DAIRY MANURE BIOGAS HYDROGEN SULFIDE SAFETY
Black & Veatch Corporation
April 2018

Introduction

Manure from dairy operations provides a favorable substrate for energy production via anaerobic digestion (AD). Other organic agricultural wastes may also be added to manure for additional energy production. AD as a waste management strategy promises numerous benefits including effective odor management, the recovery of nutrients for beneficial use, and the production of energy by capturing methane, a potent greenhouse gas that would otherwise have been emitted to the atmosphere. The most prevalent types of manure digesters include plug-flow, complete-mix and covered lagoon configurations. Operational considerations for proper AD process design include total solids content, number of stages, operating temperature (mesophilic, approximately 95 to 105°F vs. thermophilic, approximately 125 to 140°F), hydraulic retention time, agitation, process flow configuration (continuous vs. discontinuous), as well as the management strategy used for the digestate exiting the digester. Table 1 shows typical biogas composition ranges by substrate type and also includes similar values for “sour” natural gas for comparison.

Table 1. Typical Biogas Compositions

<table>
<thead>
<tr>
<th>Component</th>
<th>Manure</th>
<th>Sewage Sludge</th>
<th>Source Separated Organic Waste ¹</th>
<th>Sour Natural Gas ²</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methane (CH₄)</td>
<td>55 - 62 vol. %</td>
<td>55 - 65 vol. %</td>
<td>45 - 68 vol. %</td>
<td>60 - 95 vol. %</td>
</tr>
<tr>
<td>Carbon Dioxide (CO₂)</td>
<td>35 - 38 vol. %</td>
<td>35 - 45 vol. %</td>
<td>32 - 55 vol. %</td>
<td>5 - 20 vol. %</td>
</tr>
<tr>
<td>Hydrogen Sulfide (H₂S)</td>
<td>500 - 5,500 ppmᵥ</td>
<td>50 – 1,000 ppmᵥ</td>
<td>50 – 2,500 ppmᵥ</td>
<td>&lt;1 - 10 vol. %</td>
</tr>
</tbody>
</table>

Notes:
Percent by volume (vol.%).
Parts per million by volume (ppmᵥ).
¹. Source Separated Organic Waste could include yard and food waste.
². Sour Natural Gas implies underground deposits of natural gas containing H₂S

An emerging concept in manure AD for energy recovery applications is referred to as “clustering,” whereby several farms in close proximity convey either manure or biogas to a central location. The biogas produced provides the energy to generate electricity or the methane source for upgrading to renewable natural gas (RNG). The purpose of a cluster configuration is to achieve improved project economics and meet other project requirements such as overcoming permitting challenges and achieving environmental
compliance. Prior studies have pointed toward a “hub and spoke” model as the preferable configuration through which individual digesters located at each farm would pipe biogas via low-pressure collection pipelines (spokes) to a centralized gas cleaning and upgrading facility (hub) prior to injection into a high-pressure natural gas pipeline.

In September 2016, the California State Legislature passed Senate Bill (SB) 1383, which constituted a major amendment to the California Global Warming Solutions Act (2006) and California Integrated Waste Management Act (1989). SB 1383 requires a comprehensive strategy to reduce short-lived climate pollutants and seeks to reduce methane emissions associated with livestock manure management (40 percent by 2030 over 2013 levels) and organic waste diversion from landfills (75 percent by 2025 over 2014 levels). In June 2017, the California Public Utilities Commission (CPUC) began to develop a framework under which state gas corporations could implement at least five dairy RNG pilot projects and associated interconnection / rate recovery. As part of the rulemaking process, concerns were raised regarding the health, safety, and pipeline integrity impacts of hydrogen sulfide (H₂S) and water that may be present in the biogas collection lines. However, it was ultimately decided that H₂S would be allowed in biogas collection lines until the gas entered the utility pipeline system.

The purpose of this white paper is to elucidate the cost, safety, and management issues surrounding pipeline conveyance of biogas containing H₂S. A hazard analysis and assessment of monitoring, detection, and notification equipment in industrial environments is provided. Case studies for reference projects that include biogas transportation via pipelines are included to demonstrate how other, similar project owners are managing these matters. Finally, H₂S removal technologies, as well as their relative cost and safety characteristics are summarized.

**Hydrogen Sulfide Hazards and Management**

H₂S is a toxic and explosive gas that causes upper respiratory tract irritation and central nervous system impairment. In moist environments H₂S is acidic and corrosive. At high concentrations (≥1,000 ppmv), it can lead to unconsciousness in an instant and death within seconds without any warning. At low concentrations (≤100 ppmv), H₂S has an odor of “rotten eggs” that is offensive to humans. At high concentrations, one cannot smell it and, therefore, it becomes dangerous to those working in proximity to it.

For example, the United States (U.S.) Occupational Safety and Health Administration (OSHA) has set a “Permissible Exposure Limit” (PEL) of 10 ppmv for H₂S. Death without warning may occur at concentrations above 150 to 200 ppmv, where H₂S causes olfactory fatigue – which means the ability to smell its odor is lost. Inhalation of H₂S at a concentration greater than 1,000 to 2,000 ppmv (a level that cannot be smelled) causes the respiratory centers of the brain to become paralyzed with a few breaths, leading to rapid death. By comparison,
the concentration of H$_2$S in biogas produced during the anaerobic digestion of manure is typically 2,000 to 4,000 ppm$_v$.

**Physical and Occupational Exposure Characteristics**

- **Flammability** – H$_2$S is a highly flammable gas with a flammability range of 4.3 to 46 percent in air. Additionally, biogas diluted to approximately 10 to 30 percent in air is an explosion hazard. Open flames, sparks, and smoking must be prohibited in the vicinity and lighting and electrical equipment must be designed according to appropriate explosion proof standards. Fire extinguishment may be accomplished with water spray, powder or CO$_2$.  

- **Density** – H$_2$S has a slightly higher density than air so it tends to accumulate at the bottom of poorly ventilated spaces making it especially difficult to purge with ambient air.

- **Toxicity** – The lethal concentration of H$_2$S for 50 percent of humans for five minutes of exposure is 800 ppm$_v$.

- **Symptoms to Monitor (at two to five ppm$_v$)** – Nausea, tearing of eyes, headaches, loss of sleep. It is important to note that individuals with asthma may be more sensitive to H$_2$S exposure and may experience bronchial constriction at this low level.

- **Symptoms to Monitor (at 20 ppm$_v$)** – Possible fatigue, loss of appetite, headache, irritability, poor memory, dizziness.

- **Exposure effects following unconsciousness may include chronic headaches and poor attention span, memory, and motor function.**

**Safety-Related Case Studies and Statistics**

According to the National Institute for Occupational Safety and Health (NIOSH), H$_2$S is considered to be a leading cause of sudden death in the farm workers workplace. Some deaths occur when coworkers attempt to “rescue” collapsed victims in spaces with high H$_2$S concentrations. For instance, in an accident reported by Cornell University,  two workers died due to H$_2$S exposure in an agricultural application. In this scenario, there were four workers present. The first worker entered a drained manure holding tank to repair a gate valve. When his plug blew out of the transfer pipe, manure and gas entered the space causing him to collapse. A second coworker entered to attempt rescue and was also overcome with the gas. A third worker simply standing nearby had also started to lose consciousness until a fourth worker outside the room pulled the third man out and they

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both survived, although, the third worker remained severely disabled. The first two men did not survive.

In another study, the concentration of \( \text{H}_2\text{S} \) in raw biogas was measured to be over 5,000 ppm\(_v\). In this study, the efficiencies of \( \text{H}_2\text{S} \) removal for different biogas flow rates and water levels were conducted at 30 and 90 seconds after treatment. The \( \text{H}_2\text{S} \) measured at the upper biogas system outlet during the different intervals and water levels ranged from 1,300 – 5,200 ppm\(_v\). This amount of \( \text{H}_2\text{S} \) escaping indicates that it is not safe for human occupancy in an open system or one that leaks without proper ventilation and respiratory protection. One breath of \( \text{H}_2\text{S} \) at these levels could be fatal.

**Personal Protective Equipment**

When working in areas where exposure to low concentrations of \( \text{H}_2\text{S} \) gas may occur, a full-face elastomeric, negative pressure respirator may be worn. The full-face respirator is recommended because it supplies built-in eye protection. The full-face respirator has an assigned protection factor (APF) of 50. This means that the wearer would be protected up to 50 times the OSHA PEL. A half mask respirator may be worn as long as safety goggles are provided. The APF for a half mask is 10. The filter cartridge recommended is “Acid Gas.”

When working in areas where exposure to high concentrations of \( \text{H}_2\text{S} \) gas may occur, as with manure storage, self-contained breathing apparatus (SCBA) is required. NIOSH established an immediately dangerous to life and health (IDLH) level of \( \text{H}_2\text{S} \) at 100 ppm\(_v\). IDLH is considered the level of a contaminant that interferes with the ability to self-rescue or escape from a space where the material is present. IDLH atmospheres require the use of SCBA respiratory protection.

**Hazard Communication and Training Requirements**

OSHA’s Hazard Communication Regulation requires that employees be trained regarding the hazards associated with their jobs. Training for workers at dairy manure farms, and associated AD / biogas to RNG projects, might include:

- \( \text{H}_2\text{S} \) characteristics including its recognizable rotten egg odor and facts about olfactory fatigue.
- Normal operational and emergency procedures such as signs, signals, alarms, notifications and muster areas.
- If respiratory protection is used workers must be medically approved to wear the respirator, trained on its use, wear, fit, storage and cleaning, and annually fit tested to wear the respirator.
- If working in confined spaces, workers must be trained regarding confined space entry procedures in accordance with the OSHA Confined Space Entry Regulation,

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including how to use monitoring equipment to test the space prior to and during entry and physical characteristics of H₂S gas (e.g. how it is heavier than air so it will accumulate at the bottom of the space).

- Site-specific protocols for responding to an emergency (such as a leak), notifying emergency services, and emergency response specialized training requirements are normally established at the outset of a project by the owner and communicated to the appropriate local emergency response agencies.

**Miscellaneous Safety Considerations**

- H₂S reacts with steel to form iron sulfide which can ignite when exposed to air.
- H₂S produces sulfur dioxide (SO₂) when burned, which is also toxic.
- H₂S is highly corrosive and may lead to metal embrittlement / fatigue.
- H₂S gas detection equipment is required in areas where H₂S can be present, especially in enclosed or below grade areas (e.g. holes, trenches, reserve pits, and manholes).
- Areas where H₂S is present (including facilities, pipelines, and/or flowlines) should be properly identified with signage.
- Warning signs should be placed around manure storage systems/openings to warn visitors about the H₂S hazards. The farm is legally responsible for everyone’s safety.
- Agitation of stored manure can lead to sudden, large releases of H₂S gas. When agitating, reserve one to two feet (0.3 to 0.9 meters) of airspace above the surface to hold gas concentrations to prevent gas from escaping.

**Monitoring, Detection, and Notification Equipment**

H₂S detectors provide early warning so that the potentially harmful exposure to on-site personnel and off-site public can be minimized. Table 2 shows the fixed detection guidelines used in the oil and gas industry for H₂S by process stream concentration. An H₂S detection system installed to detect leaks depends on the on-site and off-site factors at each site. Placement of the detectors account for the following factors:

- Leakage source within the area.
- Gas density relative to air.
- Ventilation air flow patterns.

The following H₂S detector types are currently used in industrial applications:

- Electrochemical Cell – these consist of combined and enclosed electrolytic cells. As the concentration level of the H₂S increases due to an electrochemical reaction (i.e. oxidation or reduction, depending on type of cell), current flows through a circuit and gives an indication of the amount of H₂S present in the atmosphere.
Electrochemical detectors have known reliability problems in arid environments, due to dehydration. Typical response time for electrochemical $\text{H}_2\text{S}$ gas detectors are from 30 seconds up to two minutes.

Table 2. Fixed Detection Requirements for $\text{H}_2\text{S}$

<table>
<thead>
<tr>
<th>$\text{H}_2\text{S}$ Concentration</th>
<th>Fixed Detection Required?</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>&lt; 10 ppm $\text{v}$</td>
<td>No</td>
<td>This is the typical lower limit for fixed detection.</td>
</tr>
</tbody>
</table>
| 10 to 1,000 ppm $\text{v}$       | • No if gas is flammable and flammable gas detectors are installed.  
• Yes if gas is not flammable or release in liquid phase. | Detection of a release may be provided by flammable gas detectors and personal monitors. |
| 1,000 to 10,000 ppm $\text{v}$   | Yes with particular attention for areas where dispersion may be hindered. | Detection of a release shall be provided by both fixed detectors and personal monitors. |

- **Solid State** – these are constructed from a semiconducting material (e.g. metal oxide) applied to a non-conducting substrate between two electrodes. The substrate is heated to a temperature at which the presence of the gas can cause a reversible change in the conductivity of the semiconductor material. When no gas is present, oxygen is ionized onto the surface and the sensor becomes semi-conductive. When molecules of $\text{H}_2\text{S}$ gas are present, they displace oxygen ions thus decreasing the resistance between the electrodes. This change is measured electrically and is proportional to the concentration of the gas being measured. Solid state detectors have known reliability problems in humid climates, and also can become insensitive unless exposed to $\text{H}_2\text{S}$ on a regular basis (i.e. calibrated), typically every six months.

- **Point and Open Path** – the infrared (IR) method of measuring gas concentration is based on the absorption of IR radiations at certain wavelengths as the radiation passes through a volume of the gas. IR-based gas detectors can be classified as point type and/or open path gas detectors. These detectors are immune to poisoning, resistant to corrosion, and can operate in deficit or surplus oxygen as they do not suffer from reduction in sensor life on repeated exposure to gas. Optical detectors provide the advantage that they will alarm on loss of the IR signal or other failure detection, thus are effectively fail safe. Support structures for open path detectors must be rigid, robust, and decoupled from any vibration sources such as compressors. A combination of point and open path detectors will therefore generally provide the most effective design. IR point type gas detectors can have response times as fast as one second. Optical detectors can fail due to dirt on the lens. Open path detectors can fail to vibration or obstructions of light path, as well as

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dirt on the lenses and reflectors. Additionally, these detectors have another disadvantage that it is generally not possible to identify the source of emission.

- Portable – these monitors are useful gas detectors to use as a safety device that helps to detect different toxic, flammable, and combustible gases. Portable gas detectors can be calibrated with different set points. They have a relatively quick initial response time of five seconds or less when dangerous gases have been detected. Application areas for portable gas detection include personal monitoring, confined space entry, and leak detection.

Placement of detectors with the goal of providing early detection must consider potential release magnitude, momentum, and air movement. Denser gases that are heavier than air, such as H$_2$S, will sink to the ground collecting in low-lying areas of the facility. Sensors for these types of gases should be placed closer to the ground or below the release points. However, caution must be taken since placing these sensors too low to the ground may cause maintenance or performance issues. Sensors should be mounted approximately 18 to 24 inches (457 to 610 mm) above the ground, keeping them free from dirt, debris, water, or other forms of contamination. Some of the guidelines for placing the detectors include:

- Place detector close to the possible toxic gas/leak source.
- Place toxic detectors between potential leak areas and populated areas, as well as in the workers breathing zone.
- Place detectors in areas where air currents are likely to produce the highest gas concentration, including areas where gas buildup is likely, such as corners or stopping points of gas-releasing moving devices.
- Consider ease of access for functional testing and servicing.

For dairy manure AD cluster projects, the guiding principles of gas safety include containment of biogas, isolation from sources of ignition and natural or forced ventilation to prevent accumulation of hazardous gases, paying attention to density differences between component gases. Methane being lighter than air but H$_2$S being heavier than air, as noted will accumulate in low areas. A fixed detection scheme must be carefully designed to locate detectors for site-specific areas of concern. To protect operations and maintenance personnel in case of a leak along biogas collection pipelines, use of portable H$_2$S gas detectors is recommended. Any personnel assigned for maintenance and repair work should always carry a portable H$_2$S gas detector, with appropriate personal protective equipment (PPE).

Oil and gas industry best practices suggest fixed detector alarm levels for H$_2$S of 10 ppm$_v$ for an initial (warning) alarm and 15 ppm$_v$ for a secondary (action) alarm. Portable detectors will have built-in alarm levels. The triggering of an action alarm will result in emergency response procedures being initiated. Finally, it is expected that the approximate cost for a fixed detection system would be between $30,000 and $40,000 while the approximate cost for portable H$_2$S detectors would be between $350 and $500.
Reference Project Case Studies

Reference Project #1: Renewable Dairy Fuels Biogas Projects, Fair Oaks, Indiana

Fair Oaks Farms in northwestern Indiana is one of the largest and most experienced dairy manure recovery and utilization operations in the U.S. They began operating manure AD systems in 2003 for the production of electricity. In 2011, Amp Americas installed a water-wash gas upgrade system to generate RNG for vehicle usage – fueling the operation’s 42 milk delivery trucks. The RNG fuel is now dispensed into multiple truck fleets across California. The total dairy population at the 12 family-run farms feeding the central digester is estimated at 15,000 cows, which produces approximately 1.4 million cubic feet per day of biogas. The biogas for this project is piped in a 100-foot-long steel pipeline before being upgraded to RNG, after which it is transported via a three-mile-long pipeline to the local utility’s point of receipt. The Fair Oaks Farms site attracts hundreds of thousands of visitors annually and includes educational programs, tours, dining, and special events.

In discussions with project developers at Amp Americas, it was learned that a new project is under construction in the Fair Oaks township area of Jasper County. Both the Fair Oaks Farm project as well as the new project include digesters and are operated by the respective farms, while the biogas piping, gas upgrading equipment and RNG piping / interconnection are owned and operated by Amp Americas and its subsidiaries. The greatest safety concern with these projects is \( \text{H}_2\text{S} \). To mitigate these concerns, technicians are required to wear appropriate PPE as well as portable monitors. At the biogas cleaning and upgrading facility, safety showers are provided and all skidded enclosures are equipped with toxic / flammable gas monitors. In the event of a process upset or leak detection event, biogas conditioning units are isolated, biogas compressors are deactivated, and all biogas is piped to flares that are collocated with each digester.

At the existing Fair Oaks Farms plant, \( \text{H}_2\text{S} \) and \( \text{CO}_2 \) are both removed simultaneously using a water wash process. Since the biogas is not piped over any substantial distance in the existing project, dehydration is not needed. However, at the new facility biogas is dehydrated prior to entering collection piping, and \( \text{H}_2\text{S} \) will be removed via a caustic wash at the central cleaning and upgrading facility prior to \( \text{CO}_2 \) removal. In both applications, the cleaned and upgraded RNG meets local pipeline specifications. Amp Americas stated that they did not encounter any liability insurance issues with either project. Although there are no specific controls in place to prevent bacteria from being transported along with biogas, the process design in both cases adheres to industry best practices for moisture removal that should mitigate any concerns. The newest Amp Americas biogas project is expected to be operational later in 2018.

Reference Project #2: Calgren Dairy Fuels, Pixley, California

The Calgren Dairy Fuels project is a dairy manure AD cluster development being pursued by Calgren Renewable Fuels who also owns and operates a nearby grain ethanol production facility. According to Calgren, the project is currently being constructed, which when complete will include 30 miles of biogas pipeline interconnecting 14 separate dairy farms. The resultant biogas is expected to be used to fuel gas turbines that power the Calgren...
ethanol production plant and upgrade the balance of the biogas into RNG, which will be injected into a natural gas pipeline. Previously, Calgren worked with Pixley Biogas (who owns a dairy manure AD facility) to develop a large-scale mixed waste digester that became operational in 2014 and produces heat and power for the Calgren Renewable Fuels plant.

According to the project developers of the Calgren Dairy Fuels project, the raw biogas will be dried to minimize any opportunity for corrosion in their pipelines, and H₂S will be removed at a central cleaning and upgrading facility. HDPE piping will be used for all interconnecting pipelines. They state that most of the potential exposure to H₂S will be at the dairies. There are also potential exposure concerns at the inlet of the H₂S removal equipment regardless of their location and that exposure should be evaluated on a case-by-case basis. Due to the fact that they consider their unique design and risk management strategy to be proprietary, no further project information can be supplied at this time.

Hydrogen Sulfide Removal Cost and Safety Comparisons

Hydrogen Sulfide Removal Technology Summaries

For AD-derived biogas applications, one approach for H₂S control is to oxidize it by introducing air into the digester headspace. The oxygen in air reacts with H₂S to form elemental sulfur (i.e. inert particles); however, this practice also introduces nitrogen, which dilutes the energy content of the biogas. This practice may be acceptable for power generation applications, but is not suitable if the biogas is to be upgraded to RNG. Other oxidizing techniques using separate reactors are available. This white paper focuses on treatment systems using separate reactors downstream from the digester, which are intended to facilitate biogas processing for RNG applications.

There are several processes that may be used to remove H₂S from biogas streams. These include solid media, chemical scrubbing, and biological methods. In solid media (or scavenging) processes, biogas is passed through a permeable bed of media that selectively reacts with or adsorbs the H₂S. These media methods often include passive chemical reactions and require no mechanical parts or operator interfaces to make the removal process work. Some media can be regenerated and reused multiple times before replacement, while others can only be used once and must be discarded as waste when the media is exhausted and “breakthrough” of H₂S is detected in the outlet gas stream. In the case of “dry” adsorbents, regeneration requires the application of heat, which releases H₂S back into the gas phase, which is typically flared for final disposal. Disposable media does not exhibit economy of scale to the extent offered by other technologies because the cost of media is directly proportional to the amount of sulfur removed; thus, the capital cost of media based systems is lower than other technologies, while the operating costs are higher.

To increase media life and improve treated gas quality, solid media vessels are often arranged in a lead/lag configuration, requiring at least two vessels. Solid media processes are suitable for H₂S removal for biogas upgrading applications, particularly when the sulfur removed is less than 100 pounds per day. For systems removing greater amounts of sulfur investment in more costly technology with lower operating costs can offer paybacks in a short period of time.
Chemical scrubber processes remove \( \text{H}_2\text{S} \) in the biogas via contact with biogas in a packed bed and either react directly with \( \text{H}_2\text{S} \) to form a benign byproduct (e.g. liquid scavengers) or convert the \( \text{H}_2\text{S} \) to solid elemental sulfur (e.g. liquid oxidation-reduction, or redox). In liquid redox, the resulting end product is a sulfur cake that contains high moisture that can be purified for sale. A variety of liquid scavenger reactants exist, but are typically best suited for high flow rate, low \( \text{H}_2\text{S} \) concentrations making them appropriate for some biogas cleaning and upgrading applications. Alternatively, liquid redox processes use a dilute aqueous solution of iron that is circulated from the absorber (where it reacts with \( \text{H}_2\text{S} \)) to an oxidizer (where the iron solution is regenerated). Flow rates through a liquid redox system can be high, which translates to high operating costs, but this is partially offset by the high selectivity for \( \text{H}_2\text{S} \). Although chemical scrubber processes can have comparatively high capital costs, applications expected to produce more than 300 pounds of sulfur per day can have competitive lifecycle economics with solid / liquid scavenger systems due to lower operating costs.

Biological \( \text{H}_2\text{S} \) removal systems have similar process designs to liquid redox systems, but use caustic soda as removal agent and are generally more economical for low pressure applications as would be pertinent for many biogas cleaning and upgrading installations. As with chemical scrubber processes, sulfur is removed in a packed bed, with the liquid phase regenerated in a separate biological reactor. The aerobic bioreactor uses air and bacteria to convert \( \text{H}_2\text{S} \) into elemental sulfur. The alkalinity of the caustic reagent is restored in the biological oxidation process and is then recycled back to the packed bed, while the elemental sulfur slurry is pumped to a settling tank for sulfur extraction. Some disadvantages of biological removal techniques include additional monitoring requirements to ensure bacteria viability including temperature controls, use of potentially corrosive chemicals, and potential for air ingress into the biogas stream, which may require downstream removal.

Other technologies are available for the removal of \( \text{H}_2\text{S} \) from \( \text{CH}_4 \) gas streams, including water or amine scrubbing; scrubbing processes employing specialty solvents, and cryogenic methods. Water / amine scrubbing would potentially emit \( \text{H}_2\text{S} \) (or other sulfur compounds) in the stripping air vented to atmosphere or sent to a thermal oxidizer. Considering environmental and air emission requirements in California, it is anticipated that gas phase separation and subsequent discharge to the atmosphere would not be permitted. Specialty solvent processes operate in a similar manner to water / amine scrubbing processes and were originally developed for operation at larger scales than those of typical biogas upgrading applications. Thus, these processes are complex and are not considered economically viable at scales typical of biogas upgrading. Similarly, cryogenic processes are considered too expensive to be considered for biogas applications.

**Design Basis**

In order to develop a summary economic analysis for dairy manure AD clusters in California, a design basis that covers many of the typical characteristics of biogas and biogas cleaning systems is summarized in this section. Biogas from dairy manure digesters is expected to be fully saturated with water vapor and have a composition similar to the "Manure" column shown earlier in Table 1. In order to pipe the biogas any distance the moisture must be reduced to prevent condensation in the pipelines. Condensate is corrosive.
and needs to be removed from the piping. Pre-conditioning the gas by moisture removal will minimize condensate formation and remove a portion of the H$_2$S. For the purposes of this study, the biogas system is assumed to have no leaks and therefore no nitrogen or oxygen is included. RNG from gas cleaning and upgrading operations is expected to meet the specification shown in Table 3. Table 4 contains additional simplifying details for a potential dairy manure AD cluster project.

### Table 3. Typical RNG Specification

<table>
<thead>
<tr>
<th>Component</th>
<th>RNG</th>
</tr>
</thead>
<tbody>
<tr>
<td>Minimum Heating Value</td>
<td>≥ 990 BTU/SCF</td>
</tr>
<tr>
<td>Carbon Dioxide (CO$_2$)</td>
<td>≤ 3 vol. %</td>
</tr>
<tr>
<td>Moisture</td>
<td>≤ 7 lb/MMSCF</td>
</tr>
<tr>
<td>Hydrogen Sulfide (H$_2$S)</td>
<td>≤ 4 ppm$_v$</td>
</tr>
</tbody>
</table>

Notes:  
Standard cubic feet (SCF).  
Million SCF (MMSCF).

### Table 4. Dairy Manure AD Cluster Characteristics

<table>
<thead>
<tr>
<th>Characteristic</th>
<th>Range</th>
</tr>
</thead>
<tbody>
<tr>
<td>Biogas Flow from each Dairy/Digester</td>
<td>50 to 200 SCFM</td>
</tr>
<tr>
<td>Number of Dairies/Digesters in Cluster</td>
<td>3 to 10</td>
</tr>
<tr>
<td>Total Biogas Flow to Central Cleaning Facility</td>
<td>150 to 2,000 SCFM</td>
</tr>
<tr>
<td>Product RNG Flow</td>
<td>75 to 1,000 SCFM</td>
</tr>
</tbody>
</table>
| Length of Biogas Collection Pipelines | 0.5 to 2 miles (each)  
                                          | 1.5 to 20 miles (total) |

**Pre-conditioned Biogas Characteristics**

1. Size of Biogas Collection Pipelines  
2. Dew Point  
3. Temperature Range  
4. Pressure Range

<table>
<thead>
<tr>
<th>Pre-conditioned Biogas Characteristics</th>
<th>Range</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Size of Biogas Collection Pipelines</td>
<td>4 to 6 inches</td>
</tr>
<tr>
<td>2. Dew Point</td>
<td>40°F</td>
</tr>
<tr>
<td>3. Temperature Range</td>
<td>50 to 125°F</td>
</tr>
<tr>
<td>4. Pressure Range</td>
<td>1 to 15 psig</td>
</tr>
</tbody>
</table>

Notes:  
Standard cubic feet per minute (SCFM).  
Degrees Fahrenheit (°F).  
Pounds per square inch, gauge (psig).

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Biogas Pipeline Material Selection and Cost

Stainless steel, carbon steel, and polyethylene (PE) piping materials were evaluated for use for biogas collection piping systems. PE piping is recognized by many standards for transportation of natural gas and CH\textsubscript{4} (the primary component of the biogas) such as:
- API Spec 15LE Specification for Polyethylene Line Pipe.
- Title 49, CFR Part 192, Transportation of Natural Gas and Other Gas by Pipe Line.
- CSA B137.4-17 Polyethylene Piping Systems for Gas Services.

PE pipe represents over 95 percent of the pipe installed for natural gas distribution in diameters up to 12 inches (305 mm) in the U.S. and Canada. Because of PE piping’s extremely smooth inside surface, exceptional flow characteristics can be maintained, essentially 100 percent leak free fusion joints are easily obtained (assuming fusion bonding is done properly by qualified installers), and the piping will not rust, rot, pit, corrode, tuberculate or support biological growth. Caution is advised to protect PE pipe against contact with organic solvents (e.g. in the case where soils might be contaminated with oil or gasoline). Many fittings typically used for metallic pipe can be eliminated when using PE pipe because the PE pipe can be bent. PE pipe is well suited for installation in dynamic soil environments and in areas prone to earthquakes. At 140°F, PE materials retain about 50 percent of their 73°F strength (compared to PVC which loses nearly 80 percent of its strength under similar conditions).

Steels and stainless steels can be susceptible to corrosion under certain conditions. For pitting or general corrosion to occur, an electrolyte (such as produced from condensation) would be necessary. The pH of the condensate would also need to be low enough to cause significant corrosion. For a representative dairy manure biogas piping system, the pH of any condensate would be influenced primarily by the partial pressure of CO\textsubscript{2} in the gas stream. Other factors can increase the corrosion rate such as temperature (corrosion rates generally increase with increasing temperature), flow rate (rates increase with increasing flow rates), presence of electrolytes such as chlorides, and absence of H\textsubscript{2}S (in the case of CO\textsubscript{2} corrosion). Stainless steels are relatively immune to CO\textsubscript{2} corrosion, but carbon steels can be affected by CO\textsubscript{2} corrosion.

Over the decades there has been significant research on CO\textsubscript{2} corrosion on steels. In the case of expected corrosion from conditioned biogas with a dew point below the temperature of the gas stream and the gas temperature above the temperature of the pipe in contact with the ground, there will not be condensation and hence nil corrosion. If, however, the ground temperature is lower than expected or there are process upsets and some condensation does occur, there could be some localized corrosion. Based on available literature, it is roughly estimated that corrosion rates would be less than 0.5 mm per year (mm/yr), or

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0.02 inches per year (in/yr). If there is some H₂S in the gas stream, the corrosion rates should be expected to decrease. If the gas is unconditioned, the corrosion rates of carbon steel might be expected to be one to three mm/yr (0.04 to 0.12 in/yr). As mentioned, the corrosion of stainless steel (e.g. TP304L or 316L) would be expected to be nil, whether the gas is conditioned or not. Chloride stress corrosion cracking is not a concern since no chlorides are expected in the biogas.

Based on Black & Veatch budgetary quotations from reputable vendors and internal estimates for these applications, it is expected that HDPE piping costs approximately $2 to $4 per foot (ft), carbon steel piping costs $3 to $12/ft (depending on corrosion allowance), and stainless steel piping costs $15 to $25/ft. These budgetary quotations are based on 35,000 feet of pipe material only and do not represent the full installed cost for a biogas piping system in California. For carbon and stainless steels, additional (potentially significant) costs would need to be considered for exterior coatings, welding, and cathodic protection. According to industrial piping literature, two PE materials dominate the market: HDPE PE4710 and medium density polyethylene (MDPE) PE2708. While carbon steels and stainless steels should give adequate performance for biogas collection piping, PE products are superior for this application and the installed costs are expected to be lower than metallic piping.

Centralized Hydrogen Sulfide Removal

Black & Veatch analyzed potential H₂S removal costs associated with a centralized scenario using the aforementioned design basis, as depicted in the flow scheme shown in Figure 1. It was surmised that chemical scrubbing and biological removal technologies would likely be most appropriate for such applications, particularly at higher biogas H₂S concentrations. Removal costs were estimated at approximately $0.30 to $1.00 per thousand cubic feet (MCF) of biogas.

Safety considerations for centralized H₂S removal include the need for fixed detection systems for all on-site digester facilities and the centralized cleaning facility, appropriate hazard communication signage at all sites and along each biogas pipeline, comprehensive personnel training and PPE, and emergency action plans for all sites.

Figure 1. Process Flow Scheme for Centralized H₂S Removal

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**Distributed Hydrogen Sulfide Removal**

Black & Veatch also analyzed potential H$_2$S removal costs associated with the distributed scenario, once again using the same design basis information, the flow scheme for which is presented in Figure 2. Solid media would almost certainly be appropriate for distributed applications at low H$_2$S concentrations, while chemical / biological scrubbing could be competitive at the higher concentrations and flow rates examined. It was estimated that removal costs could be about $0.70 to $2.00/MCF of biogas.

![Figure 2. Process Flow Scheme for Distributed H$_2$S Removal](image)

Safety considerations for distributed H$_2$S removal include the need for fixed detection systems for all on-site digester facilities, appropriate hazard communication signage at all digester sites, comprehensive personnel training and PPE, and emergency action plans for all sites. Although the cleaning facility in a distributed configuration may not be subject to same rigorous safety management processes and hazard communication signage would not be required along each pipeline, they may still be preferable to project developers in case of a process upset upstream.

**Benchmark Cluster Project Comparison**

Black & Veatch investigated a benchmark dairy manure AD cluster project that fits within the general boundary conditions of the design basis described earlier in this white paper. The schematic in Figure 3 shows the flow rates and process blocks for such a project. For this benchmark project design, project capital and operating costs were estimated based on Black & Veatch approximations for similar projects (with and without H$_2$S removal) and publicly-available cost information, adjusted based on product capacity. For an assumed 20-year project life and five percent discount rate on capital, present worth calculations were made for centralized and distributed H$_2$S removal scenarios at typical biogas H$_2$S concentrations. The results of this economic analysis are shown in Table 5 and Figure 4. As can be seen from these benchmark project approximations, the use of distributed H$_2$S removal technologies could result in about three to 14 percent higher total project costs.
Figure 3. Benchmark Dairy Manure AD Cluster Project Schematic

Table 5. Comparison of Approximate Cost Differences for Centralized vs. Distributed H$_2$S Removal

<table>
<thead>
<tr>
<th></th>
<th>Centralized</th>
<th>Distributed</th>
</tr>
</thead>
<tbody>
<tr>
<td>H$_2$S Removal Percentage of Capital Cost</td>
<td>12-14%</td>
<td>14-21%</td>
</tr>
<tr>
<td>H$_2$S Removal Percentage of Operating Cost</td>
<td>1-8%</td>
<td>7-34%</td>
</tr>
<tr>
<td>H$_2$S Removal as Percentage of Total Project Costs (Incl. Capital and Operating)</td>
<td>7-11%</td>
<td>11-25%</td>
</tr>
</tbody>
</table>

A comparison of the safety considerations for each of the project configurations is shown in Table 6. The expected safety requirements for each configuration are compared across numerous safety program elements in a qualitative fashion using descriptive terms such as “equal,” “more,” and “less.” Overall this table shows that safety program requirements for the centralized H$_2$S removal structure are expected to be slightly more rigorous.
Figure 4. Benchmark Dairy Manure AD Cluster Project Economic Comparison

Table 6. Benchmark Cluster Project Safety Comparison

<table>
<thead>
<tr>
<th>Program Elements</th>
<th>Centralized</th>
<th>Distributed</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fixed Detection Requirements</td>
<td>Equal</td>
<td>Equal</td>
</tr>
<tr>
<td>Hazard Communication</td>
<td>More</td>
<td>Less</td>
</tr>
<tr>
<td>Personnel Training</td>
<td>Equal</td>
<td>Equal</td>
</tr>
<tr>
<td>Emergency Action Plan</td>
<td>Equal</td>
<td>Equal</td>
</tr>
<tr>
<td>Points of Greatest Exposure Risk</td>
<td>Digesters</td>
<td>Digesters</td>
</tr>
<tr>
<td>Number of Potential Failure Points</td>
<td>More</td>
<td>Less</td>
</tr>
<tr>
<td>Leading to H₂S Exposure Risks</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Conclusions and Recommendations

**Integrity of Pipes and Ancillary Components:**

Integrity of collector pipes and ancillary components (pumps, compressors, etc.) are real concerns due to the high levels (up to 5,500 ppm,) of hydrogen sulfide that could be present in dairy manure derived biogas. In moist gas it is highly corrosive in steel components, and
can cause damage to steel components over time. Appropriate materials must be selected for digester cluster applications, including the piping and the materials of construction of ancillary equipment.

**Hydrogen Sulfide Safety Issues:**

- Hydrogen sulfide exhibits both toxic and flammable characteristics, and exposure can cause death at concentrations of 150 to 200 ppm.

- For personnel working on or allowed to be in close proximity to biogas clusters and/or pipe or ancillary equipment carrying unprocessed H$_2$S gas, appropriate personal protective equipment must be worn based on the potential exposure risks. Additionally, hazard communication to all employees and visitors is the responsibility of the project owner.

- Fixed detection systems are prudent for dairy manure cluster projects, given the potential exposure risks.

- Portable monitors should be used to supplement fixed equipment when working near or visiting pipelines or process operations.

- Site-specific protocols for normal operations and emergency response should be developed for each project to include hydrogen sulfide risks and fully coordinate with the appropriate local emergency responders.

**Cluster Project Materials of Construction and Location of Hydrogen Sulfide Processing:**

- In the case studies examined in this white paper, manure is digested in clusters. The biogas from the digesters is then dehydrated near the digester and dry biogas containing hydrogen sulfide is then piped to a central gas processing facility to further remove the hydrogen sulfide and to remove other constituents to reach local RNG quality requirements.

- High-density polyethylene pipe is appropriate, widely used and economical for biogas service.

- Removal of hydrogen sulfide is expected to be more economical at a centralized location than in a distributed manner. The economic advantage of centralized removal of hydrogen sulfide should be balanced with appropriate and rigorous safety measures for those working near or visiting pipelines or processing operations.