

# Chemistry for Digesters

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# Agenda

- Microorganisms
- Organic load
- Process control
- Total and Volatile Solids
- Volatile Acids
- Alkalinity
- VA/Alk Ratio
- pH
- Process monitoring
- Importance of accurate data
- Process stream sampling
- Process ranges
- Failure indicator relationship
- Summary

# Microorganisms

- Acid formers:
  - Convert insoluble organic solids to soluble organic solids
    - Enzymes breakdown insoluble to soluble
  - Convert soluble organic solids to organic acid
    - Alkalinity and pH tend to drop
  - High energy, rapid growing
  - Not as sensitive to environmental changes

# Microorganisms

- Methane formers:
  - In a balanced system, organic acids are consumed at the same rate as produced
  - Get little energy from the organic acids, so
  - Grow slowly compared to acid formers
  - Susceptible to pH and temperature changes
  - CO<sub>2</sub> and dissolved NH<sub>3</sub> contribute to the formation of alkalinity
  - Do the work of stabilization

# What is meant by organic loading?

1. Organic Loading is the amount of food (volatile solids) fed to the digester each day.
2. It is normally calculated as pounds of volatile solids per cubic foot of digester volume per day.
3. Another way of expressing organic loadings is the relationship of the amount of volatile solids in the feed sludge to the active digester volume.

# Where does the process control of a digester begin?

1. Process control of a digester begins with control of digester loadings, both hydraulically and organically.
2. The operator must be aware of the pounds of volatile solids being pumped to the digester on a daily basis.
3. This is the means by which the operator controls and maintains the digester processes and determines digester efficiency.
4. To realize the effectiveness of process control, a program of operational and laboratory guidelines must be established and maintained.

# What are the total and volatile solids?

1. An analysis for total solids identifies the sludge concentration of the feed sludge entering the digester.
2. The water in the sludge is evaporated in an oven at 103-105°C for an hour, leaving only the residual solids which are expressed as total solids, TS.
3. Volatile solids, VS, represent that portion of the total solids that are organic in nature.
4. These volatile solids represent food matter that is to be stabilized.

# What are the total and volatile solids?

5. The total solids residue is heated in a furnace to 550°C for two hours, which will ignite the organic material in the solids, leaving only ashes, referred to as fixed solids, FS.
6. Applying these values to a formula.  
$$\text{Total solids (\%)} - \text{Fixed solids (\%)} = \text{Volatile solids (\%)}$$
7. The difference between the two weights represents volatile or organic portion and the residue after burning represents the ash or inorganic portion.

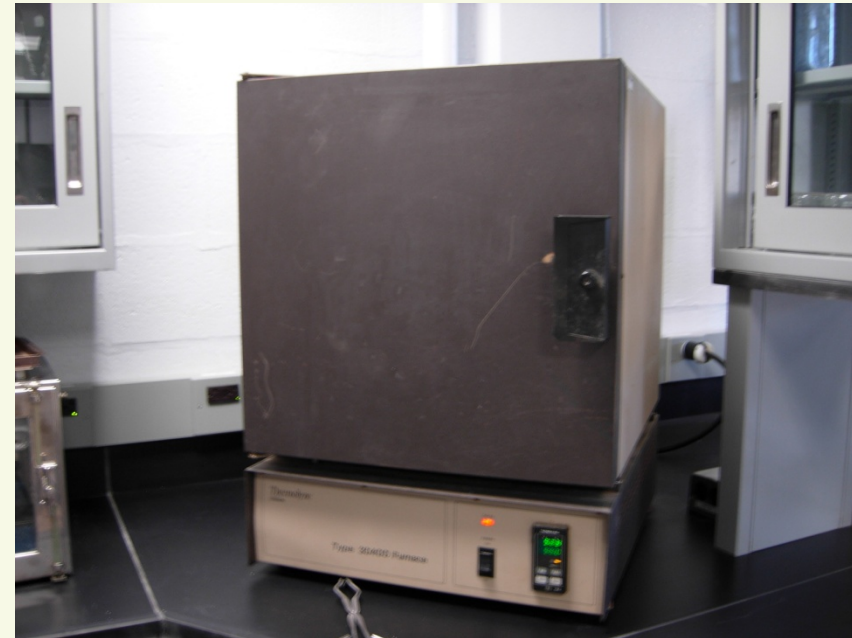


# Total and Volatile Solids

Drying Oven at 103-105°C



Furnace at 550°C



# What are other parameters to be monitored in a digester operation?

Once sludge has entered a digester, the major internal control combines two laboratory tests:

1. Volatile Acids and
2. Alkalinity

# What are volatile acids and alkalinity?

1. The alkalinity of a digester is important because it represents the ability of a digester to neutralize the acids formed during the digestion process.
2. As a result, the volatile acids should always remain low, when compared to alkalinity.

# Volatile Acids (VA)

- Volatile acid production is largely dependent on the volume of sludge fed to the digester.
  - It should be held relatively constant.
- In healthy digesters, acids will be used by the methane formers at the rate they're produced.
  - Severe changes in conc. indicates that acid-producing organisms are multiplying at a rate faster than the methane producing organisms.
  - Staff must monitor the relative change in the proportionality of the VA/Alk ratio.
- Volatile (organic) acids will typically be 50 – 300 mg/l expressed as acetic acid.

# Alkalinity (Alk)

- Sufficient alkalinity must be present to “buffer” the volatile acids formed during digestion.
- Alkaline buffers come from two sources:
  - Present and concentrated in the feed sludge.
    - Hard water, alkaline industrial wastes
  - Produced by the methane formers
    - Bicarbonates, carbonate and ammonia
  - Typically 2,000 to 5,000 mg/l expressed as bicarbonate alkalinity (mg/L  $\text{CaCO}_3$ )
- Alkalinity (fed and produced) must be in equilibrium with acid production to prevent upset.

# VA/Alk Ratio

- Indicates the progress of digestion, its stability, and is used for process control.
- The results of the volatile acids and alkalinity tests are expressed as a ratio. Example:
  - Volatile acids = 300 mg/l
  - Alkalinity = 2,000 mg/l
  - $VA/Alk = 300 / 2,000 = 0.15$
- The range of VA/Alk ratio is 0.1 to 0.35, 0.1 to 0.25 is ideal.
- VA/Alk ratio of 0.5 indicates a sour digester
- Parameters must be sampled and tested daily at start-up, no less than a minimum of three times per week during stable operation.
  - If unstable conditions are beginning to occur, or are present (trending above 0.25), test daily.

# What is the proper ratio of volatile acids to alkalinity?

1. Ideally, the VA/ALK ratio should range between 0.1 and 0.25, once it goes beyond 0.25 the operator is cautioned to back off on the feed and monitor very closely.
1. Within this range, the digester is considered healthy with good digestion taking place.
2. When the ratio begins to change, it is an indication of a potential digester upset. Trending towards 0.35 is entering the danger zone. A ratio of 0.5 indicates a sour digester.

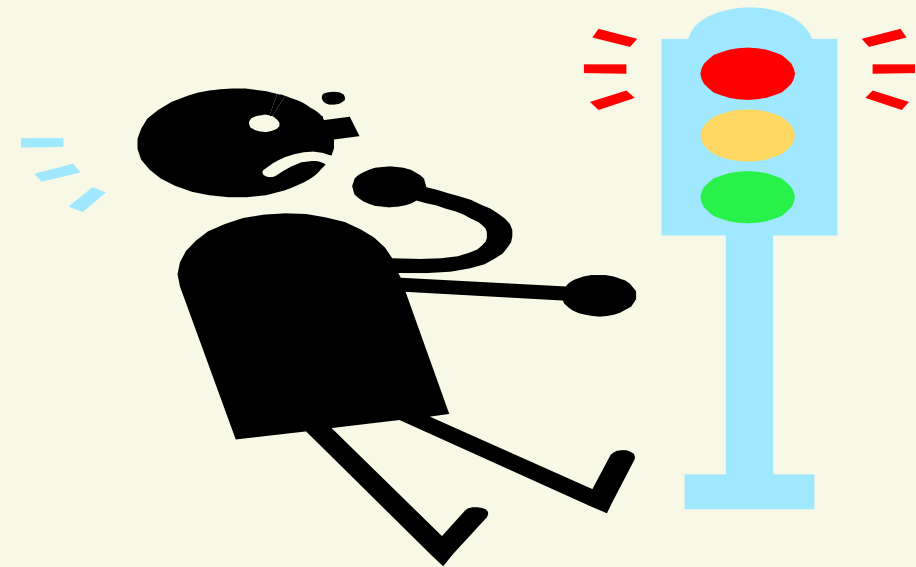
# VA/AIk Ratio

0.1 – 0.25 **green light**

0.25 + **yellow caution light**

0.35 + **red warning danger light**

0.5 **FLASHING RED LIGHT!**  
SOUR DIGESTER !!!





# Since the VA/ALK ratio is the first indicator of potential digester upset, what are some other signs which follow?

1. The process of sludge digestion generates methane and carbon dioxide gas and other trace gases.
2. Under normal circumstances, the production of methane represents 65 to 70 percent of the digester gas; carbon dioxide being 30 percent and the remaining 1 or 2 percent various trace gases.
3. Since an increase in the VA/ALK ratio is the first sign of digester trouble, an increase in this ratio will ultimately lead to an increase in carbon dioxide and a decrease in methane.

# Since the VA/ALK ratio is the first indicator of potential digester upset, what are some other signs which follow?

4. Methane production will represent less than 65 percent of the contents of the digester gas and carbon dioxide will exceed 30 percent.
5. Finally, the pH of the digester sludge will begin to drop.
6. Temperature also affects the work of the methane bacteria.

# Since the VA/ALK ratio is the first indicator of potential digester upset, what are some other signs which follow?

7. The best temperature range for the digester contents should be between 93° - 100°F and variations in temperature should **not exceed 1°F per day.**
8. In general, the detention time needed to obtain complete digestion decreases with increasing temperature since organism activity increases as temperature increases.

# pH; What is it and Why does it Matter?

- Measurement of hydrogen ion concentration of a solution indicating the relative degree of acid or base.
  - Digestion Range: 6.6 to 7.2;
  - Preferred Range: 6.8 to 7.0
  - Above 8.0, un-ionized ammonia is toxic to methane formers
  - Below 6.0, un-ionized volatile acids are toxic to methane formers
  - Below 4.5, digestion ceases
- Un-ionized molecules pass through the methane formers cell wall easily causing toxicity
  - How do you respond: change the pH which changes the un-ionized concentration preventing toxicity
    - (i.e., adding bicarbonate alkalinity)

# Wouldn't monitoring pH be the easiest method of controlling digester process control?

1. pH is one of the simplest tests that can be conducted to indicate process control and should be done at least once per shift.
2. However, there is a danger in solely relying on pH for process control because the pH changes very slowly and the digester may be completely upset before the pH changes.

# pH as a Performance Parameter

- pH is a “lagging” indicator. Why?
  - When a digester is upset, volatile acids concentration will increase neutralizing the alkalinity.
  - Once exhausted, volatile acids concentration continues unchecked and the pH drops rapidly.
  - Alkalinity masks volatile acid build-up, when the pH does drop, the digester has been sour for a long time.
- Therefore, pH is the poorest indicator of performance.

# Now that the process control parameters are known, how does an operator begin the monitoring process?

1. In order for the operations staff to effectively control the digestion process, an operator must be aware of the various sampling points and required tests.
2. A good sampling and testing program will consist of samples being collected from the same location at regular intervals.
3. Analysis of these samples will assist in informing the operations staff of digester performance and can be used to adjust the process operation

# Importance of Accurate Data

1. You must be able to trust the numbers that you get
2. Test results are only as good as the representativeness of the sample
3. Do not underestimate the importance of proper sampling technique
4. Duplicate samples on solids analyses take very little extra effort, in order to ensure that you know what you are feeding
5. Trend results



# What process streams of the digester should be sampled and what analysis should be performed?

1. The digester will have the following process streams sampled:
  - Digester feed
  - Recirculated sludge
  - Digester Gas
  - Digested sludge
2. The influent sludge to the digester, should be analyzed for total solids and total volatile solids.
3. During the recirculation of the sludge, a sample should be taken and tested for volatile acids, alkalinity, pH and temperature.

# What process streams of the digester should be sampled and what analysis should be performed?


4. A sample of the digester gas should be taken and analyzed for percent carbon dioxide using the Fyrite daily initially.

**Fyrite<sup>®</sup>**  
**Gas Analyzers**

Fast, accurate and easy to use instruments for measuring and analyzing carbon dioxide or oxygen. Fyrite Analyzers are available for either CO<sub>2</sub> or O<sub>2</sub> analysis, and each model is produced in three scale ranges.

All six instruments are similar in appearance and size, but differ in important construction details, as well as in the absorbing fluids.

Each model, therefore, is suitable only for the particular gas analysis or scale range for which it has been manufactured. Accuracy is within  $\pm 1/2\%$  CO<sub>2</sub> or O<sub>2</sub>.

The image shows two cylindrical Fyrite gas analyzers with black bases and clear upper sections containing colored liquids. A sampling probe with a yellow tip and black tubing is also visible, connected to a black pump-like device.

# What process streams of the digester should be sampled and what analysis should be performed?

5. By analyzing for carbon dioxide content and identifying the percent concentration, an accurate estimation can be made of the methane content.

# With these analyses being performed, what should an operator expect in ranges of concentration of each parameter?

1. The influent sludge to the digester should be as follows:
  - Total solids (5.6%) 6 % TS from GTs and 5% TS from TWAS
  - Volatile solid 75 - 80%
2. The sludge contents of the digester should be as follows:
  - Volatile Acids (100 - 500 mg/L)
  - Alkalinity (2500 - 5000 mg/L)
  - Temperature (93° - 100°F)
  - pH (6.6 - 7.2, 6.8 – 7.1 is preferred)

# With these analyses being performed, what should an operator expect in ranges of concentration of each parameter?

3. Digested sludge (from the digester to the sludge dewatering system) should be as follows:
  - Total solids (average 3 to 3.5%)
  - Volatile solids 60 to 65%
4. Digester gas should be analyzed for the following:
  - Methane (More than 65 %)
  - Carbon Dioxide (Less than 35 %)

# Failure Indicator Relationship

Process Indicator	Trend of Indicator	pH *	CH <sub>4</sub>	CO <sub>2</sub>	Alkalinity	Volatile Acid
pH	Down		Down	Down	Down	Up
CH <sub>4</sub> , %	Down	Down		Up	Down	Up
CO <sub>2</sub> , %	Up	None	Down		Down	Up
Alkalinity	Down	Down	Down	Up		Up
Volatile Acid	Up	Down	Down	Up	Down	

\*pH is a lagging indicator

# To summarize, what are the major guidelines to follow towards maintaining process control?

Digesters respond slowly once they have become upset.

1. To keep this situation from occurring, some of the guidelines to follow:
  - Monitor volatile acids, alkalinity, VA/ALK ratio and temperature daily. Plot these parameters against time and watch for trends.
  - Feed the digester small amounts of sludge as often as possible -- avoid shock loads of sludge.
  - Establish and maintain sludge withdrawal rates in order to maintain SRT and a sufficient amount of seed sludge in the digester.

# To summarize, what are the major guidelines to follow towards maintaining process control?

1. To keep this situation from occurring, some of the guidelines to follow (cont.):
  - Monitor volatile solids of the influent sludge daily to identify loadings to the digester.
  - Monitor carbon dioxide gas content in the digester and pH of the digester sludge on a weekly basis.



# To summarize, what are the major guidelines to follow towards maintaining process control?

2. Since the volatile acids/alkalinity ratio is the most critical parameter in the sludge digestion operation, the following are some of the corrective responses when the volatile acids/alkalinity ratio approaches or exceeds 0.35:
  - Extend the mixing time of the digester contents
  - Control heat more evenly
  - Decrease sludge input rates

# Questions?

