Biogas Upgrading – Desulfurization

Part 6: In-situ H_2S removal – chemical desulfurization

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Overview

Chemical compounds can be added to the anaerobic digester (AD) influent that directly react with the hydrogen sulfide (H_2S) gas produced before it is emitted from the digestate. The reaction causes precipitation of insoluble iron sulfide salt particles and/or elemental sulfur that tend to settle in the digester tank or in the effluent. Chemical compound options include ferric chloride (liquid) and ferric hydroxide (powder). An advantage of digester influent additives over biogas scrubbing technologies is significantly reduced capital and maintenance costs. A disadvantage is that for high biogas H_2S concentrations, additives may be limited to an initial reduction as the first step in a multi-step H_2S removal process.

Ferric chloride additive

Ferric chloride ($FeCl_3$) comes in liquid totes and is typically added to the digester influent pit using a metered dosing system. In an on-farm demonstration study[1] conducted in 2009, a 150 mg/L concentration of $FeCl_3$ was added to the influent of a plug-flow anaerobic digester. A reduction of approximately 40% of the sulfide concentration in the biogas produced was measured. Significant binding of iron ions creating iron sinks was the likely reason that further reduction of H_2S concentration was not achieved. A lack of mixing and the high suspended solids in the plug-flow digester design specifically appeared to limit the effectiveness of the $FeCl_3$ dosing system.

The addition of $FeCl_3$ in the plug-flow digester produced no measurable changes in the methane (CH_4) and carbon dioxide (CO_2) content of the biogas. Also, the precipitation of iron sulfides did not result in a measurable increase in the total solids concentration in the digester.

An estimated amount of $FeCl_3$ additive and the associated cost based on 100 lactating cow equivalents (LCE) and AD influent composition is shown in Table 1.

Ferric hydroxide additive

Ferric hydroxide ($Fe(OH)_3$) has an added characteristic of precipitating out the orthophosphate form of phosphorous (P) to reduce the plant available P in the effluent. This feature is sometimes implemented in wastewater treatment plants to meet effluent phosphorous limits by adding ferric chloride to water (e.g., in secondary clarifiers) that results in the formation of ferric hydroxide. For wastewater treatment plants that have an AD system, the use of ferric chloride upstream results in reduced hydrogen sulfide levels in the biogas.

For dairy AD, $Fe(OH)_3$ can be purchased in powder form in biodegradable bags that can be directly added in the digester influent. Since the $Fe(OH)_3$ should be evenly distributed in the AD tank, its use is better suited for complete mix AD systems. Ferric hydroxide oxidizes sulfurous compounds according to the following reactions, helping to reduce H_2S concentration in the biogas.

$$2Fe(OH)_3 + 3H_2S \rightarrow 2FeS + S + 6H_2O$$

$$2Fe(OH)_3 + 3H_2S \rightarrow Fe_2S_3 + 6H_2O$$

While both of these reactions can occur, the iron sulfide, Fe_2S_3, is unstable and can react with oxygen and convert back to ferric oxide and $Fe(OH)_3$ in a humid, aerobic environment. This regeneration effect is a major advantage for wastewater treatment plants but requires the use of a separate aerobic biogas vessel to provide oxygen from the ambient air. Aerating dairy manure digestate would be energy intensive.

It is important to carefully estimate the necessary quantity of $Fe(OH)_3$ that is needed based on the biogas production and level of H_2S (Table 1). Sulfur levels in water and feed will impact the H_2S produced and the need for additional chemical. An estimated cost is provided in Table 1 as well. Consider the possibility that the chemical commodity price may change over time. Check with local suppliers since prices and container volumes can vary.

Table 1. Ferric hydroxide ($Fe(OH)_3$) and ferric chloride ($FeCl_3$) daily usage and estimated cost per 100 LCE[A] for H_2S reduction as a function of biogas production based on AD influent composition. [2]

AD influent	Biogas production (CF/day)	$Fe(OH)_3$ lbs./day	$Fe(OH)_3$ \$/day[B]	$FeCl_3$ lbs./day	$FeCl_3$ \$/day[C]
Manure only	7,900	8.0	2.88	5.7	5.02
Manure + 10% Whey	8,690	8.8	3.17	6.3	5.54
Manure + 10% Fat/Oil/Grease	12,874	13.0	4.68	9.2	8.10

[A]Lactating cow equivalent
[B]Based on a ferric hydroxide cost of \$0.36 per pound
[C]Based on a ferric chloride cost of \$0.88 per pound

FACT SHEET SERIES: Biogas Upgrading – Desulfurization

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[1] NYSERDA, 2012. "Assessment of Biochemical Process Controls for Reduction of Hydrogen Sulfide Concentrations in Biogas from Farm Digesters". Final Report No. 12-20.
[2] Shelford, T., Gooch, C., Choudhury, A., Lansing, S. 2019. "A Technical Reference Guide for Dairy-Derived Biogas Production, Treatment and Utilization". https://ecommons.cornell.edu/handle/1813/60803.2

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