flows during media change-out or regeneration, reactors are often installed in parallel, so that when one reactor is shut down for maintenance, the other(s) can be used.

Once the media can no longer be regenerated, it must be removed and disposed of. Depending on the vessel design this can be a labor intensive process that may require manual breaking up of the spent media and removal from the vessel by shoveling; CAUTION: VESSELS ARE CONSIDERD CONFINED SPACES AND SHOULD NOT BE ENTERED WITHOUT PROPER TRAINING AND EQUIPMENT[1]. Other options are to fill the vessel with water and use vacuum trucks to remove media. Care must be taken to ensure that material removed from the vessel is kept wet, to prevent auto-ignition. Spent media can be disposed of in a landfill, composted, or field applied.

Cost

Iron sponge media retails for approximately $12 per bushel (plus shipping), and is usually sold based on the amount of ferric oxide per bushel of media (e.g. 15 lbs. Fe_2O_3 per bushel).

The annual cost of media will depend on the flowrate of biogas as well as the incoming H_2S concentration. Each pound of Fe_2O_3 will react with 0.56 pounds of H_2S. The media cost for the biogas from a 1,000 cow dairy would be ~$11,000 per year with an inlet concentration of 3,000 ppm H_2S. With regeneration this could be reduced to ~$5,500.

The required media replacement frequency and cost have led most operators of large-scale anaerobic digesters to select other technologies for primary treatment, though it remains a good option for a secondary or polishing treatment.

Iron Sponge Pros:

- Simple maintenance requirements
- No start up time required (as with biological trickling filters)
- No expensive/sensitive controls required
- Not affected by other contaminants in the gas stream (water vapor)

Iron Sponge Cons:

- Media replacement
- Labor intensive to replace media

[1]Nellie Brown 1997. Health Hazard Manual: Wastewater Treatment Plant and Sewer Workers. http://digitalcommons.ilr.cornell.edu/cgi/viewcontent.cgi?article=1001&context=manuals

Authors

Timothy Shelford, PhD tjs47@cornell.edu (607) 279-8519, ***Curt Gooch***, PE cag26@cornell.edu (607) 225-2088