

Water and Waste Water Treatment
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Module No # 12
Lecture No # 58
Stabilization of Sludge

Hello everyone, let us look at the next stage of residual management. In the first stage, we look at thickening. We wanted to increase the concentration of solids either by gravity thickening or by dissolved air floatation. Next aspect is, now that I have relatively more concentrate solids in my sludge, I want to decrease the biodegradability of this particular sludge.

If I leave it out there, it is going to stink because of anaerobic conditions, I do not want that to cause nuisance. It can attract flies and other kinds of insects or other insects too.

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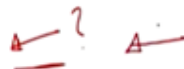


Stabilization



Let us look at the different ways we are going to achieve stabilization by.

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Methods

- Anaerobic digestion 
- Aerobic digestion
- Autothermal aerobic digestion
- Composting 
- Lime (alkaline) digestion 

Different methods one is anaerobic, firstly why anaerobic? And note that this is widely used. Sludge we have especially with the organic sludge here, we have a lot of organic concentration, if you want to do it by aerobic you need to provide oxygen. If you are doing it within a controlled system, that also can be done. But you are giving or needing to put in energy.

But with anaerobic digestion though, depending upon the by-products or the extent of optimization you are able to achieve, you can get product such as methane which can then be used for energy generation or for cooking or such but it depends upon the calorific value of here particular gas, that is one aspect to note, anaerobic digestion. Other one is aerobic digestion which will briefly look at later.

Auto thermal aerobic digestion and composting which is done in open land, you would have seen this. And lime alkaline digestion, this also we will look at later. For this session we are look at anaerobic digestion.

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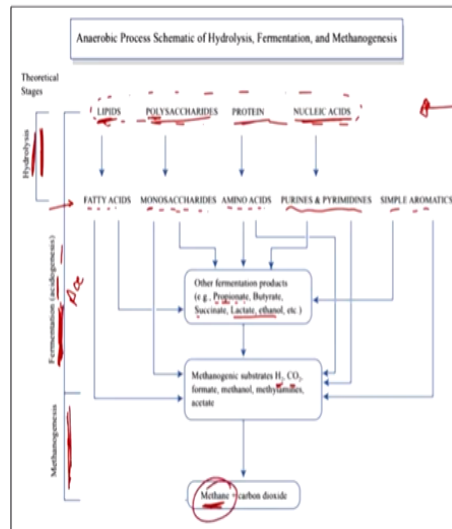


Figure by MIT OCW.
Adapted from: G. Tchobanoglous, F. L. Burton, and H. D. Stensel. *Wastewater Engineering: Treatment and Reuse*, 4th ed. Metcalf & Eddy Inc., New York, NY: McGraw-Hill, 2003, 631

Acidogenesis
Acetogenesis

Let us move on there are different stages. And note that my sludge has all these relatively complex organic matter, complex stuff well I cannot eat I cannot digest or remarkably complex products. Typically, that is why I am going to cook it or such well it is not the same analogy but even similarly for the microbes to remarkably complex organics they cannot degrade or use them well enough.

First, they have to be changed into forms that are relatively more soluble. And also, relatively easily usable by the relevant microbes as the substrate. What do we have major compounds or types of compounds of interest? We have lipids, polysaccharides, we have proteins and nucleic acids, the first stage is hydrolysis typically this is brought about by the enzymes of the microbes which are prevalent in the particular system.

That is one aspect to keep in mind, hydrolysis. And then you going to have fatty acids from lipids, monosaccharides, earlier it was poly and now monosaccharides, proteins to amino acids, nucleic acids to purines, pyrimidines and simple aromatic compounds, here we have hydrolysis and if I am trying to use kitchen waste.

We are dumping it out there that is leading to huge landfills because it going up with the inert waste and it leading to huge landfills. And there it is going to be an issue because of the kind of organic and inorganic content there I cannot treat that well. Now if I can separate it out well and I have only the organic waste after segregation, then I can have the anaerobic process too then I am just talking about another aspect which is relevant here at least in the Indian context.

That organic waste too I can have or let it undergo anaerobic digestion and get energy from it. But their hydrolysis will be pretty much slow because of the type of waste, typically people grind it with water or the sludge and create it slurry, hydrolysis is one aspect and that can be typically slow depending upon the type of compounds that you have at your inlet.

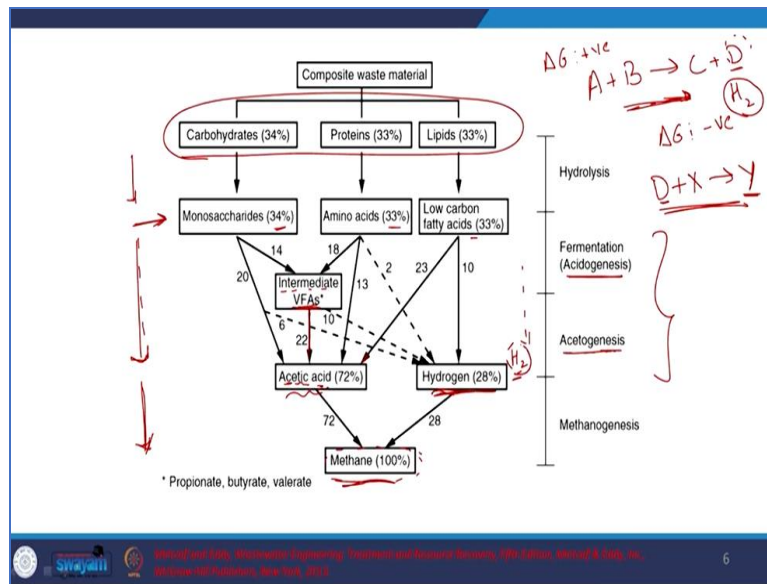
Now you have relatively simpler forms of organics. And then here we have two stages, one is acidogenesis and the other one will be acetogenesis, that something to keep in mind we will look at what it is we are going to look at or see here. As I mention here, it is going to be two aspects in conjunction and typically we are looking at fermentation.

Note that here there is no oxygen involved. In a redox process, you are going to have transfer of electrons. In the anaerobic activated sludge process, oxygen was the electron acceptor. Here if it is the fermentation the same compound will lead to relatively more oxidized and relatively more reduced compound or in the case of methanogenesis you can have hydrogen as your electron donor, carbon dioxide as electron acceptor and such.

That is something to note, we will come back to that later, what is it that we have form during the fermentation step? You have relatively complex fatty acids like propionate, butyrate, lactate and such. And then there are going to lead to formation of acetic acid, that is one aspect to know that is why acetogenesis, if I am not wrong but we will come back to that. And after that you are going have methanogenesis as in methane is formed in this step from methanogenic substances.

And hydrogen is essential, we will see why and carbon dioxide too is going to be formed in one of the products but we will look at it. 4 major stages, one is hydrolysis, acidogenesis and acetogenesis both which are under fermentation and then methanogenesis which is leading to formation of methane, let us move on.

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First I have relatively more complex organics here. And this is by COD, this percentage is by the total COD so initially I have 100%. After hydrolysis, I am going to have relatively simpler organic compounds, you can see the COD is still there. And then what is it that being formed? In the acetogenesis, you are going to have intermediate volatile fatty acids being formed.

And in the acetogenesis though you are going to have acetic acid being formed either directly some of it from these compounds after hydrolysis or from the volatile fatty acids or the intermediate volatile fatty acids that were formed. Now you see there are 2 stages, one is acetogenesis when you have the intermediate volatile fatty acids or some of it directly going to acetic acid and other one is acidogenesis.

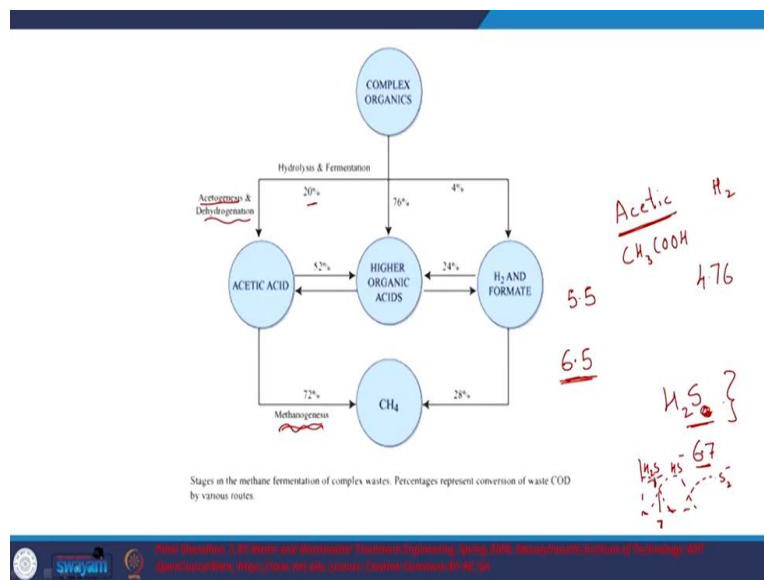
Where as I mentioned formation of acetic acid and also transformation of all these intermediate volatile fatty acids into acetic acid. And note that in this particularing process or during this process, you are going to have hydrogen being formed, so that is something to note, why is that? Later this hydrogen is going to be required for the formation of methane, that is something to keep in mind, this methane production requires acetic acid, hydrogen and if there is CO₂ that too.

One aspect to note is that if the hydrogen concentration is too high here or if it accumulates there are 3 or 4 steps one is here and if I can combine all this as 1 step and this is the third step. If sometimes this is too slow and this is too fast, what is going to happen? The hydrogen concentration is going to increase. If the hydrogen concentration is going to increase too much, A + B going to product C + D and one of this hydrogen.

Initially for this reaction to go through, if the delta G is negative that is when the microbes will try to facilitate this particular reaction. But if one of the product has accumulated because the hydrogen or D has not been used later, $D + X \rightarrow Y$, this is the methane. Because D has not been consumed and D is accumulated, so what is going to happen?

Delta G, you will not be may be favourable it might even turn to be positive then whole process can be come crashing down so that something to keep in mind. There is fine balance between hydrogen that is being produced here and the hydrogen that is been used up by the methanogens or during methanogenesis, so that something to keep in mind. And from here you are going to end up having methane, so let us move forward.

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This is the one from MIT aspect but I just wanted to mention because it is relatively simpler figure. Complex organics to higher organics, hydrolysis and fermentation here they clubbed it. But note that there are 2 aspects and then acetogenesis and dehydrogenation you are going to sometime have formation of hydrogen too or use up of hydrogen too. Key note is that we have acetic acid and also hydrogen and another aspect to note is that acetic acid, CH_3COOH , it has pKa of 4.76.

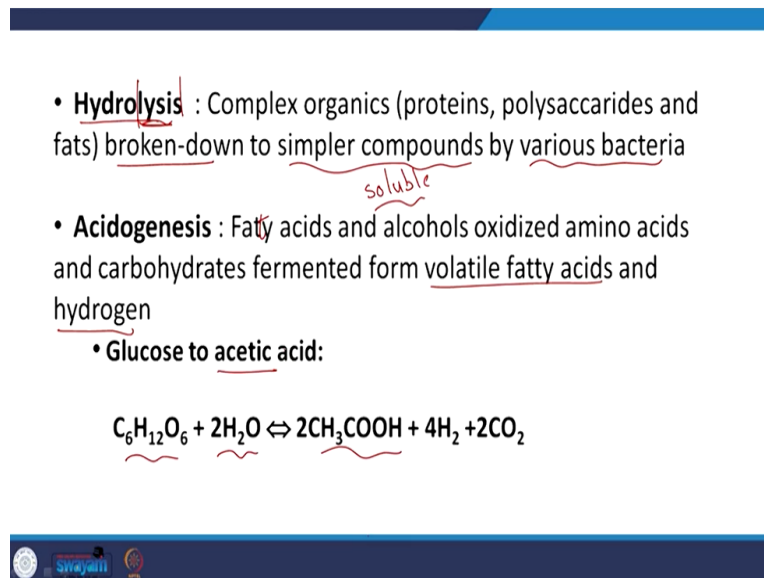
And note that this process is sensitive, one process is sensitive to pH of around 6.5 the methogenesis, the other one to around 5.5. If the PH falls considerably and especially when you have sulphide and the pKa of this around 6.7 or I think 7 let us see. We know that hydrogen sulphide something like this, this pKa is around 6 or 7 or 7 if I am not wrong. The

pH falls to around 6.5 or such, most of it will be present as H₂S only some has HS⁻ and other has S²⁻.

And this H₂S is toxic to the microbes, so here similar to is microbes are very picky. And that is why the microorganisms especially the one that leads to the methanogenesis. The methanogens are called the prima donnas. You need to really take great care of them any changes to their particular environment and they will start nagging at you. These are the prima donnas of this anaerobic digestion process where the pH

And also the toxicity of some of the relevant products which is very low in concentration or which are very low in concentration too is important so let us move forth and see what else we have.

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• Hydrolysis: Complex organics (proteins, polysaccharides and fats) broken-down to simpler compounds by various bacteria

• Acidogenesis: Fatty acids and alcohols oxidized amino acids and carbohydrates fermented form volatile fatty acids and hydrogen

• Glucose to acetic acid:

$$\text{C}_6\text{H}_{12}\text{O}_6 + 2\text{H}_2\text{O} \leftrightarrow 2\text{CH}_3\text{COOH} + 4\text{H}_2 + 2\text{CO}_2$$

The slide includes handwritten annotations: 'soluble' is written above 'simpler compounds' in the first bullet point, and 'oxidized' is written above 'Fatty acids' in the second bullet point. The slide also features a Swayam logo in the bottom left corner.

Hydrolysis, it is lysis, we are breaking something, lysis. Complex organics are broken down to simpler compounds which are more soluble. And then they can be consumed by the various bacteria and acidogenesis, what do we have? These fatty acids and alcohols are oxidized, amino acids and carbohydrates fermented to form volatile fatty acids and hydrogen.

For example glucose to acetic acid, this is one particular example but this is directly with respect to acetic acid formation. We could have chosen a better example too, we will come back to that.

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- Acidogenic Bacteria
 - Starts more quickly and can produce volatile acids faster than methanogenic bacteria
 - Fermentative and acidogenic bacteria inhibited at $\text{pH} < 5$
 - Acidogens are more robust and keep producing volatile acids when methanogens are not necessarily producing them
- Key to successful digestion is keeping Acidogens and Methanogens in balance – Monitor pH to keep track of system state

And then the other one is how is this done? We have acidogenic bacteria, they start quickly and can produce volatile acids faster than methanogenic bacteria, this was the key too that I mentioned earlier, so in this process if hydrogenic accumulate too much and it is not removed by methanogenic bacteria which can grow slowly or take time to grow. Then your system is going to fail or it is not going to be beneficial to the microbes to take the reaction forward.

Why? The delta G is now may be not favourable anymore, that something to keep in mind. One aspect to note is that as I mentioned that earlier fermentative and acidogenic bacteria are inhibited but inhibition occurs at much lower pH than the pH at which methanogenic bacteria are inhibited which is at around 6.5. But let me not digress the acidogenic bacteria which take care of acidogenesis are inhibited at pH 5 or less than 5.

As can be seen, they are robust and they can keep producing volatile fatty acids even when methanogenesis are not really thriving. But the key to successful digestion as I mentioned is from this point of view keeping acidogens and methanogens in balance. You will have to keep monitoring the pH to keep track of the system.

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- **Acetogenesis** : Conversion of complex fatty acids to acetic acid

$$\text{CH}_3\text{CH}_2\text{COOH (Propionic acid)} + 2\text{H}_2\text{O} \rightleftharpoons 2\text{CH}_3\text{COOH (acetic acid)} + 4\text{H}_2 + 2\text{CO}_2$$

- **Methanogenesis** : Conversion of acetic acid to methane and CO₂; and CO₂ and H₂ to methane

$$\text{CH}_3\text{COOH} \rightleftharpoons \text{CH}_4 + \text{CO}_2$$

$$\text{CO}_2 + 4\text{H}_2 \rightleftharpoons \text{CH}_4 + 2\text{H}_2\text{O}$$

And acetogenesis, conversion of these intermediate fatty acids or the complex fatty acids to acetic acids. That is why it is acetogenesis, so let us look at some of the relevant steps, so this way we can look at it. Earlier if I had a breakdown of a complex compound during acetogenesis into propionic acid, do I have that here or what did I have here? I have directly to acetic acid here, that is fine.

Some of these volatile fatty acids or intermediate volatile fatty acids can be propionic acid. And that now is going to undergo acetogenesis and you are going to have formation of acetic acid here. And as you can see hydrogen and carbon dioxide are given out, note that hydrogen is starting to accumulate, let us see. And then methanogenesis, this acetic acid which is formed here is going to be converted to methane and CO₂, let us see what happens.

There are 2 different kinds of microbes, imply one is the one that leads to formation of CH₄ and CO₂ from acetic acid. And the other one where CO₂ in the presence of hydrogen leads to formation of CH₄ and water. Here electron acceptor is CO₂, here electron donor is H₂, you see that H₂, where is it coming from? This H₂ is coming from here and if because the methanogens are not thriving and this does not occur this will also lead to accumulation of hydrogen here in the system.

And then this reaction which I want to go through is not going to be favourable for the microbes, that is one thing as I mentioned delta G should be negative and if too much hydrogen or one of the products accumulate, that might not be the case, so let us move on.

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• Methanogenic Bacteria

- Needed to mediate reactions are ubiquitous in nature, but at low concentrations
- Generally necessary to "seed" anaerobic reactors to get them started
- Inhibited at pH < 6.5
- Prima donnas of anaerobic digestion = very sensitive to changes in temperature and pH



Alk.

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And methanogenic bacteria, as I mentioned as the prima donnas and why do we need them? These reactions note are ubiquitous nature. For example, if I throw out any organic matter you now you are going to see methanogenesis. But they are not very much at high concentration there are low concentration. Though they are ubiquitous there present everywhere but they are present at low concentrations.

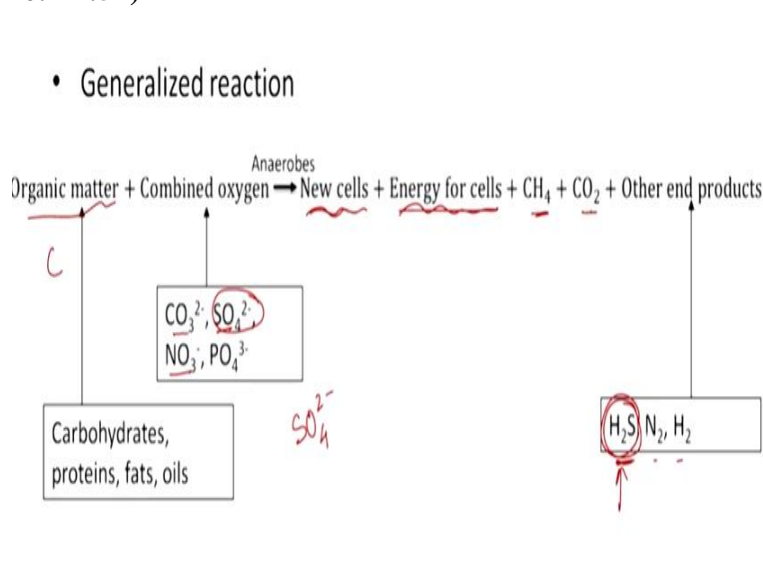
Generally in an anaerobic digester, you have to seed it. You have to get that seed from somewhere else and then put it up here, anaerobic digestors, something to keep in mind as I mentioned earlier they are very sensitive to pH. Typically neutral pH 7 and if pH is less than 6.5, you are going to have considerable effects that is why alkalinity has to be looked at, why?

Because if the pH is falling down due to the formation of acidic acid or any other particular compounds. Your acidic acids pKa is 4.76, keep that in mind. If this acidic acid HAc, I am using that acidic acid is CH₃COOH, acetate (Ac) and H. HAc and the deprotonated form is Ac⁻. As I said this is 4.76, so at most of the pH or pH 7 or 6, you see that Ac⁻ is going predominate or HAc will give out its H⁺, so pH will fall down.

If I do not have enough alkalinity in my solution to neutralize this H⁺ that is going to be formed in the system then the pH will fall down. And if the pH falls down, what is going to happen? The Prima donnas, the methanogen are going to be affected. And then the whole system is affected, why? The hydrogen is now not been consumed. If the hydrogen is not been consumed the bacteria that lead to acetogenesis or involve in acetogenesis, they would not find particular reaction favourable anymore.

That is something to keep in mind, it is a knock on effect. Lets see what eslse we have. As I mention, Prima donnas and they are very sensitive to temperature and pH too.

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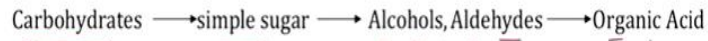
Lets just look at the generalized reaction, so you have the organic matter carbohydrates, proteins substrate and source of carbon. And what is typical electron acceptor? It can be sulphates, nitrates, carbonates or such. And anaerobes, what are they going to use it for formation of new cells? Energy for these cells they have to thrive for one is reproduction, one is the energy for this cells being functioned.

And in that process you are going to have CH₄, CO₂ and some other end products like H₂S N₂ and H₂, why H₂S? If sulphate is there and you have anaerobic conditions prevailing, sulphide can act as a electron acceptor. And if it is acting as an electron acceptor, it going to reduce and you are going to have formation of hydrogen sulphide. As I mentioned this hydrogen sulphide can lead to toxicity for the methanogens and affects the whole system, this is one aspect to understand.

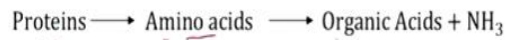
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- Breakdown pathways

1. Carbohydrates



2. Proteins

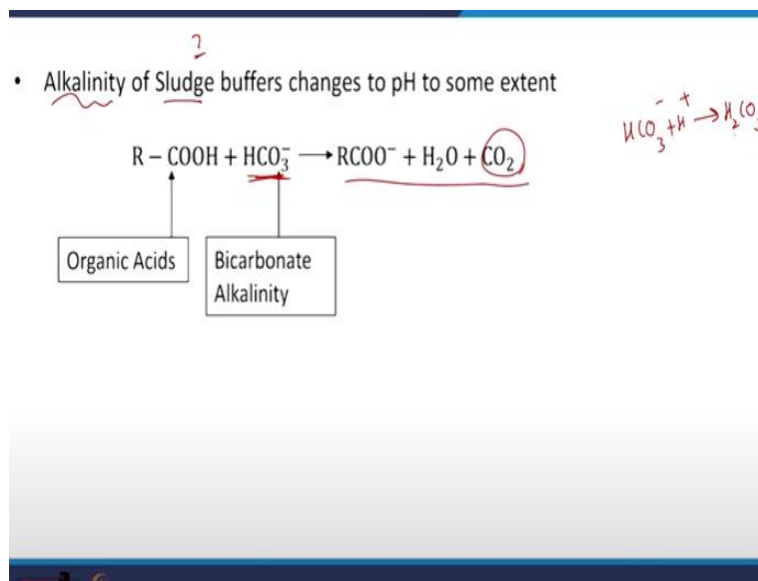


3. Fats and oils



Lets just simplify it one last time, breakdown pathways, in the hydrolysis step, carbohydrates going to simple sugar, alcohol, aldehydes and organic acids. Proteins, we are going to have amino acids and then source of nitrogen fats and oils organic acids.

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As I mentioned, alkalinity of the sludge is very much important, why is that? Acetic acid, so as you can see organic acids or even acetic acid that are going to lead to soaring of anaerobic digestors. There is a term called soaring, so that is one aspect to keep in mind. Here you have HCO₃⁻ the one that is going to be prevalent at pH 7 or near around pH 7, the inorganic carbon that can be take up H⁺.

And this way the pH is not affected or here have presented it in a different form, CO₂ instead of H₂CO₃. With that I will end today's session, so one aspect to note is that anaerobic

digestors, you have to be catering to the needs of the system primarily with respect to pH, Hydrogen build up and methanogens which are very sensitive to the temperature.

These are the aspects that has to be taken care of. The next couple of sessions we will look at the different kinds of stabilization and then more or less finish this particular course. Thank you.