Module 5:
Anaerobic Digester Start-up, Operational Monitoring, & H_2S

5.1: Four steps of AD

5.2: AD start-up

5.3: AD operation & process monitoring

5.4: Reasons for AD failure

5.5: Safety concerns

5.6: Understanding & managing H_2S

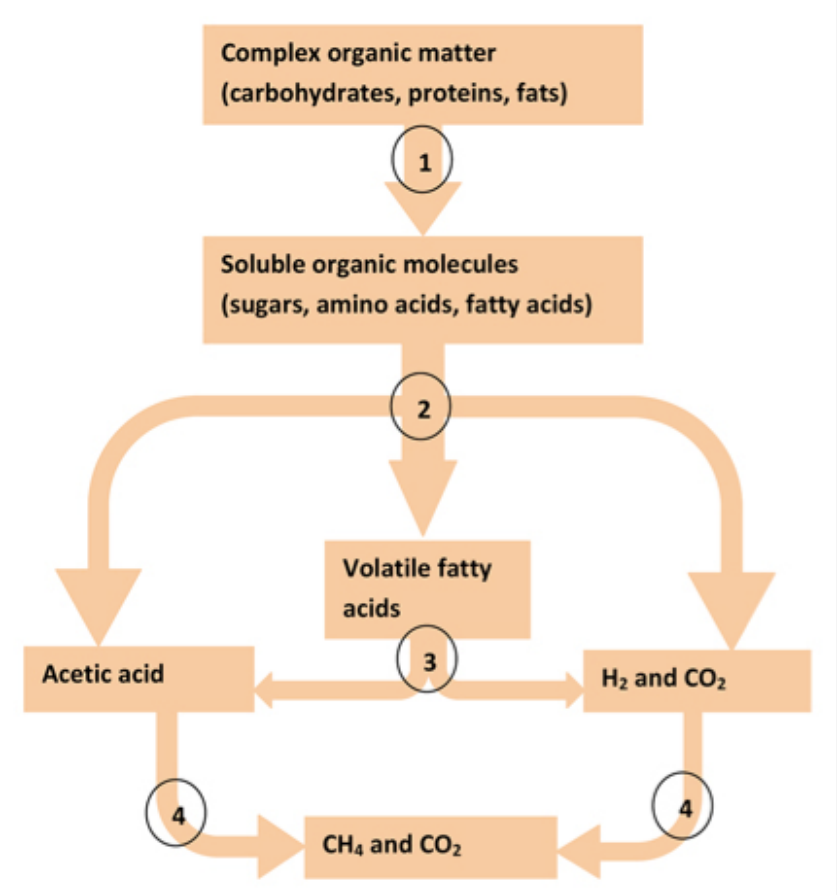
This curriculum is adapted from: eXtension Course 3: AD, University of Wisconsin

The four steps of AD

Overview of AD

AD is a complex series of biochemical reactions that are the result of the interaction of several types of bacteria. These bacteria function in the absence of oxygen gas and produce biogas, mainly methane and carbon dioxide.

The AD process occurs in 4 steps.



Step 1: Hydrolysis

Biomass is made of of very large organic **polymers** (aka biomolecules):

- Proteins
- Fats (lipids)
- Carbohydrates

Hydrolysis is a biochemical process that breaks polymers down into smaller organic molecules:

- Proteins → amino acids
- Lipids → fatty acids
- Carbohydrates → simple sugars

→ processed in step 2 acidogenesis

→ some acetate & hydrogen that goes directly to step 4, methanogenesis

Step 2: Acidogenesis (aka fermentation)

Simple organic molecules are broken down & pH drops.

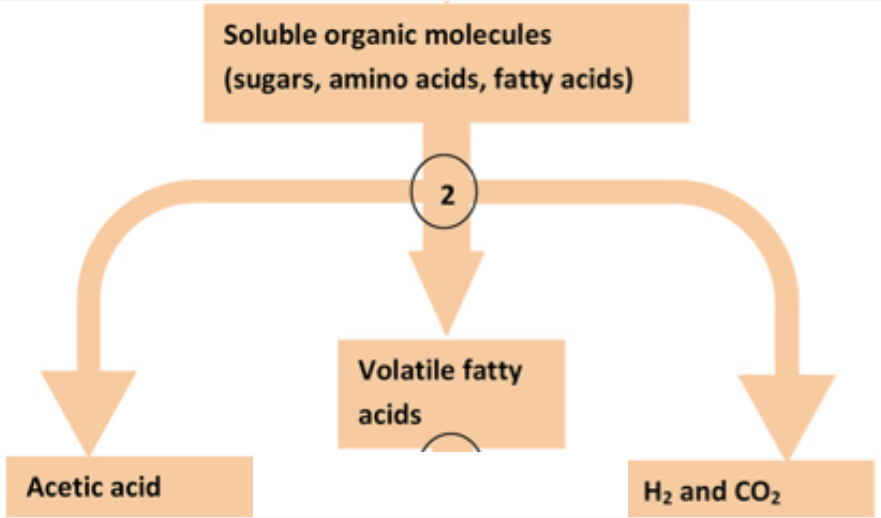
- ammonia (NH_3)
- hydrogen gas (H_2)
- carbon dioxide (CO_2)

→ Used immediately in step 4, methanogenesis

- hydrosulfuric acid (H_2S)
- volatile fatty acids (VFAs)
- carbonic acids
- alcohols

→ These acids cause pH to fall.

→ Processed in step 3, acetogenesis

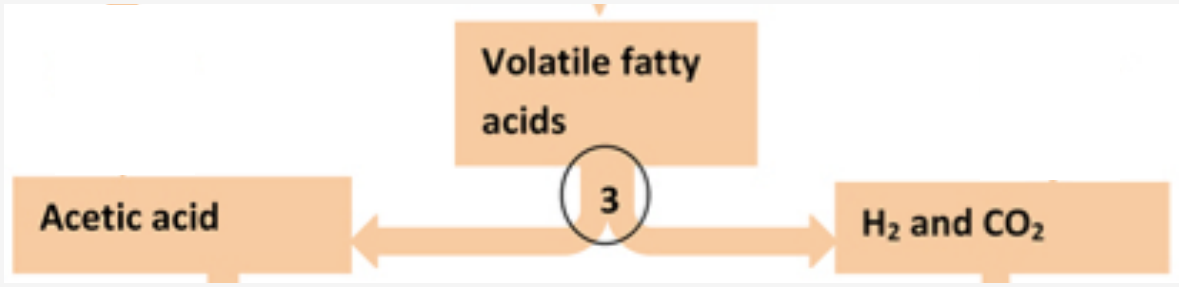


Step 3: Acetogenesis

Creation of acetic acid from remaining simple organic compounds

- volatile fatty acids (VFAs)
- carbonic acids
- alcohols

→ **acetate** (also H_2 and CO_2) → to step 4



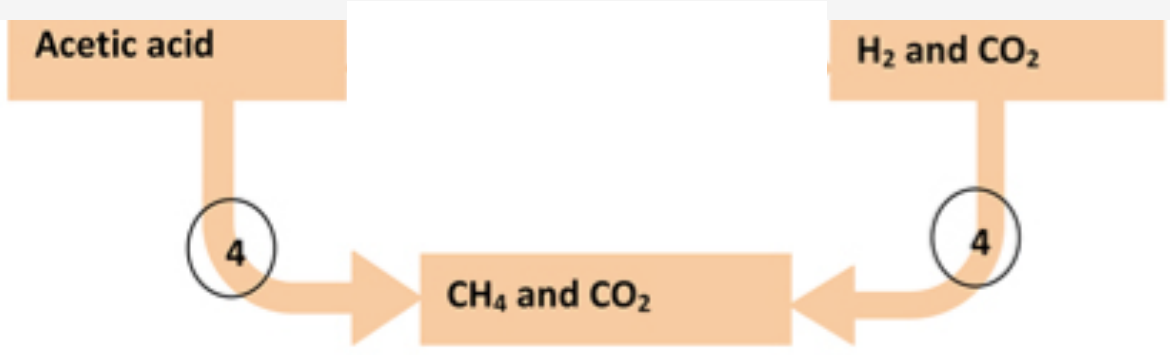
Step 4: Methanogenesis

Methanogenic bacteria turn acetate, CO_2 and H_2 into **methane** (CH_4).

$$CO_2 + 4\,H_2 \rightarrow \mathbf{CH_4} + 2\,H_2O$$

major pathway ⟶ $CH_3COOH \rightarrow \mathbf{CH_4} + CO_2$

acetate



Note that the biogas produced in step 4 contains water and carbon dioxide as well as methane.

Composition of biogas

Methane content varies somewhat with the type of feedstock used

Chemical	%
methane (CH_4)	45 - 65
carbon dioxide (CO_2)	30 - 40
hydrosulfuric acid (H_2S)	0.3 – 3
ammonia (NH_3)	0 – 1
water (H_2O)	0 - 10
nitrogen (N_2)	0 - 5
oxygen (O_2)	0 - 2
hydrogen (H_2)	0 - 1

AD Start-up

Start-up process

Monitoring the start-up processes is critical and easier than fixing a problem created by lack of care and attention.

"Seed" feedstock from an operating AD plant is often used to jumpstart AD start-up. Seeding the tank with 20 – 25% volume transfers bacteria that can grow and expand.

- *Alternatively, begin with* ***conditioned manure****: manure stored for at least 2 weeks in anaerobic conditions.*
- Fresh manure is then fed in slowly increasing volumes over the first 6 – 8 weeks of operation.
- Biogas should be produced around the fourth week of operation.
- 2 – 3 months should be allowed for bacterial populations to expand before a normal feeding schedule is started.

Flooding the gas space with carbon dioxide (or other non-oxygen gas) may speed the rate of start-up by displacing oxygen in the head space and rapidly creating anaerobic conditions.

Monitoring start-up

Monitoring several parameters helps the operator gauge the success and rate of start-up:

parameter	as methane production begins	warning sign?
pH	approaches 7	pH drops
VFA levels	decrease	VFA levels increase
biogas composition	CO_2 falls & CH_4 rises	no rise in CH_4
temperature	remains stable	becomes unstable

AD can occur at several different temperatures:

- Psychrophilic aka room temperatures
- Mesophillic temperatures should be about 100 °F
- Thermophillic temperatures should be about 135 °F

First feedings

Ideally, the first feedings after start-up should occur **continuously** and **at low rates** (or low concentrations of organic matter).

- Alternatively feed small volumes multiple times per day
- Feeding once daily is the least desirable option

Calculation of **loading (or feeding) rate** is discussed in unit 2:
Underfeeding produces less methane but has few negative consequences.

Overfeeding (volume or concentration of volatile solids):

- Inhibits production of biogas; and
- Pushes undigested VS into the digestate or effluent.

Cold weather start-up

While all start-ups require supplemental heating, **winter start-ups require very significant amounts of energy** to raise the temperatures of large volumes of cold feedstock. This represents a significant **added expense** and should be
avoided if possible.

- Plans for supplemental heat should be made if cold weather start-up cannot be avoided.

Cold weather can also cause problems with installation of valves, sensors and pumps. Ideally these items are installed, tested, and optimized prior to both start-up and the onset of cold weather.

Operation & Process Monitoring

The key to operations is 'steady state'

AD is a complex process depending on many coordinated bacterial and biochemical processes that transform complex organic material into methane.

Zickefoose & Hayes (1976) developed **seven operational procedures** to help operators reach and maintain steady state AD.

1. Set up a feeding schedule;
2. Control loading rates;
3. Control operating temperature;
4. Control mixing rates;
5. Control the quality of the slurry;
6. Control the HRT (length of digestion); and
7. Use lab tests and data to monitor the AD process and guide controls.

** See their paper for detailed checklists.*

1. A feeding schedule

The keys are:

- Minimizing excess water in feedstock; and
- Feeding continuously, or at regular intervals.

2. Control the loading rate

The loading rated depends on the mass of volatile solids fed each day and the total volume of the AD tanks.

Calculating manure volume

cylinder = $(\pi)(r^2)(h) = (\pi)(25^2)(20) = 39{,}250\ ft^3$

cone = $(1/3)(r^2)(h) = (1/3)(25^2)(5) = 3{,}217\ ft^3$

total = $42{,}521\ ft^3$

Calculating loading rate

pounds TS/day = (gallons/day)(8.34 lb/gallon)(%TS)

= (5000)(8.34)(0.065) = 2,710 lb TS/day

pounds VS/day = (lb TS/day)(%VS) = (2,710 lb TS/day)(0.69) = 1,869 lb VS/day

loading rate = (lb VS/day) / volume of manure = 1,869 lb/day / $45{,}521\ ft^3$

= 0.04 lb / day / ft^3

Average loading rates are 0.02 – 0.37 lb VS / ft^3 volume.

2. Loading rate & biogas yield

Volatile solids: generally, AD systems are loaded at a rate of 8% VS per day.

VTCAD is fed 16,000 gallons per day at full operational capacity.

$$\frac{16{,}000 \text{ gallons}}{1 \text{ gallon}} \times \frac{8.34 \text{ lb}}{2.2 \text{ lb}} \times \frac{1 \text{ kg}}{} = 60{,}654.5 \text{ kg}$$

- 8% of 60,654.6 kg = 4,852.4 kg of VS.
- Feedstock is typically 8% TS and 85% VS → 6.8% VS
- 6.8% of 60,654.5 kg is 4,124.5 kg, a bit short of 8% VS.

Biogas yield: typically 0.75 – 1.12 m^3 biogas/kg VS destroyed

VTCAD: We've been seeing about 70% destruction of VS, so:

(0.70)(4,124.5 kg VS) = 2,887.2 kg VS destroyed

Biogas range: (0.75 m^3/kg VS)(2,887.2 kg VS) = 2,165.1 m^3

(1.12 m^3/kg VS)(2,887.2 kg VS) = 3,233.2 m^3

3 - 6. Temp, mixing, slurry & HRT

3. **Temperatures** must be kept constant!

4. **Mixing** should be sufficient to mix bacteria with feedstock, and to prevent foaming and the formation of scum.

5. Feedstock controls **slurry** characteristics.

6. **HRT** and withdrawl of digestate should ensure complete digestion and destruction of odors.

7. Lab tests and operational data

Together, these data help operators to measure AD progress and to predict impending instability. In order of importance with optimal ranges.

parameter	hydrolysis tank	AD tank
VFA : alkalinity ratio	higher than AD	0.2 – 0.6
% methane		> 60 %
% carbon dioxide		< 40 %
% H_2S		< 200 ppm
pH	4.5 – 6.0	6.8 – 7.4
% destruction of VS		>> 40 %

Trends and **rates of change** are far more important than absolute values.

7. On-site testing

The operational tests suggested by Zickefoose & Hayes can, and should, be done on-site (at the digester facility). On-site testing can be done quickly and this allows problems to be nipped in the bud.

- Gas quality (methane, carbon dioxide, and H_2S levels) can be measured by sensors in the gas line or at the generator.

- VFA: alkalinity (aka the Ripley ratio is measured by acid titration of slurry sampled from the hydrolyzer or digester tank.

- Destruction of VS is determined by drying and combusting slurry samples.

Rodrigo Labatut and Curt Gooch of Cornell University created simplified testing procedures that can be performed with minimal training and using simple equipment. We've adapted their protocols for use at VTCAD and present some results here.

Determination of Ripley ratio

The Ripley ratio is the ratio of volatile fatty acids to total alkalinity (VFA : alkalinity) in slurry. This ratio is probably the most useful indicator of anaerobic digester stability that can be done on-site with minimal lab training and equipment.

Testing: 50 mL of fresh samples of hydrolyzer and AD slurries are:

- Titrated with 0.25 N sulfuric acid to three pH endpoints:
  - 5.75, 4.30 and 4.0
- NB: If samples are not fresh, loss of CO_2 gas will change alkalinity values.

Calculations: Standard titration calculations use volume and strength of acid used to calculate total, partial and intermediate alkalinities.

- TA (total alkalinity) is a measure of all bases with pKas in this range
- PA (partial alkalinity) represents bicarbonate (buffering) alkalinity
- IA (intermediate alkalinity) measures total volatile fatty acids
- The ratio of IA : PA approximates the VFA : alkalinity ratio and is called the Ripley ratio. Recommended ratio for AD tank is $\leq$ 0.8.

Ripley ratio data from VTCAD

date	sample location	sample volume (mL)	H2SO4 (N)	pH initial	H2SO4 Vi (ml)	H2SO4 Vf at pH 5.75	H2SO4 Vf at pH 4.3	H2SO4 Vf at pH 4.0
5/21/15	AD	50.0	0.25	7.21	0.0	14.4	23.0	24.7
5/21/15	AD	50.0	0.25	7.21	0.0	13.4	22.3	24.1
5/21/15	AD	50.0	0.25	7.22	0.0	13.7	22.6	24.0
5/21/15	hyd	50.0	0.25	5.04	0.0		6.8	9.8
5/21/15	hyd	50.0	0.25	5.04	9.8		16.9	20.0
5/21/15	hyd	50.0	0.25	5.04	20.0		26.8	29.9

date	Vd 5.75 (mL)	Vd 4.3 (mL)	Vd 4.0 (mL)	TA	PA	IA	Ripley (IA:PA)
5/21/15	14.4	8.6	1.70	6175	3600	2150	0.60
5/21/15	13.4	8.9	1.80	6025	3350	2225	0.66
5/21/15	13.7	8.9	1.40	6000	3425	2225	0.65
5/21/15	0.0	6.8	3.00	2450	0	1700	
5/21/15	0.0	7.1	3.10	2550	0	1775	
5/21/15	0.0	6.8	3.10	2475	0	1700	

Destruction of VS

Volatile solids (VS) are organic materials converted to biogas by AD. Effective AD will convert a significant percentage of VS to methane; conversion is called 'destruction' of VS.

Testing: Samples of feedstock and AD slurries are:

- First, dehydrated to determine total solids (TS); and
- Second, combusted to determine total volatile solids (VS).

Calculations: for feedstock vs. effluent

- TS as a percentage of initial (wet) sample mass
- VS as a percentage of initial (wet) sample mass
- Percent of TS that is VS (volatile TS)
- Percent volatile TS remaining and destroyed

VTCAD VS data

5/18/15	dish (g)	dish + wet (g)	dish + dry (g)	dish + ash (g)
prep pit	133.14	364.25	158.55	137.38
hydrolyzer	132.53	343.00	149.57	135.60
digester	131.01	340.45	141.06	133.81
effluent 1	131.04	338.95	138.60	133.58
effluent 2	134.38	348.06	141.53	136.94
solids	133.27	217.20	165.39	136.70

VTCAD VS data + results

5/18/15	wet (g)	dry (g)	ash (g)	% TS	% VS volatile TS (%)	% VS destroyed
prep pit	231.11	25.41	4.24	10.99	83.31	9.16	0.0
hydrolyzer	210.47	17.04	3.07	8.10	81.98	6.64	27.5
digester	209.44	10.05	2.80	4.80	72.14	3.46	62.2
effluent 1	207.91	7.56	2.54	3.64	66.40	2.41	73.6
effluent 2	213.68	7.15	2.56	3.35	64.20	2.15	76.5

Subtract mass of dish from mass of sample + dish

= (dry/wet)(100)

= (ash/wet)(100)

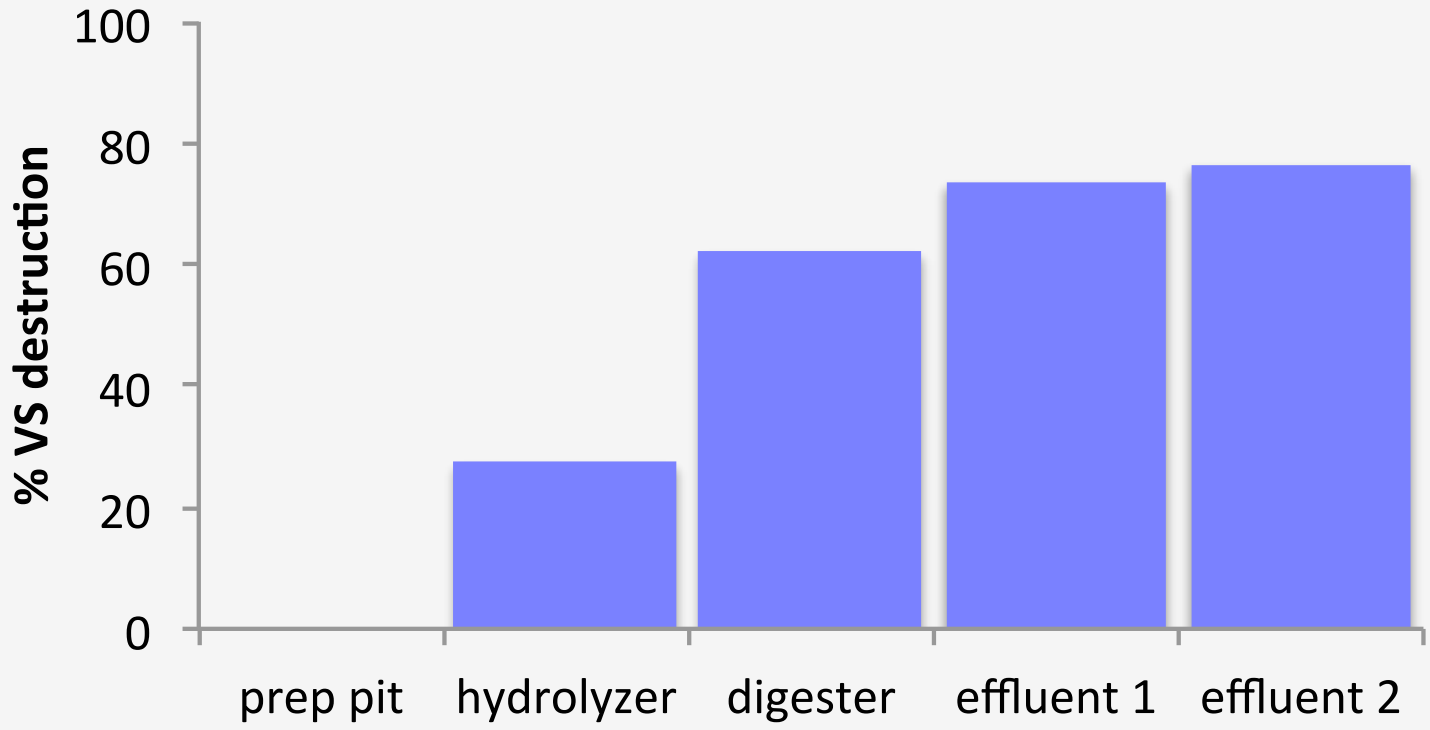
= (% TS)(% VS/100)

$$= \frac{(\%\ TS - \%\ VS)}{\%\ TS}\ [100]$$

VS destruction by VTCAD

In mid-May of 2015 feedstock was mainly manure, brewery waste, grease trap waste and glycerol.

Data shows that the digestion process was working efficiently with significant destruction of VS occurring in the hydrolyzer, and more in the digester.



VFA destruction

Since volatile fatty acids are the most available form of feedstock energy for methane producing bacteria, an efficient anaerobic digestion process should result in nearly complete destruction of VFAs.

Testing:

In order to assess the destruction of volatile fatty acids (VFAs), samples of slurry from the prep pit (undigested feedstock), hydrolysis tank, AD tank, and liquid effluent are distilled over heat. Distillation is a time consuming process requiring hot plates, and water-cooled condensers.

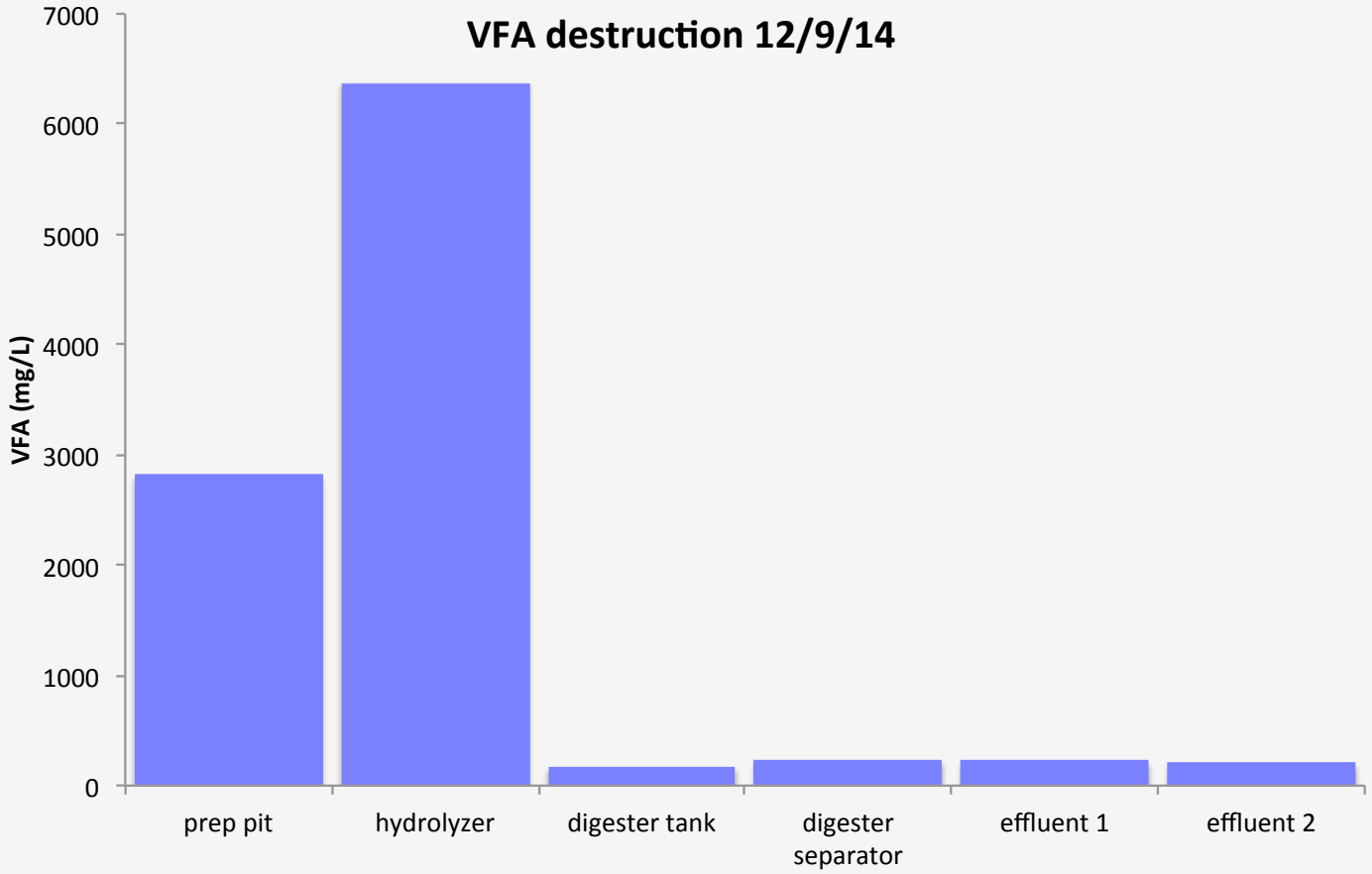
The distillate, containing total VFAs, is titrated with sodium hydroxide and quantitated using a standard acetic acid curve.

Calculations:

Standard titration calculations use the volumes of samples and concentration of the base to determine the concentration of total VFAs in each sample.

VFA destruction by VTCAD

In early December of 2014 feedstock was mainly manure.
Distillation of total VFA showed that hydrolysis released VFA from feedstock and that the AD process destroyed roughly 96% of VFAs.



Reasons for AD failure

Most failure occurs in the design phase

Prior to 1998, rates of failure for on-farm AD systems were astonishing:

- 70% failure for complete mix
- 63% failure for plug-flow

Today, long-term failure rates have been lowered by improved system design, better construction practice and the participation of more qualified and experienced companies.

However, **short-term failure** and **underperformance** are still common.

Four reasons explain most AD failures:

1. Bad design / poor installation
2. Bad choice of components
3. Poor farm management / AD operation
4. AD toxins in the feedstock

1. Bad design / poor construction

For example, **hydraulics** are often overlooked.

- While manure is flowable and pumpable it is still a semi-solid.
- Consistency can change with diet, management or season.

AD **technology providers** should be thoroughly vetted.

Grants for AD installation should include **engineering reviews** to:

- Validate design
- Ensure that AD design is appropriate for the farm and its management

2. Bad choice of equipment & materials

In the interests of keeping costs down, builders are tempted to choose less expensive or robust equipment. Farmers tend to be fiscally conservative and very cost-conscious.

There is often a cost to this approach: **"You get what you pay for."**

- Equipment failure or breakdown
- Increased need for maintenance and thus increased downtime
- Pumps and engines need to be properly sized and robust.

Examples:

- In New England, it appears that many AD facilities were over-sized using the premise that farms would expand and the extra capacity would be useful. This resulted in genset downtime and decay.
- In hindsight we can see that simplifying plumbing, using more robust valves, and having interchangeable pumps, or spare parts on hand, would have simplified early operations!

3. Poor farm management

Farmers **must be committed** to running and AD in addition to running the farm.

Successful operation requires **consistent** monitoring, operation and maintenance.

- Once the AD system is up and running this is an average daily commitment of **15 – 60 minutes per day** for the simplest AD systems using manure only.
- However, **more time will be required** during start-up, when significant changes are made, or when feedstock transportation is required.

Failures have occurred when operators cut corners. For example:

- Overfeeding for a day and then hoping the AD will run itself for 2 – 3 days.

Poor performance can becomes lead farmers to believe that the system itself is at fault and not worth their time: a self-fulfilling prophecy.

- Turning AD operations over to a **professional operator** may be a better approach for some farmers.

4. AD toxins in feedstock

Common farm chemicals and products are often toxic to the bacteria needed for AD.

Examples:

- High-protein diets can produce toxic levels of ammonia in the AD.

Common on-farm AD toxins:

- Rumensin ® and similar products (detergents)
- Copper sulfate and formaldehyde used in dairy foot-baths
- Pesticides
- Herbicides

Implementing safety procedures

AD operational precautions

Over a million AD systems are in use worldwide. Despite the obvious hazards posed their safety record is good.

Safety depends on **planning and precautions.**

- Fire prevention
- Mechanical hazards
- Statically sound construction
- Electrical safety
- Lighting protection
- Thermal safety
- Noise emission protection
- Asphyxiation & poisoning prevention
- Hygienic & veterinary safety
- Air pollution hazards
- Protection of ground & surface waters
- Nutrient overload of soil & water
- Flooding safety

Human health risks

The main risks to human health involve:

- Asphyxiation
- Explosion
- Burns
- Electrical shock
- Falls

Hydrogen sulfide is toxic

The AD process produces low to significant levels (0.05 – 4,000 ppm) of **hydrosulfuric acid** (H_2S or hydrogen sulfide) in biogas. H_2S smells like rotten eggs and is:

- Inflammable
- Colorless
- **Highly poisonous: lethal at 1.2 – 2.8 mg/L (0.117%)**
- Soluble in water, acting as a weak acid

H_2S inhibits the blood's ability to transport oxygen, causing victims to 'suffocate internally'. Initial symptoms:

- Irritation of the eyes & mucous membranes
- Nausea
- Vomiting
- Difficulty breathing
- Cyanosis
- Delirium & cramps
- Respiratory paralysis & cardiac arrest

Hydrogen sulfide exposure limits

Because H_2S is hazardous to human health, NIOSH and other agencies recommend **limiting human exposure** to H_2S:

PEL	(permissible limit)	20 ppm
REL	(recommended limit)	10 ppm
IDLH	(intermediate danger)	100 ppm

Personal or room monitors can be used to measure exposure to H_2S.

Conversion between common units:
1 ppm = 1.40 mg/m3 = 1.40 mg/1000 L = 1.40 ug/L

Entering confined spaces

Improper training on entering and working in **confined spaces** is the most common cause of accidents related to AD systems. There have been no AD-associated deaths in the US, but plenty of confined space-related deaths on farms.
No entry to, or work in, confined spaces may occur **without training**.

Once trained via OSHA, **remember** that:

- Never work alone in confined spaces
- Monitor air quality for oxygen and explosive risks
- Wear self-contained breathing apparatus (SCBA)
- Provide a continuous flow of fresh ventilated air by explosion-proof blower
- Maintain constant contact and communication with the worker to monitor their state of mind
- Wear a harness or safety belt with a lifeline attached to a support outside the tank
- Keep ignition sources far from the confined space
- Never go in after an unconscious or injured worker unless all above conditions are met

Explosions / burns

Methane is odorless, colorless, difficult to detect and highly explosive when in contact with oxygen (or atmospheric) gas.

- Lighter than air
- Therefore collects in the top of confined spaces

AD plants have been destroyed by fire and explosion!

Precautions:

- All AD buildings should be well ventilated
- All electrical wiring (lights, motors, pumps) should be explosion proof
- Gas lines should be equipped with flame-arrestors
- Gas-detection systems should be installed throughout to detect leaks

http://www.organics-recycling.org.uk/uploads/article2165/Integrating%20lessons%20learned%20from%20accidents%20into%20operators_%20behaviour%20and%20equipment%20design.pdf

Other risks at AD plants

Burns:
Contact with heating and cooling systems, the flare or genset

Electric shock:
From improper installation of equipment

Slips & falls

Collision with moving parts

Proper training, signage & fencing

Signage providing clear warning of hazards and required precautions is an essential element of a well-run AD system.

Particularly hazardous areas, like effluent ponds, and flares should be **fenced in**.

The AD operator and all personnel must be **trained**, equipped with personal protective equipment, and monitored to ensure continued good practice.

AD hazards self-assessment tool

Nellie Brown of Cornell's School of Industrial and Labor Relations has developed an assessment tool for farmers, AD operators and personnel:

> "Conducting a Safety Walk-through on a Farm: Hazards of the Manure Handling System, Anaerobic Digester, and Biogas Handling System (A Self-Assessment Guideline for Farmers)"

http://digitalcommons.ilr.cornell.edu/manuals/13/

Understanding & managing H_2S

Lowering H_2S levels in biogas

Biogas naturally contains H_2S in addition to methane and CO_2.
H_2S levels of 2,000 – 5,000 in dairy farm AD systems are typical & depend on:

1. Levels of sulfur in **feedstock**
   - Manure has abundant sulfur, generally from high-protein feed.
2. Levels of sulfur in the **water supply**
3. The **'substrate to sulfate' ratio**: in other words, the ratio of high-energy compounds to sulfate in feedstock.
   - Methanogenic bacteria grow and function best when they have access to high-energy feedstock. So increasing the 'substrate to sulfate' ratio gives methanogens the ability to effectively compete with the sulfur reducing bacteria (SRBs) that make H_2S.
4. The presence of **oxygen** in the biogas generation or storage tank.
   - Some oxygen allows sulfur-oxidizing bacteria to metabolize H_2S and convert it to elemental sulfur.

Why is H_2S a problem?

H_2S (aka hydrosulfuric acid or hydrogen sulfide) is an acid that is a gas at room temperature. The gas poses two distinct and serious dangers:

1. H_2S is **toxic to human** and animal health, & to microbial function.
   - H_2S begins to affect human health at 20 – 30 ppm.
   - H_2S enhances methane production at 0.5%, but prevents it at 6%.
2. H_2S is **corrosive** and **damages metallic surfaces** it comes in contact with.

Equipment	H_2S standards (ppm)
boiler	1,000
internal combustion engine	100
turbine	70,000
phosphoric acid fuel cell	20
molten carbonate fuel cell	10
solid oxide fuel cell	1
Stirling engine	1,000
purified biomethane	4

Magomnang & Villanueva (2014); Chynoweth & Issacson, 1987)

Acetate & H_2 are used to make H_2S

Reactions of sulfur-oxidizing bacteria that produce sulfides

$$4H_2 + SO_4^{-2} \rightarrow HS^{-1} + 4H_2O$$

$$CH_3COO^{-1} + SO_4^{-2} \rightarrow HS^{-1} + 2HCO_3^{-1}$$

acetate

$$4CH_3CH_2COO^{-1} + 3SO_4^{-2} \rightarrow 4[CH_3COO^{-1}] + 4HCO_3^{-1} + 3HS^{-1}$$

propionate

$$2CH_3CH_2CH_2COO^{-1} + SO_4^{-2} \rightarrow 4[CH_3COO^{-1}] + HS^{-1} + H^{+1}$$

butyrate

General summary from the sulfur's point of view

$$SO_4^{-2} + \text{organics} \xrightarrow{\text{anaerobes}} S^{-2} + H_2O + CO_2$$

$$HS^{-1} \longleftrightarrow S^{-2} + H^{+1}$$

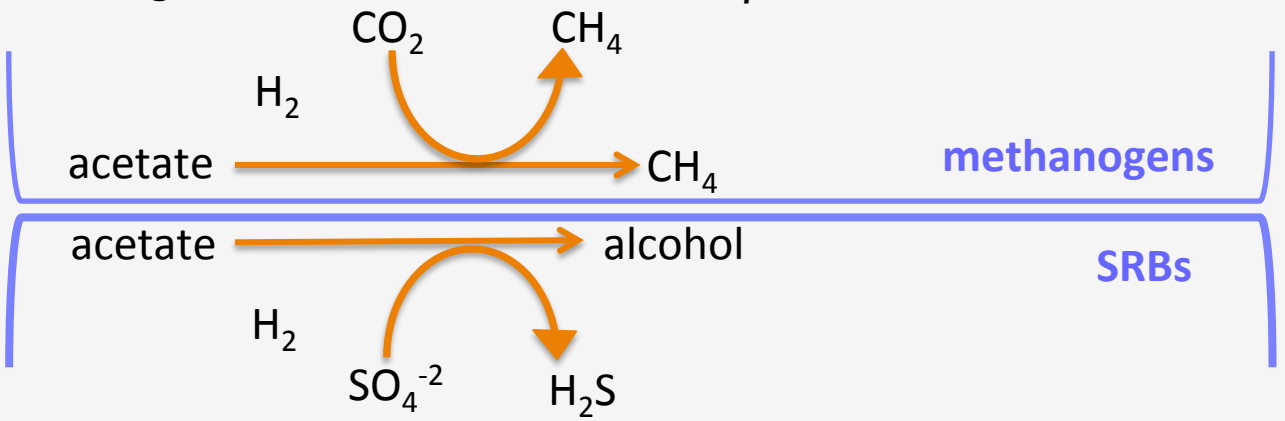
$$H_2S \longleftrightarrow HS^{-1} + H^{+1}$$

Farhan & Farhan (2006); Spreece (1996)

H_2S: a methane competitor

Digester feedstock contains a wide variety of bacteria. Two functional groups of bacteria compete for acetate feedstock (substrate) and the reducing power of hydrogen (H_2).

- Methanogens *(the good guys)*
- Sulfur reducing bacteria (SRBs) *(the competition)*



Competition from SRBs is a problem for anaerobic digesters because:

- SRBs are more robust bacteria & cope better with environmental challenge;
- SRBs reproduce more quickly than methanogens (rapid doubling);
- H_2S produced by SRBs inhibits methanogensesis.
  - H_2S has a less inhibitory effect on acetogenesis.

Negative effects of H_2S

There are many **reasons to minimize the production of H_2S**:

- H_2S competes with production of CH_4;
- H_2S inhibits production of CH_4 by methanogens;
- H_2S is highly corrosive and ruins generating engines & other equipment; and
- H_2S is highly toxic for people as well as microbes.

Methods of controlling H_2S

Prevention (pro-active):

- Low protein / low sulfur diet (feedstock)
- Addition of $FeCl_3$ to slurry to lower formation of H_2S

Treatment (reactive):

- Addition of tract amounts of oxygen to biogas space
- Post-digester scrubbing of biogas
  - Biological
  - Chemical

Diets that minimize H_2S production

To minimize production of H_2S by anaerobic digestion consider:

1. Control the amounts of **protein** in feedstock.
   - Protein is the main source of sulfur in AD diets.

2. Increase the **substrate to sulfate ratio**; the percentage of high-energy feedstock to sulfur containing feedstock.
   - 'Substrate' means high-energy feedstock that can be quickly & easily hydrolyzed and metabolized into simple organics with high levels of volatile solids.
   - High levels of VFAs give methanogens an advantage and allow them to compete effectively with SRBs.

 Gerardi (2003); Yoda (1987)

Using $FeCl_3$ to prevent formation of H_2S

When ferric chloride ($FeCl_3$) is added to feedstock, it reacts with sulfide (S^{-2}) generated as hydrolytic bacteria breakdown proteins by fermentation. **Extracellular** hydrolysis releases sulfides where the iron can react with them.

$$2\ FeCl_3 \rightarrow\ 2\ Fe^{+3} + 3\ Cl^{-1} \rightarrow +\ 3\ S^{-2} \rightarrow \boxed{Fe_2S_3}\downarrow +\ 6\ Cl^{-1}$$

The ferric sulfide (Fe_2S_3) is a **precipitate**, an ionic compound whose chemical bonds are so strong that bacteria cannot access the sulfide. So SRBs cannot metabolize the sulfur and produce H_2S.

- This prevention also gives the methanogens a competitive advantage.
- The effect of $FeCl_3$ addition is fairly rapid because it works via chemical, rather than biological, reaction with feedstock.

$FeCl_3$ caveats

Trace elements, like iron, nickel and cobalt, are required for the microbial biochemistry that is anaerobic digestion.
Addition of $FeCl_3$ can co-precipitate these ions and limit anaerobic digestion.

So, **balance is critical.**

H_2S partitions between biogas and digester slurry. A slurry concentration of 26 mg/L corresponds to 10,000 ppm H_2S in biogas.

- 1 mg/L in slurry ~ 380 ppm in biogas

Realistically, $FeCl_3$ can be used to reduce biogas H_2S levels by 50%: **mitigation**.

Remember, added $FeCl_3$ must:

1) Precipitate and remove sufficient sulfur to reduce H_2S significantly; and
2) Provide soluble iron ions for bacterial metabolism

Farhan & Farhan (2006); Speece, 1996)

Evidence that $FeCl_3$ increases AD

Bench-scale case study:

Mini-digester tests using wastewater treatment sludge digested under mesophillic conditions with a 30-day SRT were used to study the effects of ferric chloride on H_2S levels and efficiency of anaerobic digestion.

A $FeCl_3$ dose of 1.25% w/w produced these results:

- Control of H_2S;
- Reduction of volatile organic sulfur compounds that cause odor; and
- Increased volatile solids destruction.

$FeCl_3$ doses used in wastewater AD

Wastewater treatment case study:

A large wastewater plant in _____ uses a dose of:

- 0.3 gallons per minute of 40% $FeCl_3$
- That's 12 pounds per ton of feedstock TS
- At $0.10/pound, the annual cost of treatment is $73,000.
- H_2S levels are controlled.

The downside?

- The expense
- Some foaming & struvite formation

How does this compare to the dose we use at VTCAD?

16,000 gallons = 133,440 pounds = 66.72 tons

At 8% TS, that's 5.3 tons of feedstock solids per day.

At the dose above, that's 64 pounds of $FeCl_3$ or 7.68 gallons.

During 2015, we used 40 – 50 gallons of $FeCl_3$ per day!

$FeCl_3$ case study: AA Dairy (NYSEDA)

AA Dairy is a 1,000-cow dairy farm in upstate NY with a below-grade, plug-flow

AD that operates at mesophilic temperature with a 37 – 40 day HRT.

- Feedstock: 11,000 gallons of manure slurry per day (sawdust bedding)
- Biogas yield: 13,200 – 48,500 ft3/day
- Biogas quality: 34 – 40% CO_2, balance is CH_4 (60 – 66%), **4,000 ppm H_2S**
- Solids are used to create compost for commercial sale

Farhan & Farhan (2012)

$FeCl_3$ case study: slurry biochemistry

Biochemical testing of manure feedstock and $FeCl_3$-treated & digested effluent:

AA Diary	Feedstock	Effluent	EPA Dairy Avg
TS (mg/L)	74,137 (7.4%)	18,674 (1.9%)	
VS (mg/L)	21,128 (2.1%)	10,882 (1.1%)	11,600 (11.6%)
COD (ng/L)	70,800	28,985	100,000
PO_4 (mg/L)	2,408	1,198	1,550
NH_3-N (mg/L)	1,494	1,272	1,250
NO_3-N (mg/L)	1,297	274	
Iron (mg/L)	133	5.1	
Sulfate (mg/L)	2,874	4,390	
Sulfide (mg/L)	50.0	30.3	

Farhan & Farhan (2012); EPA (2002)

$FeCl_3$ case study: conclusions

- The dose of FeCl3 predicted by stoichiometry is far lower than the dose found to be effective in lab and full-scale study. Why? Hypotheses:
  - Iron is sequestered by organic material in the slurry;
  - Plug flow digesters don't provide sufficient mixing; and / or
  - Low digester ORP promotes loss of effective iron by absorption.
- Iron dosing of **150 mg/L** in feedstock:
  - Lab-scale: reduced sulfides by 40%
  - In AD: reduced biogas H_2S levels by 40%
- **Much higher doses** (250 mg/L) were required to achieve 70% reduction in H_2S
  - Mixing might increase effectiveness
- Ferrous chloride was just as effective as ferric chloride on an iron weight basis.
- Production of methane was neither increased nor decreased by $FeCl_3$.

Bottom line: The effective dose of $FeCl_3$ is best determined empirically

Farhan & Farhan (2012)

Finding the effective dose of $FeCl_3$?

The dose of FeCl3 required to keep H_2S levels at acceptable levels depends on many factors, including:

- Sulfur in the diet;
- Type and design of the anaerobic digester; and
- Operation of the anaerobic digester.

So the effective dose must be determined **empirically: by trial and error**.

1. Monitor H_2S levels daily, looking for change.
2. As soon as H_2S levels trend upward, increase the dose of $FeCl_3$.
3. Once levels of H_2S drop, lower $FeCl_3$ to levels a bit higher than before the upward trend.

Other iron salts?

A number of different salts of irons and other metals can be used to precipitate sulfur.

For example, **iron phosphate** can also be used to control H_2S levels.
Lab studies showed that this iron salt could reduce levels of H_2S in biogas from 2500 to 100 ppm.

Other effects:

- pH of digester slurry increased from 6.7 to 8.2.
- Soluble sulfides increased from 18 to 61 mg/L.

Farhan & Farhan (2006); McFarland & Jewell (1989)

Infusing oxygen to treat H_2S

It is crucial to remember combining oxygen with biogas to oxygen levels of **6-12%** creates an **explosive gas** and is **extremely dangerous**.

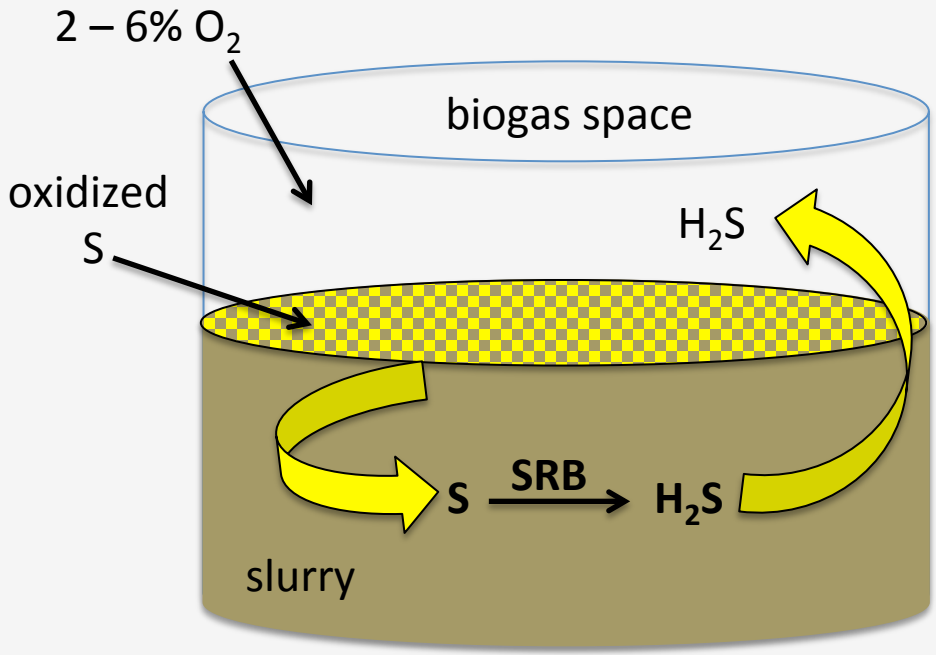
However, at lower levels of **2-6%,** oxygen in biogas creates a micro-aerophilic atmosphere that allows the growth of sulfur oxidizing bacteria (SOB) that convert H_2S to elemental sulfur (S).

- SOBs (*Thiobaccilli)* colonize and grow on the surface of the digester slurry.
- These bacteria are found in feedstock and don't need to be added.
- Oxidized, elemental sulfur deposits can be seen as yellow deposits on the surface of the slurry when oxidation is occurring.

Infusing oxygen to treat H_2S

If digester design mixes slurry well, oxidized sulfur deposits created by oxygen treatment can be mixed back into the slurry where sulfur-reducing bacteria can access the sulfur and metabolize it back into H_2S.

- This may be less problematic in plug flow digesters where mixing is minimal.



Treating biogas with oxygen in a separate gas storage tank, or in piping that delivers biogas to the genset, avoids sulfur recycling. However, it requires another tank and care and feeding of this bio-treatment system.

Post-digester biogas scrubbing

A variety of methods, both **chemical** and **biological**, can be used to scrub or purify biogas.

Drying of biogas and purification of methane to **'biomethane'** is an expensive process. Biomethane has less than 4 ppm H_2S and may be:

- Injected into natural gas pipelines; or
- Compressed for storage and / or transportation.

However, lowering (but not removing) H_2S is simpler and less expensive.

How big is your problem?

It's useful to know how much H_2S a digester produces per year in order to:

- size a scrubber;
- understand the cost of media / replacements; and
- understand the costs of disposal of used media / chemicals.

Parameters:

- Volume of biogas per day
- Concentration of H_2S (ppm)

Calculate kg of H_2S produced on an annual basis

- Remember that 1 ppm = 1.4 mg/m^3 and use metric conversions.

Typical chemical H_2S scrubbing techniques can handle 200 kg of S/day, but there is a cost to any scrubbing technology.

Chemical (absorption) scrubbers

Chemical scrubbers provide a chemical compound that react with H_2S, altering it and removing it from biogas.

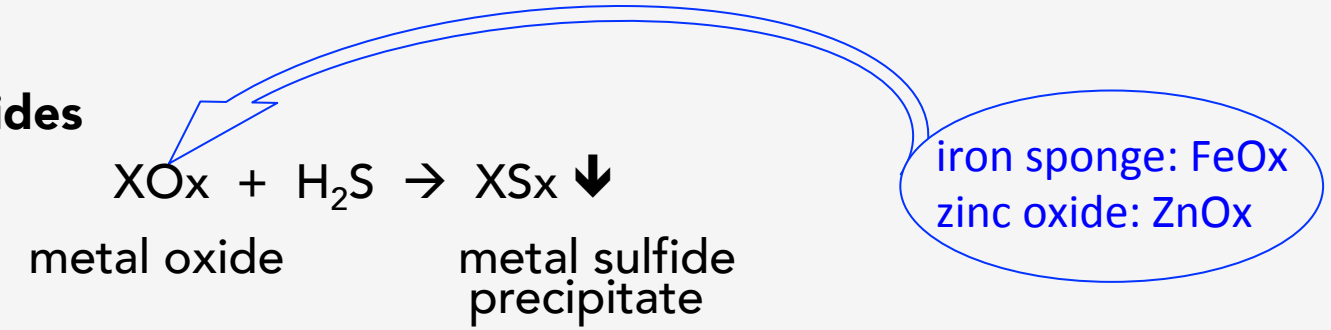
- **Metal oxides**
- **Absorbents**
- **Caustics**
- **Granular activated charcoal**
- **Water scrubbing**
- **Resins**

Soroushian et al. (2006); Farhan & Farhan (2012)

Iron sponge

Iron sponge canisters use metal oxides to precipitate sulfides out of biogas.

- **Metal oxides**



The metal oxide is consumed and must be periodically replace.

An iron sponge uses a bed (canister) of media + active ingredient.

- Media: steel wool or wood chips (often pine) [wood preferred
- Active ingredient: hydrated iron oxides (Fe_2O_3; aka rust)

Iron sulfides precipitate onto the media and can be rinsed off and filtered from the aqueous rinse solution.

Media must be replaced every 4 – 6 months.

Soroushian et al. (2006); Farhan & Farhan (2012)

Iron sponge reactions & regeneration

Iron sponge (Fe_2O_3) reacts with H_2S to form iron sulfide precipitate (1)

(1) $2Fe_2O_3 + 6H_2S \rightarrow 2Fe_2S_3 + 6H_2O$ $\Delta H = -22$ kJ/g-mol H_2S

Iron sponge can be regenerated by reaction with oxygen gas (2)

(2) $2Fe_2S_3 + 3O_2 \rightarrow 2Fe_2O_3 + 6S$ $\Delta H = -198$ kJ/g-mol H_2S

Partial <u>regeneration</u> by addition of 8% O_2 to the gas stream or by spreading the sponge out in air while continuously wet for 10 days:

- releases elemental sulfur (S); and
- enormous amounts of **heat** (exothermic ΔH); so
- **must be done with care to avoid conflagration.**

<u>Operation of iron sponge</u>:

- Operation without oxygen achieves 85% efficiency (0.56 kg H_2S/kg sponge) & requires regeneration following saturation.
- Operation with added air allows continuous (simultaneous) regeneration.

Magomnang, A-A.S.M. and Villanueva, E.P. (2014); Taylor (1956)

Iron sponge: case studies

A 2014 study conducted in **Thailand** found that simple PVC columns packed with steel wool were capable of reducing H_2S concentrations from 170 to zero ppm.

- Capacity of iron oxide for sulfide absorption ranged from 0.20 – 0.72 kg/kg
- 3 sequential iron oxide canisters were used at a flow rate of 3 – 4 L / min
- 1.9 kg of iron oxide remained effective after 17 kg of biogas were treated

A 1990 study conducted in **NY state** found that 12 lb/bushel-grade iron sponge removed 1.84 kg H2S / kg Fe2O3 when operated with 2.29% oxygen.

Magomnang, A-A.S.M. and Villanueva, E.P. (2014); Vetter (1990)

Absorbents

Absorbent media present a large and porous surface area that H_2S absorbs onto.

Media can be regenerated by:

- Heating;
- Lowering pressure; and
- Flooding with another gas to displace absorbed H_2S.

Zeolites are silicates with uniform pore size & dimensions that absorb polar compounds:

- H_2O
- SO_2
- NH_3
- Carbonyl sulfide
- mercaptans

Soroushian et al. (2006); Farhan & Farhan (2012)

Granular activated carbon

Granular activated carbon particles have huge surface areas of 4000 – 5000 square inches per ounce. Polar gases like H2S are absorbed onto these surfaces.

- These surfaces can be coated with alkaline or oxide coatings to increase reactivity & thus effective removal of gases.
  - NaOH, Na_2CO_3, KOH, KI, metal oxides are used
  - These coatings can effectively double rates or removal from 10% from untreated GAC to 20-25%
- Canisters (sometimes sequential) are packed with charcoal.
- Biogas is passed through canisters.
- When H_2S levels in treated biogas rise, canisters are repacked or replaced.
- Addition of O2 increases effectiveness.

Soroushian et al. (2006); Farhan & Farhan (2012)

Water scrubbing

The components of biogas have varying solubility in water.

Gas component	Solubility in water @ 20°C (g gas/kg water)
methane	0.023
carbon dioxide	1.70
hydrogen	0.0016
hydrosulfuric acid	3.90
nitrogen	0.018
ammonia	520
oxygen	0.044
sulfur dioxide	110

Bubbling biogas through water will remove CO_2 and H_2S as they will dissolve in the water.

- Scrubbing water will be acidic & may need to be treated before discharge.

Biological (SOB) scrubbers

Post-AD biological scrubbers use **sulfur-oxidizing bacteria** (SOBs) to destroy H_2S by oxidation of sulfur prior to combustion.
A system tested in CA in 2006 kept H_2S levels below that state's stringent air quality maximum of 40 ppm under normal conditions.

Advantages:

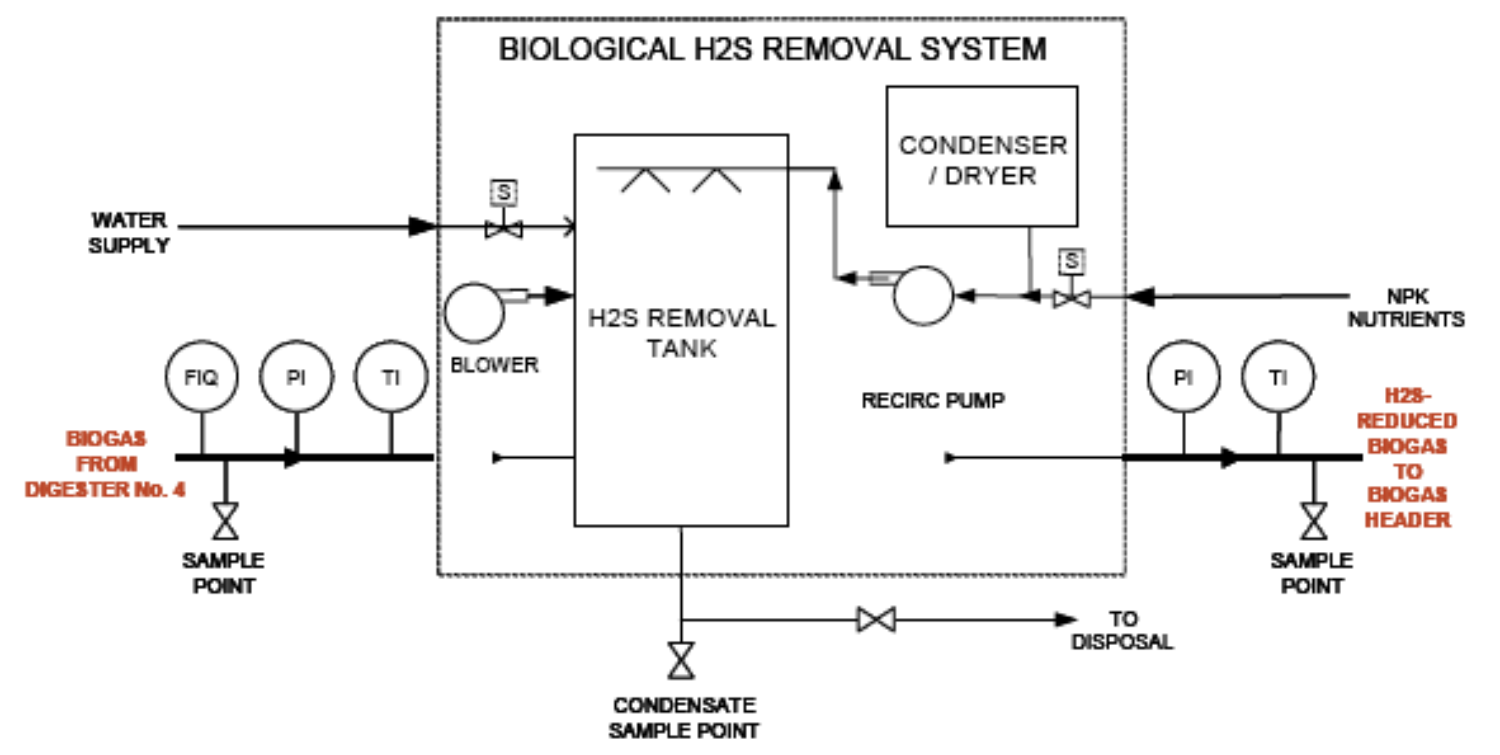
- Low energy use;
- No chemicals to store and handle
- Automated
- Long life expectancy of overall system

Cautions: Bacteria that degrade or oxidize H_2S can produce acids like H_2SO_4. Accumulation of acid lowers pH and can kill bacteria in the biological scrubber.

Example:
The IEUA RP-1 was developed as a simple single-stage scrubber in contrast to the two-stage chemical / biological scrubbers sold commercially.

IEUA RP-1

System: fiberglass tank filled with plastic media; water pump; air blower



Air was added at 5% v/v or less.

The system worked very well for > 1 month.

Drop in performance may have been due to drop in temperature from October to December (30 to 22C in scrubber) or lack of nutrients; none ever added.

Soroushian et al. (2006)

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Farhan & Farhan (2012)

Economic comparison of scrubbing

Cost comparison of H_2S removal technologies:

Technology	Capital ($)	Annual O&M ($)	Total NPV 5 years ($)	Total NPV 10 years ($)
FeClx	1.5 – 2 K	8 – 10 K	(45.8 K)	(91.0 K)
Iron sponge	40 – 50 K	1.5 – 2 K	(52.3 K)	(61.1 K)
Carbon filter	12 – 14 K	3.5 – 4.5 K	(32.2 K)	(52.3 K)
Caustic scrubber	12 – 15 K	2.5 – 3.8 K	(28.5 K)	(44.4 K)

NPV = net present value calculated from average capital and O&M costs.

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