

Sludge treatment in an Anaerobic BioReactor with external Membranes

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Abstract

This project was performed at Sjöstadverket, research facility managed by Stockholm Vatten AB. The biogas production from an Anaerobic Membrane BioReactor pilot unit was evaluated. The goal for this study was to operate the pilot unit with a Hydraulic Retention Time lower than 10 days, while promoting and evaluating biogas production.

The pilot unit contains several components. It receives primary sludge in a mixer tank. This primary sludge is then manually fed into a completely mixed bioreactor where an anaerobic degradation process occurs. This reactor is combined with a VSEP membrane unit, ensuring the separation step between permeate and concentrated sludge, the latter led back to the reactor. The temperature in the anaerobic reactor was 36°C during the entire study.

During the evaluation period, major problems came up, disturbing the continuous operation of this unit. These problems were related to an insufficient pressure provided to the membranes, resulting in an automatic stop of the pilot unit. Several changes were tried to enable the process to be operated in a continuous way. However, these new configurations did not allow operating the pilot unit for several hours, as was planned. As a consequence, the reactor was operated during at most a few hours at a time, sometimes as short as 30 minutes. Other type of problems occurred concerning biogas production measures. The registered flow did not correspond to the expected value. A leak was discovered at the axle of the mixer in the middle of June, 2007, when the level of liquid in the reactor was too low, which could explain the lack of biogas flow measured. These problems resulted in measuring from 0.17 up to 83.4 % of the theoretically calculated methane volume.

The specific methane production varied from 0.296 to 0.959 g CH₄ / g VS_{in} (average value 0.570), which is 97.7 % of the maximum theoretical value 0.584, and between 0.192 and 0.725 g CH₄ / g COD_{in} (average value 0.346), which is 98.8 % of the maximum theoretical value 0.350, if calculated values for methane production from the amount of COD reduced is used. The degree of reduction of the amount of VS varied between -11 % and 136 % (average value 75.3 %). In average, for the amount of VS, 0 % was found in the permeate, 3.9 % was accumulated in the bioreactor, and 18.5 % was withdrawn from the system as concentrated sludge. The average values for COD and TOC reduction were 98.8 % and 91.6 %, respectively. During short periods of satisfying operation, the operating pressure on the membranes was around 4 bars. Due to the variability of permeate flow (from 700 mL/min to 1500 mL/min), the flux through the membranes was in the range from 26.42 L/(m²·h) to 56.60 L/(m²·h) with a surface area of 1.59 m² for the membrane stack. The average value/median value of the organic load rate for the entire study was 4.6 / 3.9 kg VS_{in}/week, i.e. 4.9 / 4.1 g VS_{in}/(L · week). It would have required a continuous and safer operation of the pilot unit to evaluate the “maximum” organic load.

The degree of degradation of organic matter (measured as volatile solids, VS) varied between 7.6 and 69.8 % (average value 50.9 %, median value 57.5 %). The calculated hydraulic retention time for each week varied between 2.4 and 104.5 days (low influent flow that week) (average value 24.6 days, median value 14.5 days). In average, 42.5 % of the amount of Kjeldahl Nitrogen and 26.9 % of the amount of Total Phosphorus remained in the permeate. The lowest concentration of Nitrogen and Phosphorus for the permeate flow was 99 mg N/L and 15 mg P/L, respectively.

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Introduction

Urban residual sludge management is a major issue in wastewater treatment processes, as sludge management normally includes anaerobic digestion resulting in production of biogas. This gas can then be used in diverse applications (electricity, gas engine, car and bus fuel, etc.).

In this project, the evaluation of biogas production was performed in an Anaerobic Membrane BioReactor pilot unit at Sjöstadverket, Stockholm. Sjöstadverket is a research site located at the Henriksdal wastewater treatment plant.

The AnMBR (Anaerobic Membrane BioReactor) consisted of an anaerobic completely mixed reactor followed by a membrane separation stage. The goal of this study was to operate this pilot unit at a Hydraulic Retention Time lower than 10 days, at 35 – 37°C. This temperature range corresponds to an optimum for mesophilic micro-organisms. The concentration of Total Solids in the bioreactor was expected to have a value around 2 - 3 % TS. Volatile Fatty Acid's critical concentration was expected to be 500 mg/L at most, and the pH value for the operation of the pilot unit was expected to be 6.8 or higher.

The questions related to the operation of the pilot unit were the degree of Volatile Solids reduction, an evaluation of biogas production (more precisely specific methane production expressed as $\text{NL CH}_4/\text{g VS}_{\text{in}}$ and $\text{NL CH}_4/\text{g COD}_{\text{in}}$), and an estimation of the maximum organic load rate. Moreover, the pressure and flux for the membranes had to be determined. All the operational problems had to be documented with description and reasons for them to occur.

The first chapter of this report introduces the general environment and the objectives of this project. The second chapter gives the theoretical considerations regarding the operation of this pilot unit. The third chapter describes in details the materials and the methods used throughout this study. Finally the fourth chapter presents the results related to the initial questions to be answered and the comments associated.

Chapter I : Introduction and project framework

I. Overview of the working environment

I.1... in which Hammarby Sjöstadsverket is settled

A drum filter, used in one of the pilot plants (called “Line 2”) at Sjöstadsverket, generated the primary sludge that was used in this project. The influent wastewater treated in “Line 2” came from Hammarby Sjöstad and the typical characteristics (2006 as an example) are given in Table 1.

Table 1: Concentration of various parameters for influent wastewater from Hammarby Sjöstad in mg/L.

| Param. | COD | TOC | DOC | BOD ₇ | SS | Tot-P | PO ₄ -P | Kjeldahl-N | NH ₄ -N | Alk. |
|--------|-----|-----|-----|------------------|-----|-------|--------------------|------------|--------------------|------|
| mg/L | 617 | 183 | 87 | 328 | 286 | 10.7 | 7.2 | 67 | 52 | 314 |

Param. = parameter, Alk. = alkalinity

II. Details on project’s objectives

The pilot unit which was used in this study was belonging to Sjöstadsverket. It was supplied by primary sludge from Line 2 (this unit is described in details in Material and methods). It contains a completely mixed biological reactor (so-called bioreactor), operating under anaerobic conditions. It is followed by a membrane separation step (a VSEP-unit). The whole unit is called Anaerobic Membrane BioReactor (AnMBR).

The aim of the project was to operate an anaerobic digester with a Total Solids (TS) content above 5 %, and a Hydraulic Retention Time (HRT) below 10 days, at 35 – 37°C (HRT could be defined in this particular pilot unit as the volume of the bioreactor divided by the incoming flow, entering the system). To avoid clogging in the filtering steps due to high solid content in sludge streams, a TS content of 2 – 3 % in the reactor was preferred.

Volatile Solids (VS) reduction was considered as an important parameter, as it gave a good idea of the organic degradation within the bioreactor. By treating only primary sludge, the VS reduction should be at least 60 % (assuming that 75 – 80 % of the VS normally derive from primary sludge and that the degree of VS reduction in activated sludge is about 20 %).

The proceeding way was to decrease HRT continuously to reach a value of 10 days, even less if possible. This continuous decrease was allowed as long as two main parameters were kept within some predetermined values. The pH had to equal to or be above 6.8 and the Volatile Fatty Acids (VFA) concentration had to be below 500 mg/L.

After considering all these parameters and operating the pilot unit thereof, the questions that had to be answered was related to:

- the degree of VS reduction of the primary sludge.
- the gas production, expressed as NL CH₄/g VS_{in} and NL CH₄/g COD_{in}.
- the description of the operational problems. Which components were involved and why such problems occurred? Details on the provided solutions were also included.
- the pressure and flux for the membranes.
- the maximum organic loading rate.

Chapter II : Theory

I. Anaerobic fermentation and oxidation

Anaerobic digestion is a natural phenomenon taking place in various areas (sediments, some wetlands, landfills...). The main characteristic of this process is to occur without any oxygen. Under anaerobic conditions, sludge from wastewater treatment leads to biogas production, which could be used as an energy source (electricity, heat or car fuel) by burning the recovered methane. This is the main interest concerning energy issues. Depending on the temperature range within the bioreactor, different types of bacteria are active and involved in biogas production:

- psychrophilic bacteria in the range 10 – 30°C, with an optimum just below 20°C
- mesophilic bacteria in the range 20 – 45°C, with an optimum around 36°C
- thermophilic bacteria in the range 35 – 75°C, optimum in between 55 and 58°C

To be able to produce biogas, the microbial community needs steady conditions regarding operating parameters such as pH, Volatile Fatty Acids (VFA) concentration, and temperature. This community includes many different micro-organisms, with complex interactions during all the degradation process.

I.1 Description of anaerobic process

Three basic steps are involved in the overall anaerobic oxidation of a waste:

- 1 – hydrolysis
- 2 – fermentation, also known as acidogenesis
- 3 – methanogenesis

These three steps are illustrated in Figure 1. The starting point on the scheme for a particular application depends on the nature of the waste to be processed.

I.1.1 Hydrolysis

The first step for most fermentation processes is named *hydrolysis*. Particulate material is converted to soluble compounds that then can be hydrolyzed further to simple monomers. These monomers are used by bacteria that perform fermentation. Specific micro-organisms release some enzymes (proteases, lipases, etc.) able to hydrolyze macro-molecules or polymers (proteins, lipids, polysaccharides) and to turn them into simpler molecules or monomers (amino acids, fatty acids, glycerol and alcohols...).

I.1.2 Fermentation

The second step is *fermentation* (also referred as *acidogenesis*). In the fermentation process, amino acids, sugars and some fatty acids are degraded further, as shown in Figure 1. Organic substrates serve as both the electron donors and acceptors. The principal products of fermentation are acetate, hydrogen, CO₂, propionate and butyrate. The propionate, the butyrate and a large part of other volatile fatty acids and the alcohols (ethanol, glycerol) are assimilated by the autotrophic acetogenic bacteria to also produce hydrogen, CO₂ and acetate. This step is known as the *acetogenesis*. Thus, the final products of fermentation (acetate, hydrogen and CO₂) are the precursors of methane formation (*methanogenesis*).

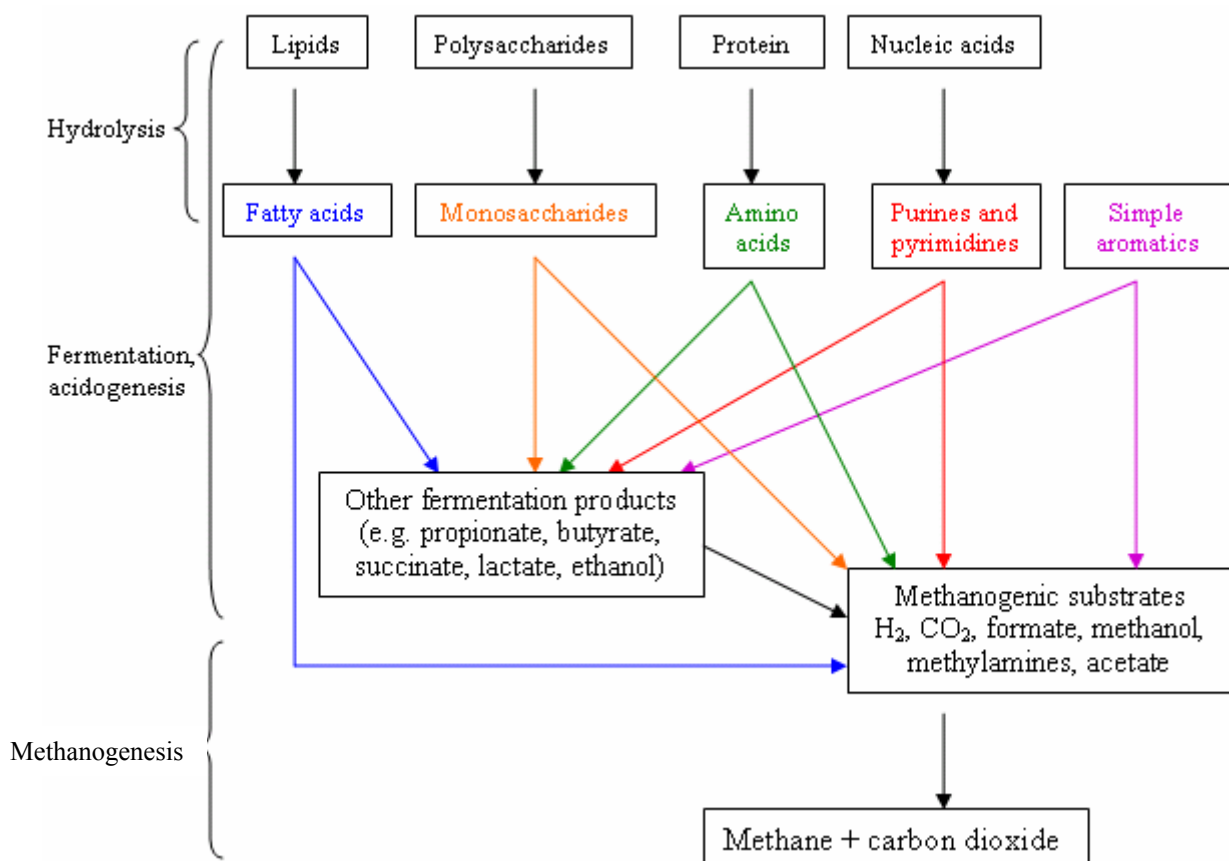


Figure 1: Anaerobic process degradation scheme¹.

I.1.3 Methanogenesis

The third step, *methanogenesis*, is carried out by a group of organisms known collectively as methanogens. Two groups of methanogenic organisms are involved in methane production. One group, named *acetoclastic methanogens*, split acetate into methane and carbon dioxide. The second group, named hydrogen-utilizing methanogens, uses hydrogen as the electron donor and CO₂ as the electron acceptor to produce methane. Bacteria within anaerobic processes, named *acetogens*, are also able to use CO₂ to oxidize hydrogen and form acetic acid. However, the acetic acid will be converted to methane, so the impact of this reaction is

¹ METCALF & EDDY, *Anaerobic fermentation and oxidation*, Figure 7-25, p 631.

minor. As shown in Figure 2, about 72 % of the methane produced in anaerobic digestion derives from acetate formation. In anaerobic digestion of sludge, the limiting step of this biological process is hydrolysis, as kinetics concerning this stage is the slowest¹.

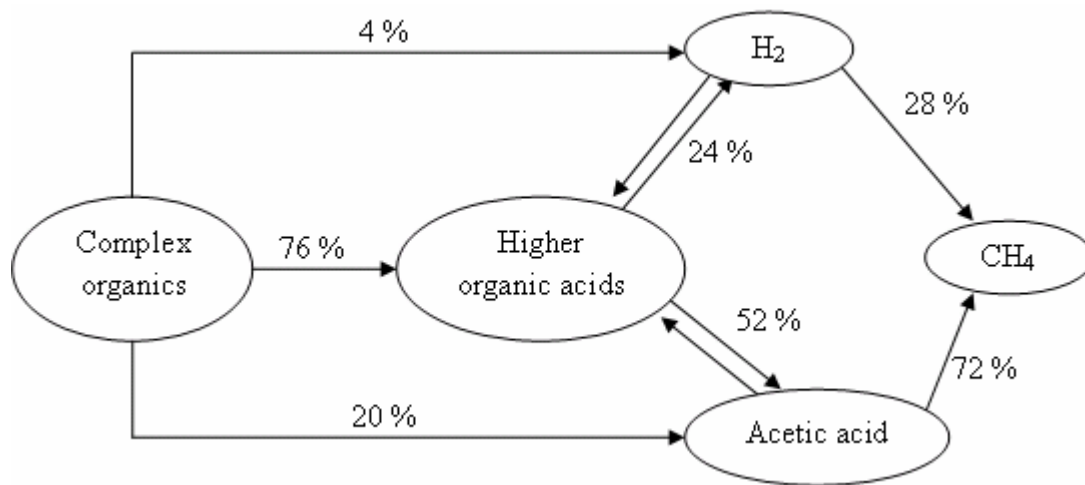


Figure 2: Carbon and hydrogen flow in anaerobic digestion process².

1.2 Microbiology and bacteria relationships under anaerobic conditions

The group of nonmethanogenic micro-organisms responsible for hydrolysis and fermentation consists of facultative and obligate anaerobic bacteria. The micro-organisms responsible for methane production, classified as archaea, are strict obligate anaerobes. Many of the methanogenic organisms identified in anaerobic digesters are similar to those found in the stomachs of ruminant animals and in organic sediments taken from lakes and rivers.

Methanosarcina and *Methanothrix* (also named *Methanosaeta*) are the only organisms able to use acetate to produce methane and carbon dioxide. The other organisms oxidize hydrogen with carbon dioxide as the electron acceptor to produce methane.

The methanogens and the acidogens form a syntrophic (mutually beneficial) relationship in which the methanogens convert fermentation end up products such as hydrogen, formate and acetate to methane and carbon dioxide. Because the methanogens are able to maintain an extremely low partial pressure of H₂, the equilibrium of the fermentation reactions is shifted toward the formation of more oxidized end products (e.g. formate and acetate). The utilization of the hydrogen produced by the acidogens and other anaerobes by the methanogens is named interspecies hydrogen transfer.

The methanogenic organisms serve as a hydrogen sink that allows the fermentation reactions to proceed. If process problems occur and if the methanogenic organisms do not consume the hydrogen produced fast enough, the propionate and butyrate fermentation will be slowed with the accumulation of volatile fatty acids in the anaerobic reactor, ending up in a possible reduction in pH³.

¹ GAY (J.), « Lutte contre la pollution des eaux », Techniques de l'ingénieur, G 1455, p 2.

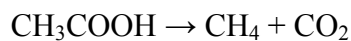
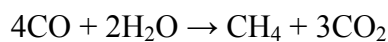
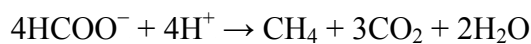
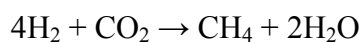
² METCALF & EDDY, *Anaerobic fermentation and oxidation*, Figure 7-26, p 631.

³ METCALF & EDDY, *Anaerobic fermentation and oxidation* 7-12, p 632.

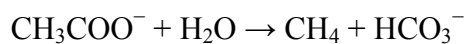
Disturbing organisms in anaerobic processes are the sulphate-reducing bacteria, which can be a problem when the wastewater contains a significant concentration of sulphate. These organisms can reduce sulphate to sulphide, which could be toxic to methanogenic bacteria. Sulphate-reducing bacteria are morphologically diverse but share the common characteristic of being able to use sulphate as an electron acceptor. They are divided into two groups, whether they produce fatty acids or use acetate. The first group of sulphate reducers can use diverse organic compounds as electron donor, oxidizing them to acetate and reducing sulphate to sulphide. The second group of sulphate reducers oxidizes fatty acids (particularly acetate) to carbon dioxide, while reducing sulphate to sulphide¹.

I.3 Stoichiometry in Anaerobic Fermentation and Oxidation

A limited number of substrates are used by the methanogenic organisms. The reactions defined as CO₂ and methyl group type reactions are shown as follows (Madigan *et al.*, 1997), involving the oxidation of hydrogen, formic acid, carbon monoxide, methanol, methylamine and acetic acid, respectively:

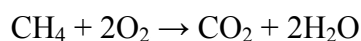


Another reaction is considered by Carlsson (2005) for methane production from acetate:



In the reaction for the acetilastic methanogens (last reaction shown in the list above), the acetic acid is cleaved to form methane and carbon dioxide.

A COD balance can be used to account for the changes in COD during fermentation. Instead of oxygen accounting for the change in COD, the COD loss in the anaerobic reactor is accounted for by the methane production. By stoichiometry the COD equivalent of methane can be determined. The COD of methane is the amount of oxygen needed to oxidize methane to carbon dioxide and water.



Under anaerobic conditions, at 36°C, the volume of methane produced with respect to COD reduced is 0.396 L CH₄/g COD, which gives 0.350 NL CH₄/g COD, (see Appendix 6 for details).

¹ METCALF & EDDY, *Anaerobic fermentation and oxidation* 7-12, p 632.

During anaerobic processes biogas is actually produced. However the interesting fraction of this gas phase is the methane gas if energetic issues are considered, as it has a lower heating value of 35 800 kJ/m³. Variable composition of biogas is given in Table 2.

Table 2: Biogas composition¹.

| Compound | Average concentration (%) |
|-------------------|----------------------------------|
| Methane | 55 to 75 |
| Carbon dioxide | 25 to 45 |
| Hydrogen sulphide | 0.01 to 1 |
| Nitrogen | 2 to 6 |
| Hydrogen | 0.1 to 2 |

Biogas has relatively high methane content, as the average methane fraction is around 64%. The aim of every recovering facility is obviously to extract as much methane as possible from the produced biogas.

1.4 Environmental factors influencing anaerobic process

➤ Influence of pH

Anaerobic processes are extremely sensitive to pH changes. A pH value near neutral is preferred and below 6.8 the methanogenic activity is inhibited. Alkaline excess values are less serious than acid excess values, as pH decrease is mainly caused by VFA accumulation. This results in methanogenic process inhibition due to the pH of the substrate².

➤ Influence of temperature

Temperature is a major concern in such processes. Temperature not only influences the metabolic activities of the microbial population but also has an effect on gas-transfer rates and the settling characteristics of the biological solids. The temperature dependence of the biological reaction-rate constants is very important in assessing the overall efficiency. According to Rodriguez Susa (2005), the main consequences are:

- increase in reaction rate, in accordance with Arrhenius relationship.
- decrease in conversion rate value, for temperature conditions out of optimum range. This is around 35°C for mesophilic process, the type of process used

¹ GAY (J.), « Lutte contre la pollution des eaux », Techniques de l'ingénieur, G 1455, p 7.

² RODRIGUEZ SUSAN (M.), « Etude d'un bioréacteur anaérobie à membranes immergées pour le traitement des eaux résiduaires », p 15.

- in this study. The bioreactor temperature remained constant during all the evaluation period, at $36^{\circ}\text{C} \pm 0.3$.
- increase in microbial decay rate, as cellular lysis is increased too.
 - affinity constant changes (k_s).

The following equation illustrates the temperature dependence for reaction rate coefficient:

$$k_T = k_{20} \cdot \theta^{(T-20)}$$

where k_T is the reaction-rate coefficient at temperature T, °C

k_{20} is the reaction-rate coefficient at 20°C

θ is the temperature-activity coefficient

T is the temperature, °C

One can notice that bacteria usually resist to a sudden decrease of temperature whereas a rapid increase might have dramatic consequences on microbial community.

➤ Influence of alkalinity

Because of the high CO_2 content in the gases developed in anaerobic processes (30 to 35 % CO_2), a high alkalinity is needed to assure pH near neutrality. An alkalinity concentration in the range of 3000 to 5000 mg/L as CaCO_3 is often found. For sludge digestion, sufficient alkalinity is produced by the breakdown of protein and amino acids to produce NH_3 , which combines with CO_2 and H_2O to form alkalinity as $\text{NH}_4(\text{HCO}_3)$ ¹.

In his Thesis review, Rodriguez Susa (2005) mentions other parameters used by different authors for anaerobic process development and monitoring:

- a very low redox potential (−300 to −400 mV)
- VFA concentration, below 3.0 meq/L
- VFA/Alkalinity ratio
- Hydrogen production
- Biogas production

1.5 Toxic and inhibitory substances for anaerobic digestion

The microbial community could be disturbed if some substances are introduced into the reactor, in addition to pH and temperature considerations. Obviously, oxygen has to be kept out of the bioreactor (under its molecular form O_2). The presence of a toxic substance does not mean that the process cannot operate. Some toxic compounds inhibit anaerobic methanogenic reaction rates, but with a diverse microbial population and low enough loading, the process can be sustained. Acclimatization to toxic concentrations is also possible. Some toxic and inhibitory compounds are given in Table 3.

¹ METCALF & EDDY, *Anaerobic fermentation and oxidation* 7-12, p 635.

Table 3: Toxic and inhibitory organic compounds for anaerobic digestion¹.

| Compound | Concentration resulting in 50 % reduction in activity (10^{-3} mol) |
|-----------------|---|
| 1-Chloropropene | 0.1 |
| 1-Chloropropane | 1.9 |
| Formaldehyde | 2.4 |
| Ethyl benzene | 3.2 |
| Vinyl acetate | 8 |
| Acetaldehyde | 10 |
| Ethyl acetate | 11 |
| Phenol | 26 |
| Propanol | 90 |

The inorganic compounds are also of main concern for inhibition of the process (heavy metals, diverse cations, etc.). Different threshold concentrations for these substances are mentioned in Table 4, and results from Stockholm Vatten's laboratory as well.

¹ GAY (J.), « Lutte contre la pollution des eaux », Techniques de l'ingénieur, G 1455, from Table 2, p 4.

Table 4: Toxic and inhibitory inorganic compounds for anaerobic digestion and results from the pilot unit¹.

| Substance | Moderately inhibitory concentration (mg·L ⁻¹) | Strongly inhibitory concentration (mg·L ⁻¹) | Results for reactor sludge (mg·L ⁻¹) | Results for permeate (mg·L ⁻¹) |
|---|---|---|--|--|
| Na ⁺ | 3500 - 5500 | 8000 | | |
| K ⁺ | 2500 - 4500 | 12000 | | |
| Ca ²⁺ | 2500 - 4500 | 8000 | | |
| Mg ²⁺ | 1000 – 1500 | 3000 | | |
| Ammonium-nitrogen NH ₄ ⁺ -N | 1500 – 3000 | 3000 | 130 - 250 | 97 - 220 |
| Sulphide S ²⁻ | 200 | 200 | | |
| Copper Cu ²⁺ | | 0.5 (soluble) 50 – 70 (total) | 4.5 (total) | < 0.02 |
| Chromium Cr(VI) | | 3 (soluble) 200 – 250 (total) | 1.5 (total) | < 0.02 |
| Chromium Cr(III) | | 2 (soluble) 180 – 420 (total) | 1.5 (total) | < 0.02 |
| Nickel Ni ²⁺ | | 30 (total) | 0.78 (total) | 0.027 |
| Zinc Zn ²⁺ | | 1 (soluble) | 10000 (mg/kg TS) | 20 (mg/kg TS) |
| Silver Ag (total) | | | 0.085 | < 0.02 |
| Cadmium Cd (total) | | | 0.012 | < 0.005 |
| Mercury Hg (total) | | | 0.018 | < 0.05·10 ⁻³ |
| Lead Pb (total) | | | 0.46 | < 0.05 |
| Iron Fe (total) | | | 220 | 2.0 |

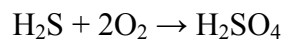
One can notice that the concentrations from the reactor sludge are below the “strongly inhibitory concentration” values for the considered heavy metals. Regarding ammonium-nitrogen, the highest concentration found in the bioreactor is far below the “moderately inhibitory concentration” range. The conclusion which could be drawn is that inorganic compounds within bioreactor should not be a problem regarding anaerobic digestion inhibition. Details on heavy metals analyses performed by Stockholm Vatten’s main laboratory are available in Appendix 1.

- Influence of sulphide production

Oxidized sulphur compounds, such as sulphate, sulphite and thiosulphate, may be present in significant concentrations in some industrial and to some degree municipal wastewaters. These compounds can serve as electron acceptors for sulphate-reducing bacteria, which

¹ METCALF & EDDY, *General design considerations for anaerobic treatment processes 10-2*, from Table 10-5, p 991 and personal data.

consume organic compounds in the anaerobic reactor and produce hydrogen sulphide (H₂S). Based on the following stoichiometry for H₂S oxidation, 2 moles of oxygen are required per mole of H₂S, just as for methane oxidation.



Thus, the amount of H₂S produced per unit COD is the same as for methane (0.40 L H₂S/g COD used at 35°C, 0.350 NL H₂S/g COD at 0 °C and 1 atm). Hydrogen sulphide is malodorous and corrosive to metals. Combustion products formed from sulphur oxidation are considered air pollutants. In contrast to methane, H₂S is highly soluble in water, with a solubility of 2650 mg/L at 35°C, for example.

The concentration of oxidized sulphur compounds in the influent wastewater to an anaerobic treatment process is important as high concentrations can have a negative effect on anaerobic treatment. Sulphate-reducing bacteria compete with methanogenic bacteria for COD and thus can decrease the amount of methane gas production¹. While low concentrations (less than 20 mg/L) of sulphide are needed for optimal methanogenic activity, higher concentrations can be toxic.

- Influence of ammonia

Ammonia toxicity may be of concern for anaerobic treatment of wastewaters containing high concentrations of ammonium or proteins and/or amino acids, which can be degraded to produce ammonium. Free ammonia (NH₃), at high enough concentrations, is considered toxic to methanogenic bacteria. The amount of free ammonia is a function of temperature and pH. The toxicity threshold may vary depending on operating conditions and acclimatization time.

I.6 Synthesis regarding anaerobic processes operation

A review of the main advantages and drawbacks is presented here, to sum up the key ideas concerning anaerobic processes needs and operational parameters (based on “Wastewater Engineering”, Metcalf & Eddy, 2003).

First, one can consider the following positive points:

- Less energy required.
Anaerobic processes may be net energy producers instead of energy users, as it is the case for aerobic processes. The energy produced in an anaerobic way takes into account methane produced, thus an evaluation of this total amount of energy could be made by considering the energy content of methane (35 846 kJ/m³ at 0°C and 1 atm)². A part of this energy can be used to increase the wastewater temperature to the mesophilic temperature range for instance. The net energy produced is still higher than the energy required.
- Less biological sludge production.

¹ METCALF & EDDY, *Anaerobic suspended and attached growth biological treatment processes 10-2*, p 994.

² METCALF & EDDY, *The rationale for anaerobic treatment 10-1*, p 985.

Because energetics of anaerobic processes result in lower biomass production by a factor of about 6 to 8 times, sludge processing and disposal costs are greatly reduced. This is a major advantage over aerobic treatment.

- Methane production.
Methane production, a potential energy source and therefore the main interest of anaerobic digestion
- Fewer nutrients are required.
Fewer nutrients are required by comparison to aerobic processes. The cost for nutrient addition is much less for anaerobic processes, as less biomass is produced.
- Smaller reactor volume and less space required.
Smaller reactor volume and less space required, as anaerobic processes generally have higher volumetric and organic loads than aerobic processes.
- Rapid response to substrate addition.
Rapid response to substrate addition after long period without feeding.
- Treating pollutants.
A very good ability for treating pollutants such as PAH (Polycyclic Aromatic Hydrocarbons), PCB (PolyChlorinated Biphenyls) and nitrogenous organic compounds¹.

However, all these aspects have to be balanced by negative considerations:

- Longer start-up time.
Longer start-up time to develop necessary biomass population, as micro-organisms growth is very slow. Reaching equilibrium for given conditions is also rather long, by comparison to aerobic processes. The microbiological system might be complex, including several types of micro-organisms, thus optimal conditions may not be reached at the same time.
- Much more sensitive.
Much more sensitive to the adverse effect of lower temperatures on reaction rates, pH dependent and extremely sensitive to environmental changes. A population of micro-organisms may be more susceptible to problems due to toxic substances.
- May require alkalinity addition.
Alkalinity concentrations of 2000 to 3000 mg/L (as CaCO₃) may be needed in anaerobic processes to maintain an acceptable pH with the high CO₂ concentration in gas phase. If this amount of alkalinity is not available in the incoming influent wastewater or cannot be produced by proteins and amino acids degradation, it might be costly to purchase a chemical for increasing the alkalinity.
- May require further treatment.

¹ RODRIGUEZ SUSA (M.), « Etude d'un bioréacteur anaérobie à membranes immergées pour le traitement des eaux résiduaires », p 10.

May require further treatment with an aerobic treatment process to meet discharge requirements. Aerobic treatment can also follow anaerobic steps for effluent polishing. Series reactors of anaerobic-aerobic treatments could be used, getting benefits from both processes.

- Production of odours and corrosive gases.
Potential for production of odours and corrosive gases. Under anaerobic conditions, sulphate can be an electron acceptor and can form H_2S for instance.

II. Description of the Anaerobic Membrane BioReactor pilot unit (AnMBR)

II.1 Considerations regarding biological reactors including external membranes

Membrane Biological Reactors (MBRs) consist of a biological reactor (so-called bioreactor) with suspended biomass and solids separation by micro filtration membranes (pore size ranging from 0.1 to 0.4 μm). These biological reactor systems may be used both with aerobic and anaerobic suspended growth bioreactors to separate treated water from active biomass.

The goal of such systems is to combine a bioreactor and micro filtration as one unit process for wastewater treatment. It could replace, in some cases, the solid separation function of secondary clarification and effluent filtration. The ability to eliminate the secondary clarification and to operate at higher mixed liquor suspended solids concentration provides the following advantages¹:

- higher volumetric loading rates, and thus shorter reactor Hydraulic Retention Times (HRT)
- longer Solids Retention Times (SRTs) resulting in less sludge production, as well as a total separation from HRT
- operation at low Dissolved Oxygen (DO) concentrations, potential for simultaneous nitrification-denitrification in long SRT designs
- high-quality effluent (low turbidity, bacteria, Biological Oxygen Demand [BOD]...)
- less space required for wastewater treatment

Membrane bioreactor systems have two basic configurations. The integrated bioreactor uses membranes immersed within the reactor whereas in the recirculated MBR, the mixed liquor circulates through a membrane stack situated outside the reactor. In this study, a recirculated MBR has been used. An overview of the main components and streams is shown in Figure 3.

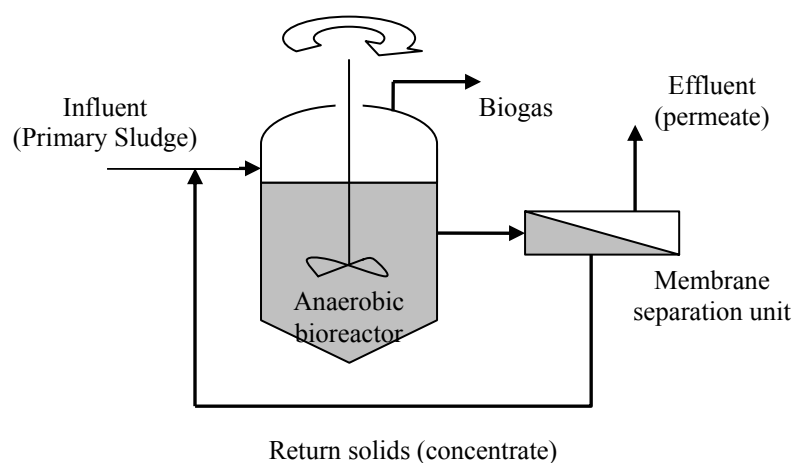


Figure 3 : Anaerobic bioreactor with external membrane separation².

¹ METCALF & EDDY, *Biological treatment with membrane separation* 8-9, p 854.

² METCALF & EDDY, adapted from Figure 10-11, p 1027.

Using this membrane separation configuration enables the process to reach longer SRT values as almost all the solids are captured and recycled back to the bioreactor. It could result in a maximum removal of VFA and degradable soluble COD substances. The suspended solids capture could also result in a significant improvement in effluent quality, with a low suspended solids concentration in the outgoing permeate. These considerations should allow anaerobic reactors to produce an effluent quality equal to aerobic secondary treatment processes¹.

Membrane fouling and loss of active cells are critical issues for the proper operation of the whole pilot unit. To control fouling, high liquid velocities must be maintained across the membrane. High pumping flow rates across the membrane may lead to the loss of working bacteria due to cell lysis. Organic fouling problems are typically caused by the accumulation of colloidal particles and bacteria on the membrane surface. Inorganic fouling is due to the formation of precipitates, a consequence of a rise in the pH as the flow passes through the membrane and CO₂ dissipate from the liquid. Membrane fouling will be discussed in a further part of this chapter.

To avoid fouling problems, a “special” type of membrane module has been installed as part of the pilot unit. Details on its operational principles are given in this section.

II.2 VSEP operating principles and properties

II.2.1 General description of the membrane filtration unit

The VSEP (*Vibratory Shear Enhancement Processing*) has been developed by NEW LOGIC Research Inc. since 1987, as an enhanced liquid/solid separation system. The model used at Sjöstadverket, known as “Series L/P”, is a laboratory or pilot unit, designed for a semi-industrial purpose. The “L mode” enables to evaluate the performance of a single membrane within a specific application. In the “P mode” operation, small scale filtration can be performed. During this study, the pilot unit has only been used in the “P mode” configuration.

In the first seconds of operation, the pressure has to be built up in the pilot unit and especially within the membrane stack. A minimum pressure of approximately 2.5 bars is required before the vibrations start, to avoid damaging the membranes with the oscillating motion. The displacement pump used to supply sludge to the membranes should enable the system to provide a pressure up to 12 bars. The VSEP unit has been designed so that this pump works in two modes; concentration and purge.

During the concentration phase, the closed valve ROV-03 (see Appendix 2) stops the concentrate flow just after the cross flow filtration step (so-called “dead-ends filtration” in this configuration). The pump operates at a given frequency, adjustable if the “feeding” pressure for the membranes is different from the nominal value. Indeed, the pump frequency is increased (respectively decreased) by the control system if this pressure is lower (respectively higher) than the expected value. A typical operating frequency is in the range 15 – 20 Hz. During the purge phase, the valve ROV-03 is open and the concentrate is sent back to the bioreactor. The pump frequency automatically increases to its maximum value to balance the pressure drop within the membranes. This maximum value may vary depending on the

¹ METCALF & EDDY, *Other anaerobic treatment processes 10-6*, p 1026.

application (sludge with a high Total Solids [TS] content for instance). It has been set to 60 Hz during the evaluation period.

The concentration phase lasts 90 seconds, and the valve ROV-03 is then open for 15 seconds to enable the concentrate to reach the bioreactor. This cycle is permanently reproduced during the operation period. The control system automatically records several parameters such as feeding pressure, concentrate pressure, permeate flow, temperature, and others that can be controlled from and shown on the operating screen of the VSEP unit (Lindblom, 2007).

The separation membranes are round and flat. They are piled up in order to form a stack. This stack is placed on top of a torsion spring.

The torsion spring is agitated by a vibrating motion, imposed by an eccentric weight. An AC engine spins this eccentric weight at a variable frequency and it is coupled to a seismic mass which supports all these components. Thus, the resonant spring-mass system transfers the vibrations directly to the membranes. According to instructions given by the manufacturer, amplitude for the vibrations should never exceed 1 inch (2.54 cm). The operational amplitude is actually in the range 0.70 – 0.85 inch. The parameter that efficiently controls this amplitude is the engine frequency. During the evaluation period, this frequency has been set to 51.25 Hz.

A simplified scheme of this oscillating system is represented in Figure 4.

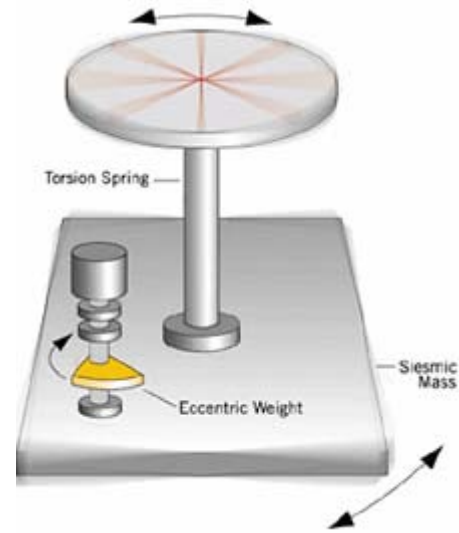


Figure 4 : VSEP resonating drive system¹.

II.2.2 Details on membrane stack

The membrane stack is composed of 19 double sided Membrane Tray assemblies, that is to say 38 membranes in total. A standard unit comprises 10 trays with two feed holes and 9 trays with only one feed hole (called “diverters”). During the installation of the membrane stack, the trays and the diverters are alternately placed on top of each other. The feed hole of the diverters is also positioned in an alternating way, once on the left side, once on the right side.

¹ NEW LOGIC RESEARCH Inc, *Technology*, <http://www.vsep.com/technology/index.html>, Figure 4.

This configuration enables the permeate and concentrate flows to be completely separated, as shown on Figure 5.

The feeding sludge reaches the membranes and is filtrated. The fluid going through the membranes is the permeate. It is drained to centre channel by drain clothes, in between the membranes and the stainless steel tray support. The concentrate is collected at each level of the stack and drained to the lower tray, until it reaches the bottom of the stack. The concentrate is collected and removed with the ROV-03 valve opening. Plastic and metallic “o-rings” avoid leaks in the whole pile.

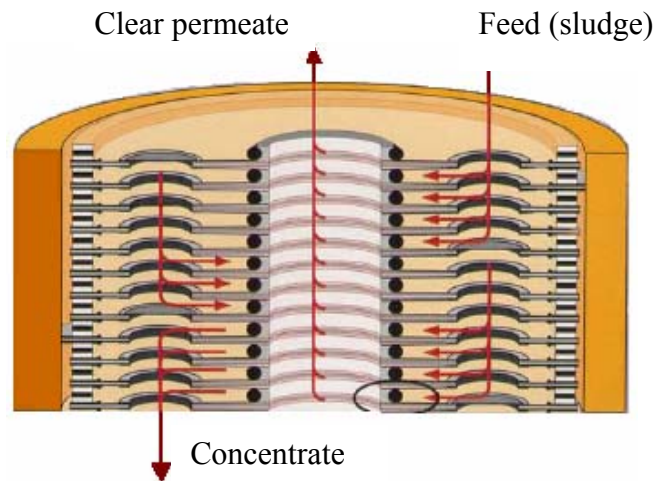


Figure 5 : Flow diagram through the membrane stack¹.

The separation process used in this pilot unit is a micro filtration process, which implies an operating range of 0.08 – 2.0 μm . The typical constituents removed are the particles composing the Total Suspended Solids (TSS), turbidity, some micro-organisms, some bacteria and viruses. The permeate contains water and dissolved solutes². Some details and characteristics regarding the membranes themselves are developed in a further chapter (see Material and methods).

II.2.3 Vibration effects and practical application

The main advantage of the VSEP pilot unit is to avoid fouling resulting from daily use. Indeed, this is a major issue in membrane separation processes, as it is a long-term loss regarding sludge treatment capacity and permeate flow rate. This phenomenon is due primarily to the formation of a boundary layer that builds up naturally on the membrane's surface during the filtration process. In addition to decrease the flux capacity and performance of the membrane, this boundary layer acts as a secondary membrane reducing the efficiency of the membrane in use.

A reason for this particles deposit on the membrane surface is that the majority of shear created by the turbulent flow takes place outside the boundary layer. Therefore, it cannot efficiently remove retained particles. This is why traditional cross-flow membranes plug and foul. This inefficient use of shear accounts for the eventual loss of flux experienced in traditional systems over time. Figure 6 illustrates this deposit phenomenon.

¹ VSEP Brochure, *A separate revolution*, p 9.

² METCALF & EDDY, from Table 11-17, p 1106.

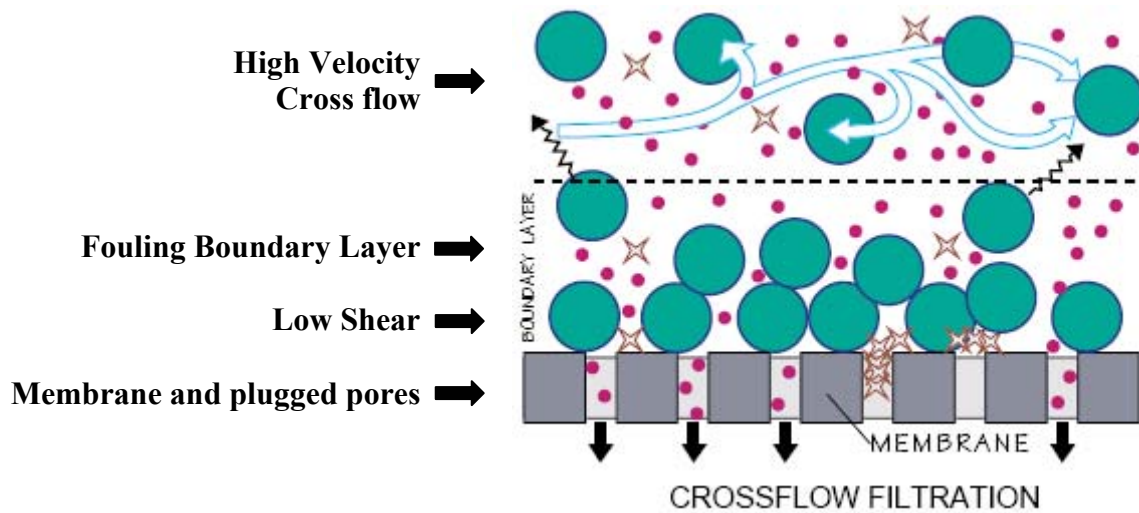


Figure 6 : Illustration of membrane fouling¹.

To prevent the membranes from fouling, intense shear waves could be applied at their surfaces. This is how the VSEP operates. The feed sludge remains nearly stationary, moving in a leisurely flow between parallel membrane elements. Shear cleaning action is created by vigorously vibrating the membranes in a direction tangent to their faces. The shear waves produced by the membrane's vibration cause solids and foulants to be lifted off the membrane surface and remixed with the bulk material flowing through the stack². Thus, the liquid can flow through the membrane pores unhindered. The shear rate applied at the membrane surface is approximately 150,000 inverse seconds. This principle is shown in Figure 7.

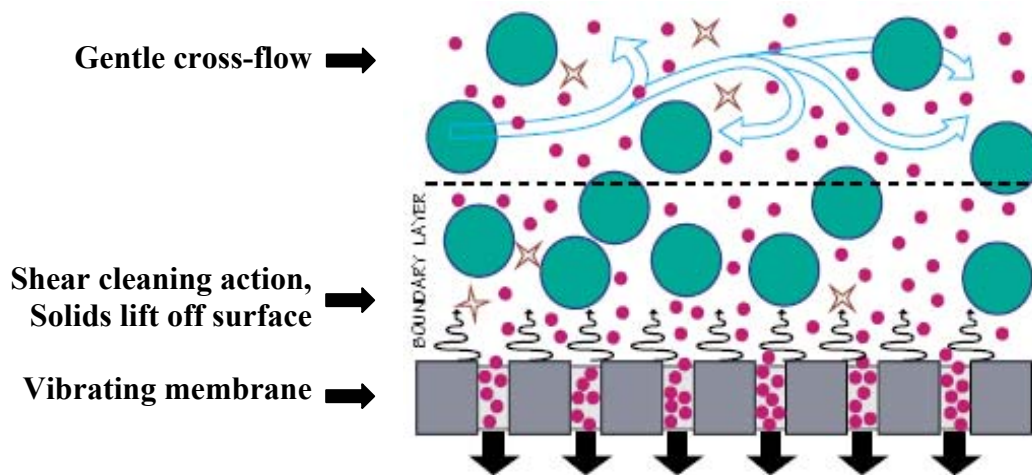


Figure 7 : Effects of shear waves on membrane surface³.

According to NEW LOGIC RESEARCH Inc. documentation, nearly 99 % of the total energy used is converted to shear at the membrane surface (VSEP Brochure, *A separate revolution*, p 6). However, this statement is rather hard to check. The shear waves are obviously linked to the AC engine frequency. The only way to control the efficiency of this shear motion is by

¹ VSEP Technical Manual, *Technical overview*, p 7.

² NEW LOGIC RESEARCH Inc., *Technology*, <http://www.vsep.com/technology/index.html>

³ VSEP Technical Manual, *Technical overview*, p 7.

checking the membrane stack amplitude (operating range is 0.70 – 0.85 inches, as mentioned previously).

These shear waves are actually needed to avoid membrane fouling. Therefore the permeate flow is more or less maintained at a constant value (some fluctuations result from variations in the feeding pressure). It is very important to know the total volume of permeate produced by the membranes for a given period of operation. By knowing the amount of permeate generated and led out of the system, a precise volume of Primary Sludge (PS) could be introduced in the bioreactor. The HRT is clearly dependent on this way of proceeding and this is why a problem free operation of the VSEP unit is required. Lowering the membrane fouling risk is then essential. The use of this VSEP separation technique meets this requirement.

II.3 Membrane fouling

The term *fouling* is used to describe the potential deposition of existing solid material from the feed stream on the element of the membrane. Fouling can be either reversible or irreversible¹. Membrane fouling is an important consideration as it affects cleaning requirements, operating conditions and performance. The main consequence observed is a decrease in the permeate flux (permeate flow through the membranes). Membrane fouling includes the following phenomena: colloids and particles deposition at the surface, deposition inside the pores due to particles or insoluble substances (struvite, calcite, magnesite, etc.), and organic compounds adsorption at the surface or in the pores of the membrane.

Constituents in wastewater that can bring about membrane fouling are identified in Table 5.

Table 5: Constituents in wastewater responsible for membrane fouling mechanism².

| Type of membrane fouling | Fouling (cake formation sometimes identified as bio film formation) | Scaling (precipitation) | Damage to membrane |
|---------------------------------|---|---|---|
| Responsible constituents | Metal oxides Organic and inorganic colloids Bacteria Micro-organisms concentration Concentration polarization | Calcium sulphate Calcium carbonate Calcium fluoride Barium sulphate Metal oxide formation Silica | Acids Bases extreme pH values Free chlorine Bacteria Free oxygen |

Fouling of the membrane can occur in three general forms:

- a build-up of the constituents in the feed water on the membrane surface
- the formation of chemical precipitates due to the chemistry of the feed water

¹ METCALF & EDDY, from Table 11-16, p 1105.

² METCALF & EDDY, from Table 11-18, p 1118.

- damage to the membrane due to the presence of chemical substances that can react with the membrane or biological agents that can colonize the membrane

These different phenomena could be modelled as a serial resistance system, as shown in Figure 8 (Rodriguez Susa, 2005)

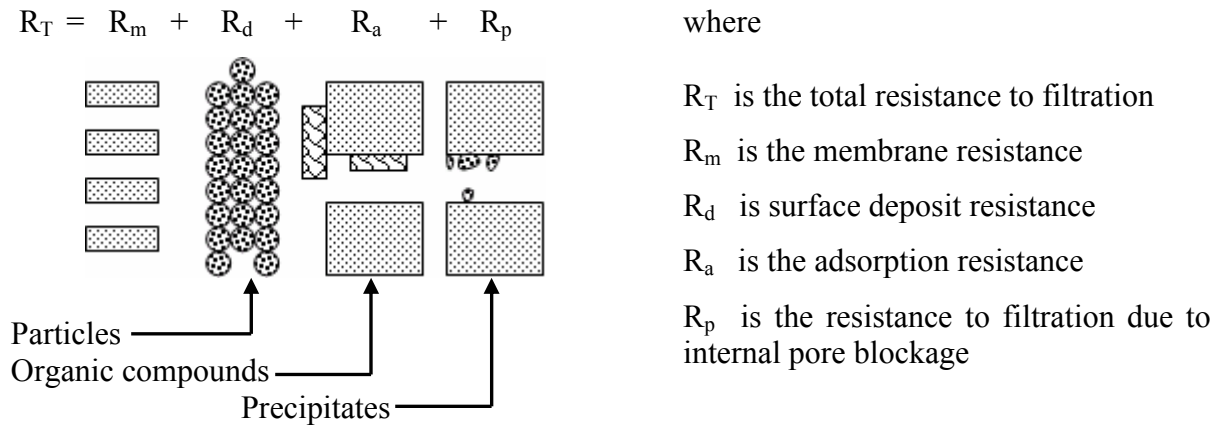


Figure 8: Serial resistance conceptual model¹.

In the case of membrane fouling caused by build-up of solids, three mechanisms could be considered. They result in resistance to flow due to accumulation of material within or around the pores. These mechanisms, *pore narrowing*, *pore plugging* and *gel/cake formation* caused by concentration polarization, are defined below, according to Metcalf & Eddy (2003) “Wastewater Engineering, Treatment and Reuse” description.

Gel/cake formation may happen when most of the solid matter in the feed water is larger than the pore sizes or molecular weight cut-off of the membrane. Concentration polarization could be described as the matter build-up close to or on the membrane surface that causes an increase in resistance to solvent transport across the membrane. This particular phenomenon will always occur within a membrane system, whatever the operating conditions would be. However, the formation of a gel or a cake layer is an extreme case of polarization where large amount of matter is actually accumulated on the membrane surface.

Pore plugging and pore narrowing will occur only when solid matter contained in the feed water is smaller than the pore size or molecular weight cut-off. *Pore plugging* occurs when particles fitting the pore size become stuck in the pores of the membrane. *Pore narrowing* consists of solid material attached to the internal surface of the membrane, thus resulting in narrowing the pores. These mechanisms are illustrated in Figure 9.

¹ RODRIGUEZ SUSANA (M.), « Etude d’un bioréacteur anaérobie à membranes immergées pour le traitement des eaux résiduaires », Figure I.9, p 33.

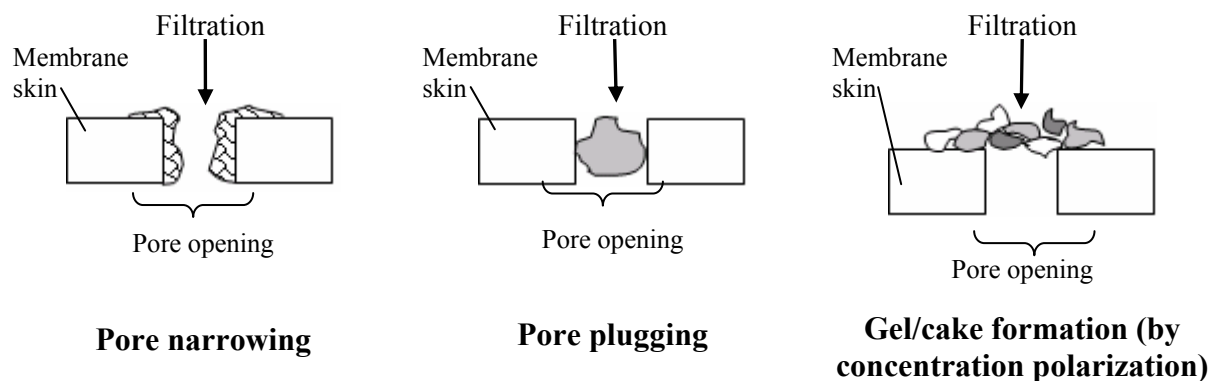


Figure 9: Modes of membrane fouling¹.

The main operating parameter affected by membrane fouling is the permeate flux, as previously mentioned. However, it is rather difficult to describe a general behaviour for permeate flux within anaerobic membrane bioreactor systems. In his literature review, Rodriguez Susa points out that several authors have observed a permeate flux decrease when micro-organisms concentration within the bioreactor increases. Some of these authors suggest operating the system below critical flux conditions. The critical flux is defined as the permeate flux for which membrane fouling becomes measurable. This critical flux is a characteristic of the fluid/membrane/hydrodynamics system around the membrane.

According to this review, within external loop systems, the critical flux depends on circulation velocity inside the membrane module and therefore fluxes are higher with higher circulation speeds. Within such external systems, the permeate flux is dependent on pressure, circulation velocity, temperature, micro-organisms concentration, viscosity, sludge rheology, biological activity and effluent biodegradability. But this flux depends also on the amount of fouling matter and organic matter concentration. Some authors noticed that the permeate flux decreased while HRT decreased as well. As a consequence, the operating transmembrane flux varies a lot with effluent concentration.

II.3.1 Influence of biomass concentration and structure

In his review, Rodriguez Susa (2005) states that most of the authors have observed a permeate flux decline while micro-organisms concentration increases within the bioreactor. However, the degree of decrease in permeate flux varies. In the case of a membrane bioreactor with external loop, an example has been mentioned. The permeate flux decrease could be caused by biomass concentration increase, adsorption phenomena, pore plugging, and concentration polarization. By considering the same configuration, the flock size reduction of anaerobic sludge would probably lead to an increase of filtration resistance.

II.3.2 Influence of organic substances

Results from Rodriguez Susa's review show different impact assessments regarding soluble matter, colloids and particles involved in organic fouling. According to Choo and Lee (1996a, 1996b, 1998), colloids are responsible for membrane fouling. 83 % of total resistance to filtration is caused by the phase containing colloids, whereas flocculated micro-organisms are responsible for 18 % of total resistance to filtration. Moreover several authors state that

¹ METCALF & EDDY, adapted from Figure 11-41, p 1118.

soluble organic substances are mainly responsible for gel layer formation in anaerobic membrane bioreactors. Undigested compounds could partly be held responsible for membrane fouling.

II.3.3 Influence of inorganic substances

Precipitations are much more important in anaerobic processes than in aerobic processes, as ion and organic molecule concentrations are higher in treated effluents, under anaerobic conditions. Iron sulphur precipitates have been observed as well as struvite precipitates ($\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$). They are one reason of membrane fouling. Other common precipitates responsible for membrane fouling within anaerobic processes are calcium phosphate ($\text{Ca}_3(\text{PO}_4)_2 \cdot x\text{H}_2\text{O}$), hydroxyl apatite ($\text{Ca}_5(\text{PO}_4)_3\text{OH}$), newberyite ($\text{MgHPO}_4 \cdot 3\text{H}_2\text{O}$), calcite (CaCO_3) and magnesite (MgCO_3). It is rather difficult to draw conclusions about their contribution into the fouling, although parameters for precipitate formation under anaerobic conditions are known (high pH values, high concentrations as NH_3 , Mg, Ca and PO_4).

Interactions between organic and inorganic substances in filtration cake formation must be taken into account as well. He *et al.* (2005), referring to a study, stated that “the inorganic precipitate generated during anaerobic digestion could play an important role in the consolidation of biomass cakes on membrane surface and this resulted in severe membrane fouling”. They draw the following conclusion: “Membrane autopsy revealed that the main component of the fouling layer was the bio film bound with inorganic components.”

II.3.4 Reversible and irreversible fouling

Rodriguez Susa (2005) defines reversible fouling as a fouling that can be easily removed with clear water flushing whereas irreversible fouling cannot be eliminated with such washing. Other types of washing procedures are used to get rid of this particular fouling (for example, chemical washes). They could be estimated by considering the permeate fluxes before and after the washing steps, respectively with clear water and chemical solution. Both types of fouling are involved in resistance to filtration, added to membrane resistance itself. Total resistance to filtration could be modelled as previously by using a serial-resistance model. With these considerations, an expression for the total resistance could be:

$$R_T = R_M + R_R + R_{IRR}$$

where R_T is total resistance to filtration

R_M is the membrane resistance

R_R is resistance due to reversible fouling

R_{IRR} is resistance due to irreversible fouling

Regarding irreversible fouling, Rodriguez Susa notices that continuous loss in permeate flux may be caused by organic molecules adsorption (intermediate substances from anaerobic metabolism for instance) and/or deposition of inorganic precipitates and organic particles on membrane surface. However, details and characterisations on particular compounds involved in this phenomenon are not developed. The following conclusion has been drawn. Most of the irreversible fouling comes from organic substances and is due to adsorption of this type of compounds.

As previously mentioned, reversible fouling could be easily eliminated by clean water flushing. It is rather difficult to determine whether or not a particular phenomenon is mainly responsible for this kind of fouling under anaerobic conditions, among adsorption, cake formation and precipitation. It depends on sludge composition, operating conditions, type of membranes used and if they are immersed or a part of an external loop.

II.3.5 Observations from the pilot unit

One can think that permeate flow and therefore permeate flux should decrease with time, as a consequence of fouling. But this situation was not observed with a normal operation of the pilot unit, it was the other way round. Permeate flow increased over time until a “physical” limit allowed by the membrane module. At the very beginning of a new operation period, the system usually has a permeate flow around 750 mL/min whereas at the end, a common permeate flow value is 1500 mL/min.

This phenomenon was considered by Rodriguez Susa in his Ph.D. review, and a possible explanation for these flow and flux increases over time is the temperature influence. Indeed, Ross *et al.* (1990) got an improvement in permeate flux by 2 % per additional degree within their bioreactor. Hogetsu *et al.* (1992) measured a permeate flux increase from 32 L/(m²·h) at 40°C to 43 L/(m²·h) at 47°C. This trend concerning flux improvement due to temperature increase could be related to¹:

- a decrease in sludge viscosity
- a general enhancement in biological activity, perhaps resulting in a higher organic substances consumption (responsible for membrane fouling)

One could also consider influence of temperature on pore size. The membrane module is settled in a hall which temperature is assumed to be constant at 20°C. After a few minutes of operation, sludge from the bioreactor at 36°C could have increased membrane temperature by contact. This 16°C variation in temperature might have an influence on membrane behaviour regarding fouling and ability to let permeate cross different layers.

¹ RODRIGUEZ SUSA (M.), « Etude d'un bioréacteur anaérobie à membranes immergées pour le traitement des eaux résiduaires », p 27.

Chapter III: Material and methods

The pilot unit used in this study is described in this chapter. The two main components of this unit are the bioreactor and the membrane separation unit. In this chapter, reference is also made to all devices within this pilot unit.

The methods followed to operate this unit, the way samples were taken and stored, the analyses, and related calculations are explained as well.

Consequences of the operation of this pilot unit referring to different problems faced during the whole evaluation period are listed. The solutions found or in need to be improved are also presented.

I. Technical description of the Anaerobic Membrane BioReactor unit (AnMBR)

I.1. Storage of primary sludge in the mixer tank

The starting point of the whole process could be considered as the agitated tank containing primary sludge (see Appendix 2). This tank is cylinder-shaped, with a conical part at its bottom, supplied by Good Tech MRAB. The total surface area is 1.3 m² and its volume is 1.5 m³. A propeller ensures the content of this tank to be agitated. A wooden board diving from the top of the tank towards the bottom conical part was added to promote mixing.

The primary sludge stored in this tank comes from a drum filter, which settings can be changed to increase (or decrease) TS content within primary sludge. Indeed, sensor level in the drum filter, backwashing, drum rotation angle, polymer and sludge addition are factors that may contribute to increase dry solids content (Karczewska, 2006). During the evaluation period, backwashing parameter was changed to try to increase TS content, without being totally successful. The final purpose of increasing TS content in PS is obviously to raise the TS content within bioreactor sludge.

Several “batches” of PS were made. “Fresh” PS with a proper TS content was added into the bioreactor for example during week 16, resulting in one of the highest TS values for the bioreactor (1.1 %). Expected sludge concentration in the reactor was 2 - 3 % TS.

Monitoring TS content of primary sludge was performed over the whole study. Samples were taken after 30 minutes agitation at least. A one litre container was dived and filled at a depth of around 20 cm below the PS surface. A part of this sludge was then poured into a smaller container, convenient to perform analyses. This 30-minute agitation period was aimed to balance deposition phenomenon occurring over night, while the mixer tank was not agitated.

Just below the mixer tank, a displacement pump enabled primary sludge to be pumped through a hose, directly to the bioreactor. Its brand is Netzsch Mohnopumpen, year 2002, operating at 60 Hz, for 0.63 kW and 1700 rot/min. However, operational frequency was around 18 Hz as settings could not be changed. It resulted in a mean PS flow of 700 mL/min, from the bottom of the mixer tank to the bioreactor.

I.2 The BioReactor, major component of the pilot unit

The bioreactor is settled outside the main hall, sheltered by a roof. In this reactor, an anaerobic process occurs, thus producing biogas. It is a 2-meter high cylinder, and has an inner diameter of \varnothing 0.950 m. The volume would have been 1.4 m³ for a totally filled reactor. It is assumed to be completely mixed (continuous agitation with a propeller).



Figure 10: Anaerobic bioreactor¹.

Figure 10 illustrates the previous description. A pre-sedimentation tank can be seen to the right. Here, primary sludge was introduced. A direct connection leads primary sludge to the agitated part of the reactor.

Temperature within the bioreactor can be adjusted. Hot water hoses circle the reactor and a thermostat enables the water temperature to be set. Moreover, on its top, a hand valve could be opened or closed to control hot water flow. Therefore, temperature of anaerobic activated sludge could be set this way.

During this study, temperature within the bioreactor remained stable at $36^{\circ}\text{C} \pm 0.3$, right in the optimum range for mesophilic conditions.

The level of sludge in the reactor is measured by a pressure sensor and displayed on the central control system screen. This level is given as a percentage. 100 % of 2 metres corresponds to 1.4 m³. During the evaluation period, the level was first kept more or less constant, around 60 %, i.e. roughly 850 L. In a second phase, the level was increased up to 70 % (about 990 L). The bioreactor was never filled to its maximum capacity, as an unoccupied volume was required to allow biogas first to leave the sludge phase and second to be collected and removed from the reactor.

Biogas produced is then led to a Schlumberger gas flow meter to monitor total biogas production. Prior passing through this gas flow meter, biogas goes through condensate trap (containing glycol). Serious problems occurred in biogas measuring system during the evaluation period. They are discussed in detail in a further part of this chapter.

I.3 Technical considerations regarding the membranes

As mentioned in the Theory chapter, 19 doubled side membranes are piled to form a stack that ensures a separation step. The membranes used during this study have been supplied by Nordcap. Their pore size is 0.1 μm . They are made of Teflon and Polypropylene, and the

¹ CARLSSON (A.), *Sewage treatment in an anaerobic membrane bioreactor with a VSEP unit*, Figure 7, p 12.

drain clothes are made of Polyester. The total area of the membrane stack is 1.59 m² (Carlsson, 2005).

Figure 11 gives an overview of the whole membrane unit, where the membrane stack could be seen in the top central part of the picture. The operating “feeding” pressure was set around 4 bars. At this pressure, the permeate flow produced is close to the maximum flow but requires a lower feeding pressure (4 bar instead of 10 bar, based on results from Carlsson, 2005).



Figure 11: VSEP unit (membrane stack and electrical engine)¹.



Figure 12: Old membranes during changing².

The membranes previously described are new ones that have been installed to replace damaged membranes. The whole membrane stack was changed. A picture illustrates this operation (Figure 12). This step was necessary, as the damages were really serious. They were due to fouling, low pressure while vibrations occurring, perhaps development of a bio film at membrane surface. It is difficult to state which was the main phenomenon responsible for these damages.

Regarding permeate flux through the membranes, the monitored values were satisfying in spite of the huge range they covered. Indeed, in normal operation of the pilot unit, permeate flow varied from 700 mL/min up to 1500 mL/min. These values correspond to 42 L/h and 90 L/h, respectively. Thus, considering the total surface area of the membrane stack (1.59 m²), the values for the flux varied from 26.42 L/(m²·h) to 56.60 L/(m²·h). The average pressure was around 4 bars so this parameter cannot be held responsible for such a wide range of flux. A general behaviour has been observed. At the beginning of its operation, the VSEP unit has a lower permeate flow than after 60 or 90 minutes in operation (respectively 700 or 800 mL/min, 1500 mL/min). This could be explained by the increase in temperature over operating time (see Theory).

¹ Personal picture, Sjöstadverket, 06/08/2007.

² Personal picture, Sjöstadverket, 03/29/2007.

I.4 Other components of the pilot unit

To avoid excess clogging due to anaerobic activated sludge, two filters are placed just before the membranes (see Appendix 2). The main filter was supplied by EATON Filtration. It is contained in a metallic filter house, which volume is 15.5 L, 2006. This filter is bag-shaped and could be carried like a bag. It is so-called and will be referred to as a bag filter. It is made of polymers, its diameter is 18 cm and it is around 45 cm long, the pore size is 0.6 mm. The maximum operating conditions are 10 bars for the pressure and 120°C for the temperature. The second filter is smaller, 6.5 cm in diameter and about 13 cm long. Its pore size is 0.5 mm, so it actually works in complement to the bag filter and retains a part of the particles that went through the bag filter.

Three pumps are used in the pilot unit. The recirculation pump P-02 and the “feeding” pump P-01 (see Appendix 2) are both from Netzsch Mohnopumpen, 2002. The feeding pump is usually operated at a frequency varying from 14 to 25 Hz when the pilot unit starts. During the purge phase, its frequency increases up to 60 Hz (see Theory). Its power is 0.63 kW and the maximum rotation velocity is 1700 r/min.

The recirculation pump P-12 is a little bit more powerful, effect 0.86 kW, for a maximum rotation velocity of 1650 r/min. This model has been installed recently in order to fix problems related to low feeding pressure.

The centrifugal pump P-12 has been manufactured by ABB Motors. At 60 Hz, its power is 0.45 kW and its rotation velocity reaches 3440 r/min. During the last weeks of the study, this pump was only used for flushing and washing procedures. These changes were made to solve the low feeding pressure problem, as mentioned above.

Other components of interest for the pilot unit are the different valves. Indeed, they are controlled by the central system and they allow the fluids (permeate, sludge and concentrate) to circulate through the whole pilot unit. ROV-02, ROV-03 and ROV-05 (see Appendix 2) have been manufactured by BEGRA. These pneumatic valves are solenoid valves, operating in the pressure range from 1.5 to 8 kgf/cm².

II. Different methods and procedures applied to the operation of the pilot unit

II.1 Several phases during the study

According to the “Research plan”, four stages should have been fulfilled. The first step was the cleaning and preparation of the pilot unit, particularly the membrane module. The bioreactor was fed with primary sludge.

The second step included the beginning of the sampling programme. Primary sludge was introduced into the bioreactor as well. All operational parameters should have been checked to confirm the proper operation of the pilot unit.

The next stage concerned membrane substitution, as the old membranes were seriously damaged as previously mentioned. The bioreactor was still fed with primary sludge.

The final step was actually the evaluation period. HRT was decreased, see Table 10, when operational conditions enabled the pilot unit to be operated properly. Primary sludge was added in various amounts, from a few litres (20 L) to 150 L.

Serious mechanical problems disturbed this planning, resulting in a few days of constant operating conditions. Therefore the results are not totally satisfying, even if all the previous stages were fulfilled. These problems will be described in a further part of this chapter.

II.2 Sample taking and storage

The samples were taken in small plastic buckets, dedicated to one substance. Analyses related to parameters indicating a proper anaerobic process were performed every day, while chemical analyses were carried out once a week at Sjöstadsverket. Moreover, all these analyses were performed by Stockholm Vatten's main laboratory (accredited), based on mixed samples from a whole week. Indeed, permeate, primary sludge, and removed sludge samples were recovered every day and mixed to have a representative sample covering an entire week. Bioreactor sludge was recovered as a daily sample and sent to the main laboratory as well.

Continuous sampling from permeate flow ended up in a bucket, which was placed into a cooled box (temperature 7°C). Settings for this continuous sampling are made for recovering 0.3 L of permeate as soon as 3 L of permeate have passed through valve ROV-02 (see Appendix 2). Samples taken all week long are stored in a cooled automatic sampler, at approximately 7°C, before being mixed.

Filtration is required for recovering primary and reactor sludge filtrate, in order to perform chemical analyses describe in the next point. The filters used for this purpose were manufactured by Munktell, with 1.6 µm pore size, grade "MGA".

Removed sludge from the bag filter (liquid and thick sludge) was poured into a barrel, which was vigorously agitated. This step is necessary to homogenize as much as possible removed sludge. The mixed content of this barrel was then transferred into plastic flasks and stored in a cooled automatic sampler.

II.3 Pilot unit monitoring and analyses

➤ pH measures

The pH meter used was supplied by WTW, model pH 330i. The electrode was changed on April, 5th, 2007. Calibration was made before every single use, with buffer solutions from Merck, pH 7.00 and pH 4.00 at 20°C. Only two buffer solutions were needed in order to set a calibration slope, directly calculated by the pH meter. Most of the measures were below pH value 7.00, so it was consistent to use calibration buffer solutions with such pH values.

pH analyses were performed daily for primary sludge, reactor sludge and after satisfying operation of the unit for permeate and concentrate.

➤ TS and VS parameters

Total Solids (TS) were measured every day for primary sludge and reactor sludge, as a mean of monitoring variations occurring within the mixer tank and the bioreactor. TS are defined as "the residue remaining after a wastewater sample has been evaporated and dried at a specified

temperature (103 to 105°C)¹”. The main laboratory also performed this kind of analysis but with a weekly sample, thus with extracts collected over a week.

As mentioned before, sludge samples were taken below primary sludge surface in the mixer tank. The sampling point is about a third of the bioreactor height. Both sludges are poured in small metallic pans and let dry 24 hours at 105°C, in a convenient oven. TS content is calculated by considering the mass after drying m_d , the total wet mass m_t and the pan mass m_p :

$$\text{TS [\%]} = \frac{m_d - m_p}{m_t - m_p} \cdot 100$$

Volatile Solids (VS) were only measured by the main laboratory, based on the same weekly sample supplied for TS analyses. VS are defined as “solids that can be volatilized and burned off when the TS are ignited (500 ± 50°C)²”. Results from the laboratory actually give complementary fraction of VS, that is called “GR” (stands for Glödresten, the inorganic part of TS, see Appendix 1). Therefore, VS fraction is deduced from the GR values:

$$\text{VS [\%]} = 100 - \text{GR [\%]}$$

These two methods are performed under Swedish standard procedure, SS 028113-1 for both TS content and GR.

➤ Chemical analyses for monitoring and efficiency evaluation

Chemical analyses were performed at Sjöstadsverket either to check operating conditions or to have a rough evaluation of process efficiency. Results from the main laboratory were received more than a week after sending the samples, so that was also a faster way to get some results confirming a safe operation of the process.

These tests concerned COD, Ortho Phosphate (PO₄-P), Ammonium-Nitrogen (NH₄-N), Nitrate (NO₃-N) and Volatile Fatty Acids (VFA). They were performed with Dr Lange cuvette tests, practical for quick investigations (see Appendix 3 for details). Measures were made with a spectrophotometer Xion 500, Dr Lange.

➤ Methane content monitoring

Methane content was measured in the total biogas flow, every morning at the same time. This was made in order to evaluate and compare biogas and thus methane production from one day to another. The percentage (in volume) of methane was measured with an EX-METER II from Auer MSA.

To avoid introducing water inside this CH₄-meter, a water trap was built with a small plastic flask. Through a thin pipe, incoming biogas fills up this little bottle and potential water drops are trapped within this container, while biogas can escape using an outgoing pipe towards the methane meter.

➤ Membrane cleaning

¹ METCALF & EDDY, *Physical Characteristics 2-3*, from Table 2-4, p 43.

² METCALF & EDDY, *Physical Characteristics 2-3*, from Table 2-4, p 43.

Chemical cleaning was made at least once a week, sometimes twice a week to make sure the membranes were totally clean. The chemical product used for this purpose was P3-ultrasil 11, from Ecolab. It is a strong alkaline powder detergent for membrane filtration units. It contains sodium hydroxide and EDTA.

Prior to cleaning the membrane, a few changes have to be done regarding hose connections. The pilot unit has to be in “recirculation mode” (SP-02 closed), and the clear water pipes and P-12 pump have to be connected to the main pipe network to introduce water towards the bag filter (see Appendix 2).

The washing procedure includes three stages. The first step is a classical flushing of the membrane stack, with tap water, during 10 minutes. Then an alkaline solution is made in the T-13 tank with pH in between 11 and 12. This solution is introduced to the membranes via the normal “feeding” way, during 30 minutes. The membrane stack is then rinsed with “warm” water at around 25°C for a few minutes. During the whole procedure, feeding pressure must remain stable at 2.5 bars. It could be adjusted with the HV-04 valve. The system has to be changed to its initial settings (previous hose connections, opening/closing of some valves) before the system is taken into operation again.

III. Problems that occurred during the evaluation period

III.1 The main problem with a low feeding pressure

A minimum sludge pressure has to be supplied to the membranes before the vibrations start, the so-called “feeding” pressure. This pressure is set to 2.5 bar (see Theory) and the system cuts out automatically if the feeding pressure is below this value for 10 seconds or more. Therefore, maintaining the feeding pressure above 2.5 bars and around 4 bars for a satisfying operation is fundamental. It is the key parameter and this is why feeding pressure was carefully checked while the pilot unit operated.

During many weeks, and particularly at the beginning of the study, the pilot unit could not be operated in a proper way as the system was not able to provide the minimum required pressure. So after a few minutes, the control system turned off all operating devices. Several reasons resulted in this situation.

Concretely, the system did not provide a sufficient pressure to the “feeding” pump P-01. A pressure gauge on its suction side did not show any pressure, meaning that sludge flow before the feeding pump was not high enough. Thus this pump was not able to supply the membrane stack with appropriate sludge flow. The P-01 pump worked perfectly. Its stator was changed during week 11. When its frequency was voluntarily forced, the feeding pressure did not reach the minimum value anyway. The conclusion was drawn that the problem related to how high the provided pressure was before the feeding pump, referring to process sketch (Appendix 2).

An investigation was made regarding the bag filter. One of the goals of the study was to increase the TS content of the bioreactor sludge, so primary sludge with the highest TS content possible was introduced in the reactor. After a few weeks, the TS concentration of the bioreactor sludge started to increase. This operating parameter could have an influence on bag

filter clogging. Indeed, as the amount of solids in the sludge was enhanced, particles were even more numerous, thus promoting accumulation on filter walls. This was considered as a filtration cake, which basic formation mechanisms could be compared to those mentioned in membrane fouling theory. The consequence was a pressure drop, as less flow could cross the filter walls. This pressure loss was responsible for not providing enough sludge to the feeding pump. However, this type of bag filter was designed to operate with higher TS content than the one within the bioreactor sludge. So theoretically, it could not explain clogging and pressure drop observed. In practice, bag filter clogging occurred more rapidly since the TS content was increased, so there might be a link in between.

Another kind of filter was available, a metallic one, with a similar pore size than the bag filter. They were switched for a try, to check the possibility of using this metallic filter. The result was even worse. This metallic filter was clogged in a few minutes. To supply the suitable flow to the feeding pump and so to overcome the pressure drop after the bag filter, the frequency of the recirculation was increased from 50 % to 100 % of its capacity. The sludge flow within the recirculation loop was higher than previously but this modification did not improve the value of the feeding pressure towards the membrane stack. Operating the system at a lower pressure did not work either. The settings were changed to supply the membranes at 3.5 bars but the pressure value could not be kept steady. A temporary solution found was to stop the pilot unit when the pressure became unstable and to clean the bag filter i.e. to remove all the sludge accumulated and forming the “filtration cake”. The system was then started up for a new period. So actually, the overall operation of the pilot unit was composed of two semi-periods, which was not satisfying.

The problem was the same even by proceeding with two operation stages, as described above. The feeding pressure could not be supplied in an efficient way. Moreover, additional problems occurred. The centrifugal pump P-12 suddenly required an electrical current of several amperes, which made the contactor to open in the central fuse box. P-12 was taken apart and its three-blade wheel was changed. Finally, after a meeting with a pump consultant, a pressure valve was added in the hose leading the sludge back to the reactor, in the recirculation loop. The purpose was to adjust manually this valve so as the sludge flow and thus the pressure in the bag filter could be maintained at a suitable value. The feeding pump could then supply the membrane stack with a sufficient pressure. This system was installed and an improvement was observed, but it did not totally solve the problem. After several tries and deeper investigations, a new pipe network was built around the recirculation loop to disconnect the centrifugal pump during normal operation. This pump was only used for membrane flushing and washing procedures. This configuration is illustrated in the scheme in Appendix 2. The pressure valve 2 (nameless) was also adjusted. During concentrate “purge” phases, the concentrate flow towards the bioreactor could be so high that pressure within the membrane stack could drop rapidly. So by adjusting this valve, the pilot unit could operate in rather steady operating conditions.

The consequences of this low feeding pressure problem were first obviously a delay in the evaluation planning. Second, some days the pilot unit was stabilized enough, i.e. to have a steady permeate flow removed from the system, to add the corresponding primary sludge volume. But these additions could only be possible one or two days a week, in a completely irregular way. Therefore, to plan and to introduce a constant organic load into the bioreactor was very difficult and somehow disturbing for the bacterial community. Third, parameters such as HRT could not remain stable during this period, so the operation of the pilot unit in this situation was far from the suitable operating conditions defined in the research plan.

Due to inability to ensure constant influent flow of primary sludge to the bioreactor, the operation of the pilot unit was not in a steady state.

III.2 Problem related to biogas production measuring system

Monitoring the biogas production was an essential requirement. Obviously, this implies that the flow meter had to measure the right biogas volume to indicate reliable results. That was not the case during the whole evaluation period of investigation. The measured flow through the flow meter was reduced to a few litres per day while primary sludge was added into the bioreactor, i.e. biogas production should have been at its maximum.

At the beginning of the study, the pilot unit could not be operated properly due to previously detailed problems. Therefore, only a few litres of primary sludge were introduced within the reactor, explaining the low biogas (and methane) volume produced. This situation lasted until week 14. It was then possible to operate the unit and to add a larger but still not satisfying volume of primary sludge. During the sporadic feeding of the reactor with primary sludge each day (half an hour to a few hours at a time), the HRT went down to 10 days or less during the time that the reactor was fed. In Table 10, the HRT is calculated as an average value during the week and is for that reason much higher as there was not any incoming flow during nights and weekends. The biogas production measured was really low and far from the expected value. An investigation regarding the entire collection and measuring system was necessary. At first, no leakages were found among the pipes and hoses networks. Researches focused on the flow meter. The oil level was adjusted by introducing mineral oil and air tightness was reinforced by adding a plastic gasket around a control bolt. The measured biogas flow was closer to the theoretical value. However, after a few days, technical problems occurred again in the pilot unit, so once again primary sludge could be added into the bioreactor and the biogas production dropped.

Once these problems had been fixed and primary sludge could be introduced in the right amount, a new kind of disturbance appeared, involving the biogas flow meter. Its unexpected behaviour (“reverse” flow was observed, the needle indicating the grading went backwards and the accumulated total volume decreased) was the reason for a careful inspection of the measuring system. This examination did not allow noticing any leakage or perturbation. At the beginning of June, 2007, an expert for device calibration from JTI¹ inspected the flow meter, finding no dysfunction. He suggested skipping a liquid trap in which biogas passed through before reaching the flow meter, as this trap might be involved in the biogas leakage. He also advised to connect a plastic flask prior to the flow meter, to recover possible oil spill.

During week 23, it seemed that a proper biogas volume was measured after modifying the measuring system as described above. Finally, in the middle of June, it was discovered that biogas was leaking from the bioreactor from where the axle of the mixer enters the reactor. When the sludge filled the bioreactor to a level of 65 %, biogas was leaking, but when the sludge filled the reactor to a level of 70 % most of the leakage but not all stopped. Due to this lack of accuracy regarding the measured values, the results are unreliable and have to be carefully considered. Theoretically calculated values for methane production were instead used in the report. From a mass balance over the reactor, the reduced amount of COD as

¹ Swedish Institute of Agricultural and Environmental Engineering.

g/week was found, and these values were then multiplied with the factor 0.350 NL CH₄/g COD_{reduced} giving the methane production for each week.

III.3 Difficulties regarding primary sludge transfer

Carrying primary sludge from the mixer tank to the bioreactor was first made with 12-litres buckets (filled up to 10 litres), to be as accurate as possible concerning primary sludge volume. In order to add this sludge in a smooth way, during a couple of hours, using pump P-10 (situated just below the mixer tank) was considered as an option.

A hose was then connected from this pump to the top of the bioreactor. The average sludge flow was 700 mL/min and the frequency was estimated to around 18 Hz. This incoming flow to the reactor could balance the permeate flow led off the system, at least at the beginning of a new period of operation of the pilot unit. However, as the permeate flow used to increase after a few minutes, the volume removed from the system was higher than the incoming volume of sludge. This situation required to complement the missing volume with sludge buckets. Increasing the frequency of pump P-10 was an alternative. However, it was not possible to change the settings in a convenient way. Whatever the modifications were, the frequency remained the same. Thus, the function of pump P-10 was crucial for the operation. Furthermore, careful attention to the sludge level within the bioreactor was important (otherwise the system could have turned off by itself, as a safety measure at low levels in the reactor).

The inability to increase the frequency of pump P-10 combined with the consequences from the “low feeding pressure” problems led to serious difficulties in providing a continuous and smooth primary sludge volume over an operational day. So the organic load introduced within the bioreactor was highly variable during most of the evaluation period. The permeate flow was measured with a flow meter.

Chapter IV : Results and discussion

I. General monitoring of the bioreactor

I.1 pH monitoring

As previously explained, pH is one of the most important parameters for anaerobic processes (the methanogenic stage could be strongly inhibited, see Theory). Thus, a daily monitoring was performed during this study. The aim was to check the environmental conditions for the bacterial community and prevent this community from being irreversibly damaged.

The primary sludge was monitored as well, to be sure not to introduce low-pH sludge within the bioreactor, which could disturb bacteria. The results are plotted in Figure 13.

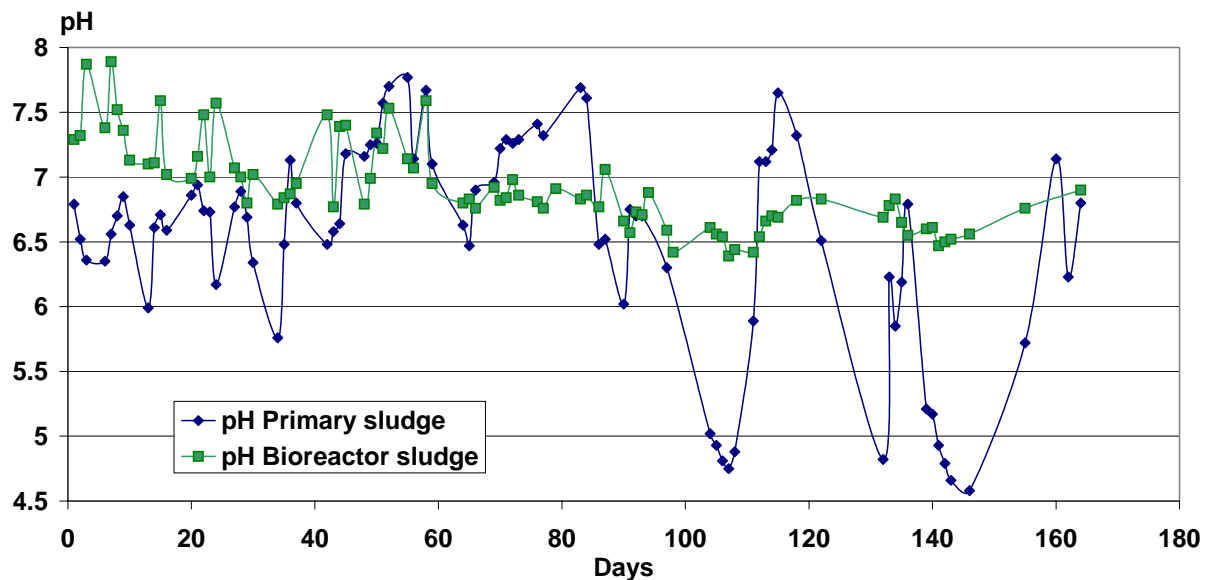


Figure 13: pH in primary sludge and bioreactor sludge over time (from February, 28th, 2007 (day 1) to August, 10th, 2007 (day 164)).

One can notice that pH for bioreactor sludge is in the range 6.4 – 7.9. It is a little bit low, referring to the “Research plan” where it is stated that pH should be above 6.8. However, it is nearly always above 6.5. No obvious decrease in the specific biogas production was detected during the weeks with a pH lower than 6.8.

From day 58 to 82 (week 18 - 20), small amounts of primary sludge was added, due to serious technical problems. One can observe that pH within the bioreactor remains rather stable during these days. During the period from day 83 to 94 (week 21 - 22), the operation of the reactor was problem free, with an average HRT of 8 - 14 days. A stable operation was also found during weeks 25, 28, 29, and 32; days 111-117, 133-146, and 160-167. Between days 30 and 58 (week 14 - 17), a variable amount of primary sludge was introduced in the bioreactor per day. This irregularity might explain the tendency of the bioreactor pH curve (fluctuations and small peaks), even if a quantified correlation has not been found. Despite low pH values in the primary sludge during three weeks, below 5, the pH value in the reactor

was equal to or above 6.4. During three other occasions, the pH value in the primary sludge was high, above 7.5, but the fluctuation in the bioreactor was low compared to adjacent weeks.

I.2 Monitoring of VFA

Monitoring this parameter is an efficient way of checking anaerobic process operation. Volatile Fatty Acids are intermediate compounds along the anaerobic reaction chain. Therefore one can have a precise idea of the balance between VFA production and consumption, meaning sufficient production and consumption rates for the bacteria involved. Moreover, VFA can inhibit an anaerobic process at high concentrations (see Theory). This is the other reason for monitoring these compounds.

VFA were measured within primary sludge (PS), bioreactor sludge and permeate. The lowest concentration detectable is 50 mg/L and as no other ranges for VFA tests were available many concentrations below this value are not accurately known. However, this situation is not a huge problem, as the main operating condition concerning VFA was set to be below 500 mg/L, in the “Research plan”. This condition was fulfilled during the whole evaluation period.

The results indicate that VFA concentration within the bioreactor sludge was detectable (i.e. above 50 mg/L) during the first weeks of monitoring, from day 1 to day 42 (week 9 - 14). Nevertheless, the concentrations were not continuously detectable during this period, meaning that some days the VFA concentration was below 50 mg/L. The VFA concentration varies from around 18 to 162 mg/L, which is far below the highest tolerable concentration of 500 mg/L. From day 43 to the end of the study, VFA concentration in the bioreactor sludge was nearly always below 50 mg/L, and between 51 and 57 mg/L during four days, except for day 122, 476 mg VFA/L, and day 136, 73 mg VFA/L.

By considering these results, one can draw the conclusion that VFA consumption occurred with a suitable rate, meaning that the methanogenic stage was satisfactory in the bioreactor.

VFA concentration in the outgoing permeate was also measured every day when the pilot unit was in operation. The values are nearly always lower than 50 mg/L, except for day 37, 139 mg VFA/L, two days during week 21 and week 22 (day 87 and 90), 51 mg VFA/L, day 113, 99 mg VFA/L, day 143, 68 mg VFA/L, and day 156, 125 mg VFA/L. Regarding VFA in the PS, the purpose of daily monitoring was to check that a degradation process had not started and that it was possible to add PS in the bioreactor with an appropriate VFA concentration. The values vary from below 50 mg/L to 874 mg/L during week 9 - 23, and from 112 to 2067 mg/L during week 24 - 32. The high concentration during the first period could be explained by the lack of agitation in the mixer tank during 2, 3 or 4 days. This situation happened when the pilot unit met serious problems and so there was no need for mixing the primary sludge in the mixer tank. During the second period, there was a shortage of personnel and as a result of that probably lack of agitation in the tank with primary sludge.

A general trend could be noticed. VFA concentration in primary sludge was rather high (up to 900 mg/L) after a period without any agitation and drops rapidly after one or two days of mixing to be below the lowest detection limit (50 mg/L).

In this chapter, values are presented with too high accuracy on purpose, especially in the tables, to make it easier for the reader to follow the calculations. In reality, the values are much less accurate.

I.3 Monitoring of Total Solids (TS)

The goal was to increase TS of bioreactor sludge up to 2 %, referring to the research plan, and keeping it between 2 and 3 %. To have a precise idea of the changes, TS was measured at least twice a week and every day during stable operation conditions. These analyses were performed in the laboratory at Sjöstadsverket and in Stockholm Vatten's main laboratory. The sludge samples sent to the main laboratory are taken once a week.

Despite the amount of PS added, the TS concentration of the bioreactor sludge did not reach 2 %. The results are plotted in Figure 14 and Figure 15. The maximum TS values of bioreactor sludge were 1.1 % during weeks 16, 24, and 32 (red dots) and spikes at around 1.5 and 1.2 % TS (blue dots). This is partly due to the rather low TS concentration of added PS with values mainly from 0.6 to 1.6 % TS (minimum 0.35 %TS; maximum 3.4 % TS).

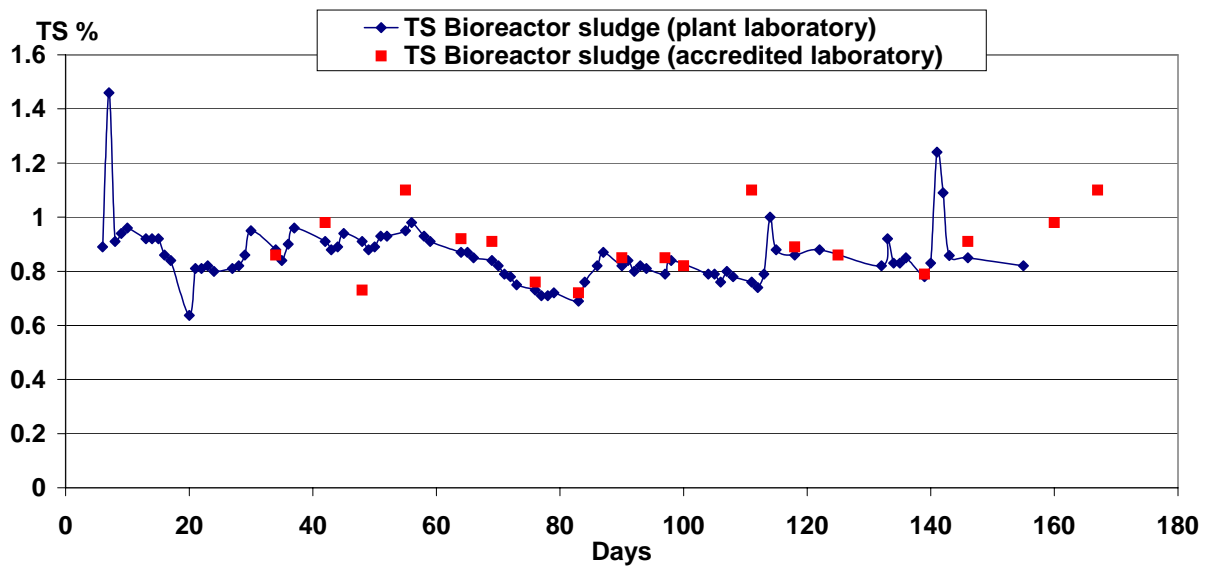


Figure 14: TS concentration for bioreactor sludge over time (from March, 5th, 2007 (day 6) to August, 13th, 2007 (day 167)).

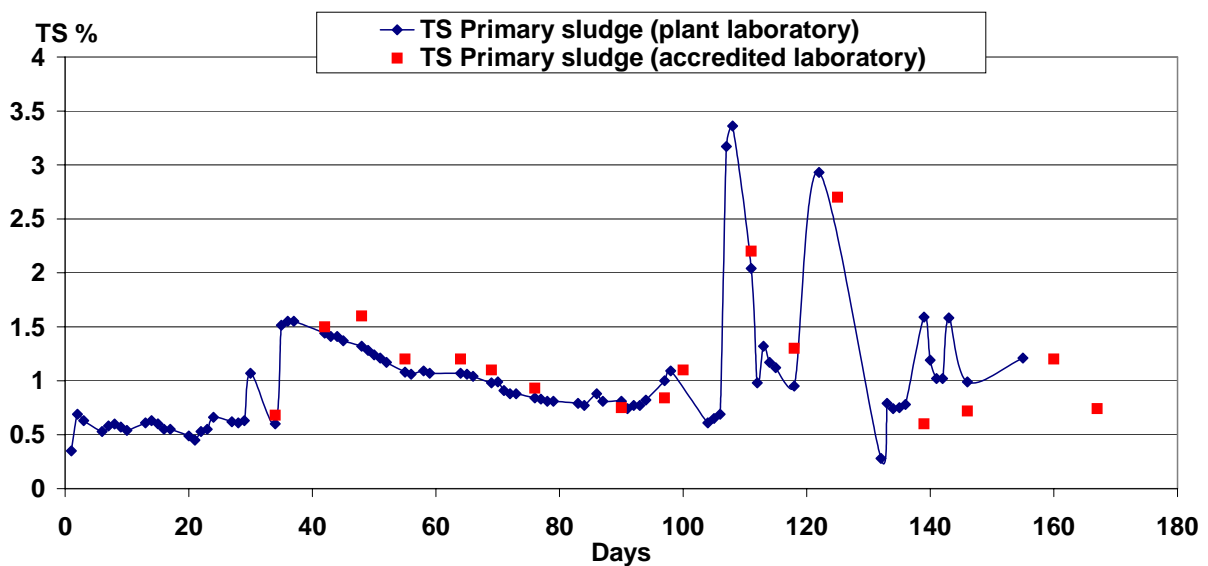


Figure 15: TS concentration for primary sludge over time (from February, 28th, 2007 (day 1) to August, 13th, 2007 (day 167)).

Varying amounts of PS were added in between day 27 and day 56 (week 13 - 16). This might explain the oscillation observed in TS content for bioreactor sludge. It was not possible to introduce a constant volume of PS during this period. At day 83 (week 21), an attempt to decrease the HRT below 10 days was made by adding a predetermined amount of PS every day. One can notice a slow increase in the TS concentration starting on this particular date and continuing for a week.

The results from the main laboratory are rather close to the daily monitoring performed at Sjöstadverket in most of the cases. However, reliability of measures for week 19 (around day 70) is questionable due to indications of lack of accuracy in measurement and analyses during this week.

II. Results related to methane production

II.1 Potential methanogenic activity

An activity test was performed in May 2007 to evaluate the potential activity of current bacteria community within the bioreactor sludge. The sample was taken after a period in which introduction of PS was irregular.

AnoxKaldnes, in Lund (Sweden) was responsible for carrying out this test. The results show a maximum methane production of 58 mL, lower than the 65 mL theoretical value. This maximum production is reached after 11 days, which is 2 days longer than in the previous test (August 2006). Nevertheless, the activity measured is considered satisfactory at the test temperature (20°C) and the response as relatively fast (see Appendix 4). But this test temperature was not representative as an operating temperature within the bioreactor (36°C).

II.2 Calculated gas production

Regarding the concentration of methane in the biogas, the measured percentages varied with a highest value of 77 % during the study. The lowest values are not correlated to any particular problems for the pilot unit. They happened in periods when PS was added and when PS was not added. Therefore it is rather difficult to link these momentary problems to a special phenomenon. It may be a result of air leaking into the system and passing the methane concentration meter.

Due to technical problems detailed in “Material and methods”, the measures of biogas flow are not reliable. Instead, a theoretical methane production as NL CH₄/week was calculated from the calculated value of g COD_{reduced}/week, which was given by mass balances. The cumulative methane volume, both measured and calculated, and the percentages of methane contained in the biogas flow are presented in Figure 16 from February, 28th to August, 13th. In week 32 (days 160 to 166), the closest correlation between measured and calculated methane was found, see Table 6, where 79.4 % of the expected methane production was measured. From Figure 16, it is obvious that the measured methane flow is not accurate and thereby meaningless.

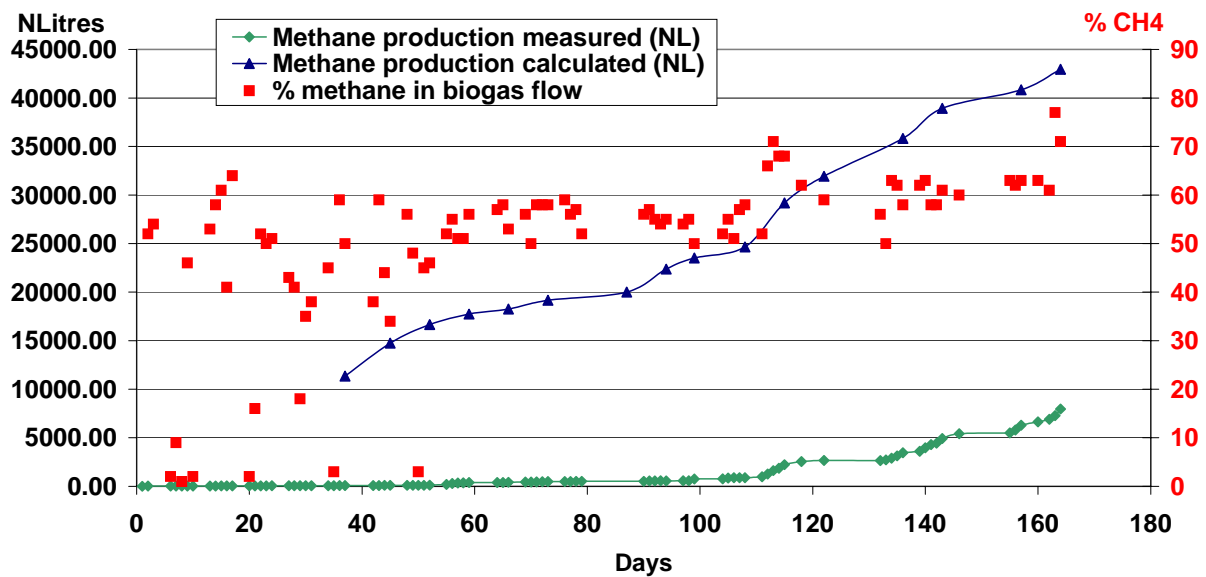


Figure 16: Cumulative measured and calculated methane production (1 atm, 0 °C) and methane concentration within total biogas flow over time (from February, 28th, 2007 (day 1) to August, 13th, 2007 (day 167)).

Around one fourth of the values for the concentration of methane in the biogas were below 50 %. The lowest percentages are not correlated to special operating conditions but one can notice that prior to day 50, the introduction of PS within the bioreactor was not done in a regular way. Since day 52, a significant amount of PS has been added and the methane content in the biogas flow was above or equal to 50 %. No values, except values for calculated methane production, are shown in Figure 16 during week 21 (day 80 - 89) as a result of problems with the biogas flow meter and the methane concentration meter, during week 27 (day 123 - 131) as a result of various problems, and during week 30 (day 147 - 154) probably as a result of a shortage of personnel.

Referring to the maximum percentage for the current bacterial community in the bioreactor, i.e. 58 %, the measures show rather good values, particularly after day 52. Indeed, all the percentages are in between 50 and 77 % from this date. Therefore, by only considering this percentage of methane in the total biogas flow, the results are satisfying. For the period starting on day 55 until the end (in which high PS volumes have been introduced), the methane content varied from 86 % to 133 % of the expected methane content. The reference was the maximum potential methane production determined from AnoxKaldnes activity test (58 % CH₄ of the volume in biogas flow).

For 1 g of COD reduced, 0.350 NL of methane should be produced (see Appendix 6). Reduced COD, which results in methane production, could be calculated by a mass balance according to the formula

$$\text{in} + \text{produced} = \text{out} + \text{accumulated}$$

where reduced can be seen as a negative production in the formula. Both the effluent permeate and the sludge from the bag filter are taken out of the system. The accumulated amount of COD from one week to another can be either positive or negative and is affected

both by the level of liquid in the bioreactor and the concentration of COD in the bioreactor. In COD terms, the formula can be written as

$$\text{COD}_{\text{red}} = \text{COD}_{\text{in}} - (\text{COD}_{\text{eff}} + \text{COD}_{\text{sludge}} + \text{COD}_{\text{acc}})$$

where COD_{red} is the amount of COD used to methane production (reduced) (g/week)

COD_{in} is the COD amount in primary sludge (g/week)

COD_{acc} is the accumulated COD amount within bioreactor (g/week)

COD_{eff} is the COD amount in permeate (effluent) (g/week)

$\text{COD}_{\text{sludge}}$ is the COD amount removed with sludge from bag filter cleaning (g/week)

As an example, for week 16, COD concentrations were 15 000 mg/L for primary sludge and 120 mg/L for permeate. VS percentage in mass for disposed sludge is given by:

$$\text{VS} [\%] = \text{TS} \cdot (1 - \text{GR})$$

Thus, for week 16, VS percentage in mass for disposed sludge is $1.8 \cdot (1 - 0.274) = 1.307 \%$.

The total weight of sludge removed from the system this week was 15.84 kg.

The weight of VS removed from the system could be evaluated to $0.01307 \cdot 15.84 = 0.207$ kg VS removed. An assessment of COD removed can be made by assuming the ratio COD/VS equals to 1.0864 g COD/g VS (from analysis of bioreactor sludge), that is to say $\text{COD}_{\text{sludge}}$ is approximately $0.207 \cdot 1.0864 = 0.225$ kg or 225 g COD removed.

In the beginning of the week, the level in the bioreactor was 65.8 % of 2 metres and the COD concentration was 13 538 mg/L. In the beginning of next week, these values were 64.8 % and 12 000 mg/L. The accumulated volume was $0.475 \cdot 0.475 \cdot 3.14159 \cdot 2 \cdot 64.8/100 - 0.475 \cdot 0.475 \cdot 3.14159 \cdot 2 \cdot 65.8/100 = 0.919 - 0.933 = -0.014 \text{ m}^3$ or -14 litres. The accumulated amount of COD was $0.919 \cdot 12\ 000 - 0.933 \cdot 13\ 538 = -1605$ g COD.

During this period, 270 litres of permeate were removed from the system. The amount of VS of the primary sludge multiplied by the degree of degradation in the reactor was calculated to 1.46 litres, which equals the reduced volume of VS in the reactor. The influent volume of primary sludge is $V_{\text{primary sludge}} = V_{\text{permeate}} + V_{\text{sludge}} + V_{\text{accumulated}} - V_{\text{produced}} = V_{\text{permeate}} + V_{\text{sludge}} + V_{\text{accumulated}} + V_{\text{reduced}} = 270 + 15.84 - 14 + 1.46 = 273$ litres. The amount of COD reduced is then:

$$\begin{aligned} \text{COD}_{\text{red}} &= \text{COD}_{\text{in}} - (\text{COD}_{\text{eff}} + \text{COD}_{\text{sludge}} + \text{COD}_{\text{acc}}) \\ \text{COD}_{\text{red}} &= 15.00 \text{ g/L} \cdot 273 \text{ L} - (0.12 \text{ g/L} \cdot 270 \text{ L} + 225 \text{ g} - 1605 \text{ g}) \\ \text{COD}_{\text{red}} &= 5444.8 \text{ g} \end{aligned}$$

The theoretical volume of produced methane according to Appendix 6 is then:

$$V_{\text{methane}} = 0.350 \text{ NL/g COD} \cdot 5444.8 \text{ g COD} \approx 1907 \text{ NL}$$

The volume of methane as normal litres for this week was 21.17 NL CH_4 calculated to normal litres from the measured volume 22.22 L CH_4 . This means that only 1.1 % of the theoretical methane production was actually measured during this week.

Therefore, by considering all the results provided by the main laboratory and by applying the same reasoning to the entire evaluation period, Table 6 and Table 11 could be presented. Details on calculations for other weeks can be found in Appendix 5.

Table 6: Theoretically calculated and measured methane volumes in NL/week.

| Week | Calculated CH ₄ volume (NL) | Measured CH ₄ volume (NL) | Methane measured with respect to calculated volume (%) | Lowest level in the reactor during the week (%) | Average level in the reactor (%) |
|------|--|--------------------------------------|--|---|----------------------------------|
| 8 | nva | nva | nva | 50.4 | 59.3 |
| 9 | nva | 10.94 | nva | 52.8 | 60.6 |
| 10 | nva | 3.83 | nva | 51.0 | 58.0 |
| 11 | nva | 15.54 | nva | 50.5 | 62.4 |
| 12 | nva | 15.45 | nva | 57.5 | 65.4 |
| 13 | nva | 11.35 | nva | 55.7 | 64.0 |
| 14 | 11346 | 19.46 | 0.17 | 55.9 | 64.4 |
| 15 | 3398 | 15.52 | 0.46 | 57.8 | 65.9 |
| 16 | 1907 | 21.17 | 1.11 | 55.6 | 65.4 |
| 17 | 1084 | 281.87 | 26.00 | 55.7 | 63.8 |
| 18 | 520 | 25.27 | 4.86 | 57.3 | 63.0 |
| 19 | 909 | 69.40 | 7.63 | 56.7 | 66.9 |
| 20 | nva | 22.37 | nva | 63.5 | 70.6 |
| 21 | 850 | nva | nva | 53.1 | 63.4 |
| 22 | 2362 | 59.13 | 2.50 | 55.7 | 67.7 |
| 23 | 1145 | 191.13 | 16.69 | 59.6 | 67.2 |
| 24 | 1128 | 142.89 | 12.67 | 58.5 | 64.8 |
| 25 | 4543 | 1312.42 | 28.89 | 57.4 | 70.0 |
| 26 | 2735 | 426.01 | 15.58 | 57.3 | 69.4 |
| 27 | nva | 0 | nva | 59.1 | 68.8 |
| 28 | 3915 | 774.94 | 19.79 | 55.1 | 70.4 |
| 29 | 3085 | 1474.05 | 47.78 | 59.0 | 69.2 |
| 30 | nva | 493.62 | nva | 66.0 | 68.4 |
| 31 | 1921 | 876.00 | 45.60 | 64.1 | 67.5 |
| 32 | 2097 | 1665.06 | 79.39 | 50.2 | 67.3 |
| 33 | nva | nva | nva | 66.0 | 66.2 |
| mean | 2684 | 360.34 | 20.61 | nva | 65.8 |

nva = no value available

These very low recovering values are due to serious problems in the measuring system (see Material and Methods for details). A leakage could explain this poor volume recovery. To avoid a leakage from points close to the axle, the level of liquid in the bioreactor had to be at

least 70 % (of 2 metres). From the values for the lowest level in the reactor during the week in Table 6 above, it is obvious that this was not the case during the time of investigation, although the average level in the reactor reached 70 % during some weeks.

In Table 7 below, volumes of different fractions are shown. The volume reduced is calculated from the volume of influent VS that is reduced according to the degree of degradation, see Table 10.

Table 7: Volumes of different fractions in litres (L).

| Week | Influent primary sludge (L) | Reduced volume of sludge (L) | Effluent permeate (L) | Effluent sludge from bag filter (L) | Volume accumulated within bioreactor (L) |
|------|-----------------------------|------------------------------|-----------------------|-------------------------------------|--|
| 8 | 625 | nva | 551 | 0 | 74 |
| 9 | 2496 | nva | 2526 | 0 | -30 |
| 10 | 932 | nva | 965 | 0 | -33 |
| 11 | 486 | nva | 368 | 0 | 118 |
| 12 | 1330 | nva | 1329 | 0.57 | 0 |
| 13 | 430 | 1.38 | 461 | 1.52 | -34 |
| 14 | 1271 | 11.65 | 1238 | 1.34 | 20 |
| 15 | 372 | 3.55 | 359 | 1.00 | 8.5 |
| 16 | 273 | 1.46 | 270 | 15.84 | -14. |
| 17 | 178 | 1.05 | 140 | 64.02 | -27 |
| 18 | 60 | 0.30 | 40 | 16.70 | 2.8 |
| 19 | 189 | 0.74 | 60 | 31.50 | 96 |
| 20 | 68 | nva | 55 | 0 | 13 |
| 21 | 443 | 1.74 | 517 | 53.60 | -129 |
| 22 | 888 | 3.65 | 722 | 71.33 | 91 |
| 23 | 383 | 2.47 | 368 | 55.06 | -43 |
| 24 | 98 | 1.24 | 86 | 15.35 | -4.3 |
| 25 | 862 | 2.96 | 731 | 55.90 | 72 |
| 26 | 263 | 1.12 | 253 | 25.04 | -16 |
| 27 | 0 | nva | nva | 0 | 0 |
| 28 | 1015 | 3.24 | 956 | 44.50 | 11 |
| 29 | 813 | 2.17 | 783 | 43.68 | -16 |
| 30 | 174 | nva | 166 | 12.92 | -5.7 |
| 31 | 446 | 0.30 | 459 | 16.61 | -30 |
| 32 | 1033 | 1.61 | 999 | 25.90 | 7.1 |
| 33 | nva | nva | nva | 0 | -4.3 |
| mean | 630 | 2.39 | 600 | 29.07 | 5.4 |

nva = no value available

II.3 VS reduction of primary sludge in the bioreactor

In the same way as for COD, the VS reduced could be calculated according to the formula

$$\text{in} + \text{produced} = \text{out} + \text{accumulated}$$

where reduced can be seen as a negative production in the formula. Both the effluent permeate and the sludge from the bag filter are taken out of the system, but in this case TS_{permeate} is zero thereby giving no VS in the permeate either. The accumulated amount of VS from one week to another can be either positive or negative and is affected both by the level of liquid in the bioreactor and the concentration of VS in the bioreactor at the beginning and at the end of the week evaluated. In VS terms, the formula can be written as

$$VS_{\text{in}} + VS_{\text{produced}} = VS_{\text{permeate}} + VS_{\text{sludge}} + VS_{\text{accumulated}}$$

or

$$VS_{\text{red}} = VS_{\text{in}} - (VS_{\text{sludge}} + VS_{\text{acc}})$$

The degree of reduction is defined by the ratio:

$$\text{Degree of reduction} = \frac{VS_{\text{red}}}{VS_{\text{in}}} = \frac{VS_{\text{in}} - VS_{\text{sludge}} - VS_{\text{acc}}}{VS_{\text{in}}}$$

where VS_{red} is the amount of VS reduced (kg)

VS_{in} is the amount of VS introduced as primary sludge (kg)

VS_{sludge} is the amount of VS removed from the system as sludge (kg)

VS_{acc} is the amount of VS accumulated in the reactor (kg)

Using the results from the main laboratory, VS_{in} is calculated as:

$$VS_{\text{in}} = Q_{\text{in}} \cdot TS \cdot (1 - GR)$$

VS_{sludge} is calculated in the same way, except that Q_{out} , TS and GR for the disposed sludge are considered. VS_{acc} is found by considering the variation within the bioreactor sludge in between two following weeks. All the results are shown in Table 8.

Table 8: VS of different fractions in kilogrammes (kg).

| Week | VS_{in} primary sludge (kg) | VS_{red} in bioreactor (kg) | VS_{out} as sludge (kg) | VS_{sac} in bioreactor (kg) | VS_{degree of reduction (%)} |
|-------------|--|--|--|--|---|
| 8 | nva | nva | 0 | nva | nva |
| 9 | nva | nva | 0 | nva | nva |
| 10 | nva | nva | 0 | nva | nva |
| 11 | nva | nva | 0 | nva | nva |
| 12 | nva | nva | nva | nva | nva |
| 13 | 2.36 | nva | nva | nva | nva |
| 14 | 16.70 | nva | nva | 1.21 | nva |
| 15 | 5.15 | nva | nva | -1.64 | nva |
| 16 | 2.74 | -0.05 | 0.21 | 2.59 | -1.92 |
| 17 | 1.79 | 2.44 | 0.88 | -1.53 | 136.4 |
| 18 | 0.54 | 0.42 | 0.17 | -0.04 | 77.4 |
| 19 | 1.41 | 1.86 | 0.10 | -0.54 | 131.5 |
| 20 | nva | nva | nva | -0.36 | nva |
| 21 | 2.87 | 1.28 | 0.95 | 0.64 | 44.5 |
| 22 | 6.35 | 4.12 | 1.70 | 0.53 | 64.9 |
| 23 | 3.74 | 2.99 | 1.04 | -0.29 | 79.9 |
| 24 | 1.92 | -0.21 | 0.19 | 1.93 | -11.0 |
| 25 | 8.62 | 9.11 | 0.92 | -1.41 | 105.7 |
| 26 | 5.18 | 5.08 | 0.47 | -0.37 | 98.2 |
| 27 | 0 | 0 | 0 | 0 | nva |
| 28 | 5.19 | 5.10 | 0.42 | -0.33 | 98.3 |
| 29 | 4.82 | 2.92 | 0.89 | 1.01 | 60.6 |
| 30 | nva | nva | nva | 0.04 | nva |
| 31 | 3.89 | 3.39 | 0.38 | 0.12 | 87.3 |
| 32 | 5.59 | 4.63 | 0.63 | 0.32 | 82.8 |
| 33 | nva | nva | nva | nva | nva |
| mean | 4.64 | 2.87 | 0.64 | 0.10 | 75.3 |

nva = no value available

Some results are clearly unreliable. They correspond to analyses made during weeks when the pilot unit did not operate for a sufficient time to provide representative samples. This point will be discussed in the last part of this chapter.

One can notice the variability of reduction percentages, from -11 to 136 % (average value 75.3 %). Results from week number 21, 22, 23, 28, 29, 31, and 32 seem more reliable, as the pilot unit was operating for a sufficient time during these weeks. A mass balance of the amount of VS over the bioreactor is presented in Figure 17.

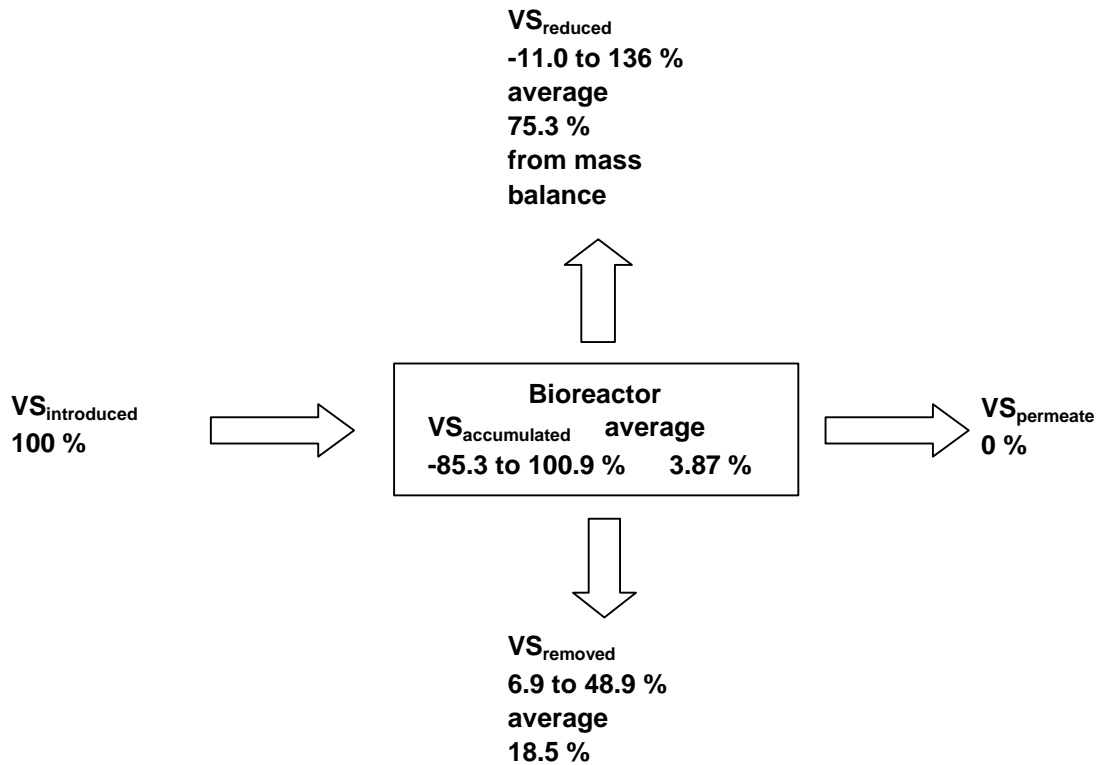


Figure 17: Mass balance of VS over the bioreactor.

II.4 Specific methane production corresponding to COD and VS introduced in the system

Referring to the research plan, one of the goals of this study was to evaluate the gas production, more specifically the methane production, with respect to added VS (NL CH₄/g VS_{in}). This evaluation could be made from the previous results. The corresponding specific methane production with respect to added COD (NL CH₄/g COD_{in}) is also presented in Table 9.

The produced volume of methane as NL is calculated from the reduced amount of COD for each week times the factor 0.350 NL CH₄/g COD (see Appendix 6 and Appendix 5), which is the maximum theoretical value. The value of NL CH₄ (see Table 6) is then divided by the amount of COD and VS, respectively, added to the system as g/week with the primary sludge (see Table 8 and Table 11). If the primary sludge has a quotient of 1.482 g COD/g VS (from laboratory analysis of the primary sludge), the maximum possible gas production would be 0.519 NL CH₄ / g VS_{in}, (0.350*1.482). If some values with COD calculated from TOC/COD quotients for PS are included in the quotient used, the highest possible gas production would be 0.350 NL CH₄/g COD * 1.6669 g COD/g VS = 0.584 NL CH₄ / g VS_{in}. The specific methane productions are given in Table 9.

Table 9: Methane production related to COD and VS load (from primary sludge).

| Week | NL CH ₄ / g COD _{in} | NL CH ₄ / g VS _{in} |
|------|--|---|
| 8 | nva | nva |
| 9 | nva | nva |
| 10 | nva | nva |
| 11 | nva | nva |
| 12 | nva | nva |
| 13 | nva | nva |
| 14 | 0.331 | 0.679 |
| 15 | 0.345 | 0.660 |
| 16 | 0.465 | 0.696 |
| 17 | 0.380 | 0.605 |
| 18 | 0.725 | 0.959 |
| 19 | 0.438 | 0.643 |
| 20 | nva | nva |
| 21 | 0.192 | 0.296 |
| 22 | 0.274 | 0.372 |
| 23 | 0.230 | 0.306 |
| 24 | 0.397 | 0.588 |
| 25 | 0.310 | 0.527 |
| 26 | 0.346 | 0.528 |
| 27 | nva | nva |
| 28 | 0.367 | 0.754 |
| 29 | 0.262 | 0.641 |
| 30 | nva | nva |
| 31 | 0.269 | 0.494 |
| 32 | 0.203 | 0.375 |
| 33 | nva | nva |
| mean | 0.346 | 0.570 |

nva = no value available

The specific biogas production, expressed per amount of COD introduced to the bioreactor, varied from 0.192 to 0.725 NL CH₄ / g COD_{in} with an average value of 0.346 NL CH₄ / g COD_{in}. This could be compared with the maximum theoretical value of 0.350 NL CH₄ / g COD, which gives that 98.8 % of the COD introduced was converted to methane. The specific gas production, expressed per amount of VS introduced to the bioreactor, varied from 0.296 to 0.959 NL CH₄ / g VS_{in} with an average value of 0.570 NL CH₄ / g VS_{in}. This could be compared with the maximum theoretical value of 0.519 NL CH₄ / g VS, which gives that over 100 % of the VS introduced was converted to methane (110 %), which is not possible. Compared with the value 0.584 NL CH₄ / g VS, 97.7 % of the added VS was converted to methane. It is, however, doubtful if TOC analysis can be used in these calculations.

Regarding the organic material, from Figure 18 it is shown that 98.8 % of the amount of COD is reduced (median value 96.4 %), from Figure 17 it is shown that 75.3 % of the amount of VS is reduced (median value 81.3 %), and from Figure 20 it is shown that 91.6 % of the amount of TOC is reduced (median value 91.3 %). The value for COD is consistent with the value found in the discussion of the specific biogas production above. For VS, the values differ. This is probably due to the transformation factor 1.482 g COD/g VS for primary sludge, which probably not applies for all samples of primary sludge taken in this investigation. The factor 1.6669 g COD/g VS for primary sludge is consistent with the value 97.7 % reduction of VS introduced to the bioreactor, but the factor is questionable. The median value 81.3 % is closer to the values for COD and TOC. For TOC, the value 91.6 % reduction seems to be more in agreement with the value 98.8 % reduction of COD. The differences are explained by the fact that COD, VS, and TOC all are based on different types of analysis. Overall, the reduction of organic material, which produces methane gas, is high according to average values although the values greatly fluctuate. The retention time is, however, high in the system as a result of the problems with continuous operation. With an expected HRT of less than 10 days instead of 24.6 days, the reduction of organic material might have been lower.

Referring to VS_{in} , three groups of results seem to appear in Table 9; one for weeks 14, 15, 16, 28, and 29 with values around 0.68 NL $CH_4/g VS_{in}$, one for weeks 17, 24, 25, and 26 with values around 0.56 NL $CH_4/g VS_{in}$, and one for weeks 21, 22, 23, 31, and 32 with values around 0.35 NL $CH_4/g VS_{in}$. In the same way when interpreting COD_{in} , four groups of results seem to appear; one for weeks 16 and 19 with values around 0.45 NL $CH_4/g COD_{in}$, one for weeks 14, 15, 17, 24, 25, 26, and 28 with values around 0.35 NL $CH_4/g COD_{in}$, one for weeks 22, 29, and 31 with values around 0.27 NL $CH_4/g COD_{in}$, and one for weeks 21, 23, and 32 with values around 0.20 NL $CH_4/g COD_{in}$.

II.5 The maximum organic load rate, degree of degradation, and hydraulic retention time

The term “maximum” is not a proper word, as no evaluation was voluntarily made with different loads. Indeed, estimating the effects on changing load would have required more time, therefore this kind of conclusions could not be drawn.

The expression “maximum” refers to the highest organic load tolerated by the microbial community without any change in their activity. Regarding the experiments performed with the pilot unit, the highest load introduced within the bioreactor was 16.7 kg $VS_{in}/week$, see Table 8, which corresponds to 18.3 g $VS_{in}/(L \cdot week)$, see Table 10, (g VS of primary sludge per L bioreactor volume and week), during week 14. It does not mean that it is the “maximum” organic load that could be applied to the system. More experiments are necessary to determine this point. The average value for the load was 4.6 kg $VS_{in}/week$, which corresponds to 4.9 g $VS_{in}/(L \cdot week)$, (median values 3.9 kg $VS_{in}/week$ and 4.1 g $VS_{in}/(L \cdot week)$). The conversion, i.e. the degree of degradation was 50.9 % as an average value or 57.5 % as a median value. As a result of previously mentioned problems, the bioreactor was operated intermittent not continuously and, hence, the hydraulic retention time varied great. An operation time of 30 minutes per day obviously could not give any controlled HRT. The intention from the beginning, however, was that keep the HRT below 10 days. This was also accomplished during the few minutes of operation that were achieved. In Table 10, the HRT and degree of degradation are given as average values for each week. An average

value of 24.6 days (median value 14.5 days) was accomplished during the entire period of investigation.

Table 10: Organic load, degree of degradation, and HRT.

| Week | g VS _{in} / (L · week) | Degree of degradation (%) | Hydraulic retention time (d) |
|------|---------------------------------|---------------------------|------------------------------|
| 8 | nva | nva | 9.4 |
| 9 | nva | nva | 2.4 |
| 10 | nva | nva | 6.2 |
| 11 | nva | nva | 12.8 |
| 12 | nva | nva | 4.9 |
| 13 | 2.60 | 58.3 | 14.8 |
| 14 | 18.29 | 69.8 | 5.0 |
| 15 | 5.52 | 69.0 | 17.6 |
| 16 | 2.96 | 53.3 | 23.8 |
| 17 | 1.98 | 58.7 | 35.5 |
| 18 | 0.61 | 54.7 | 104.5 |
| 19 | 1.49 | 52.4 | 35.2 |
| 20 | nva | nva | 102.8 |
| 21 | 3.19 | 60.8 | 14.2 |
| 22 | 6.61 | 57.5 | 7.8 |
| 23 | 3.93 | 65.9 | 17.4 |
| 24 | 2.08 | 64.8 | 65.7 |
| 25 | 8.68 | 34.4 | 8.1 |
| 26 | 5.27 | 21.7 | 26.1 |
| 27 | no feed | no feed | no feed |
| 28 | 5.21 | 62.4 | 6.9 |
| 29 | 4.91 | 45.0 | 8.4 |
| 30 | nva | nva | 39.1 |
| 31 | 4.06 | 7.6 | 15.0 |
| 32 | 5.86 | 28.9 | 6.5 |
| 33 | nva | nva | nva |
| mean | 4.90 | 50.9 | 24.6 |

nva = no value available

The degree of degradation in the bioreactor was calculated as

$$\text{Degradation degree } [\%] = \left(1 - \frac{\text{GR}_{\text{in}} * \text{VS}_{\text{out}}}{\text{GR}_{\text{out}} * \text{VS}_{\text{in}}}\right) * 100 \quad (\text{in}=\text{primary sludge, out}=\text{reactor sludge})$$

where GR represents the inorganic part of TS and VS represents the organic part of TS.

III. Results regarding organic issues

In addition of biogas production efficiency, monitoring of organic parameters was performed as well. Analyses were focused on Nitrogen and Phosphorus under various forms. The organic content was analysed as Chemical Oxygen Demand (COD), Total Organic Carbon (TOC), and Volatile Solids (VS).

III.1 COD reduction

COD analyses were both performed by the main laboratory (SS 028142-2) from weekly mixed samples, and analysed directly at Sjöstadsverket once a week. Samples of primary sludge, reactor sludge and permeate were analysed, in order to notice changes at different stages of the anaerobic process. Disposed concentrated sludge was analysed for TS and VS. COD for the disposed concentrated sludge was calculated from the factor 1.0864 g COD/g VS from reactor sludge. The degree of reduction is calculated from mass balances according to Appendix 5 and the formula:

$$\text{Degree of reduction} = \frac{\text{COD}_{\text{reduced}}}{\text{COD}_{\text{in}}} = \frac{\text{COD}_{\text{in}} - \text{COD}_{\text{permeate}} - \text{COD}_{\text{sludge}} - \text{COD}_{\text{accumulated}}}{\text{COD}_{\text{in}}}$$

Table 11: COD of different fractions in grammes (g).

| Week | COD _{in} (g) | COD _{reduced} (g) [calculated] | COD _{permeate} (g) | COD _{out} (g) [disposed sludge] | COD _{accumulated} (g) [in reactor] | COD _{degree} of reduction (%) |
|------|--------------------------|---|--------------------------------|--|--|--|
| 8 | nva | nva | nva | 0 | nva | nva |
| 9 | nva | nva | nva | 0 | nva | nva |
| 10 | nva | nva | nva | 0 | nva | nva |
| 11 | nva | nva | nva | 0 | nva | nva |
| 12 | nva | nva | nva | nva | nva | nva |
| 13 | 3224 | nva | 61.7 | nva | nva | nva |
| 14 | 34310 | 32396 | 231.9 | nva | 1682 | 94.4 |
| 15 | 9861 | 9702 | 44.2 | nva | 115 | 98.4 |
| 16 | 4097 | 5445 | 32.4 | 225 | -1605 | 132.9 |
| 17 | 2850 | 3095 | 18.2 | 951 | -1215 | 108.6 |
| 18 | 718 | 1486 | 4.40 | 180 | -953 | 207.0 |
| 19 | 2075 | 2596 | 4.32 | 105 | -631 | 125.1 |
| 20 | nva | nva | nva | 0 | -396 | |
| 21 | 4433 | 2426 | 56.9 | 1032 | 918 | 54.7 |
| 22 | 8611 | 6745 | 79.4 | 1845 | -58 | 78.3 |
| 23 | 4979 | 3269 | 40.5 | 1129 | 540 | 65.7 |
| 24 | 2842 | 3220 | 4.45 | 211 | -594 | 113.3 |
| 25 | 14650 | 12971 | 102.3 | 997 | 581 | 88.5 |
| 26 | 7904 | 7809 | 25.3 | 507 | -438 | 98.8 |
| 27 | 0 | 0 | 0 | 0 | 0 | |
| 28 | 10655 | 11179 | 89.5 | 458 | -1071 | 104.9 |
| 29 | 11785 | 8808 | 106.8 | 969 | 1901 | 74.7 |
| 30 | nva | nva | nva | | 400 | |
| 31 | 7138 | 5485 | 46.7 | 408 | 1199 | 76.8 |
| 32 | 10330 | 5988 | 130.9 | 690 | 3521 | 58.0 |
| 33 | nva | nva | nva | 0 | nva | nva |
| mean | 8262 | 7664 | 63.5 | 693 | 216 | 98.8 |

nva = no value available

From the results in Table 11, one can notice a high but fluctuating percentage of COD reduction with an average value of 98.8 % for the entire study. The percentage of organic matter reduced to form methane changes depending on the weeks considered, with respect to initial amount introduced within the bioreactor, as shown in Table 11 and Figure 18, where the reduction of the amount of COD varies between 55 and 207 %. Values higher than 100 % refers to weeks with increasing amount of COD in the reactor (negative accumulation), see Table 11. As can also be seen in Figure 18, 16.0 % reduced COD from measurements of methane gas flows is not a realistic value. This is due to the technical problems with leakage

discussed earlier. Calculating directly from the mass balance, the more realistic value of 98.8 % COD reduced is received. The efficiency of this anaerobic process could be considered as satisfactory.

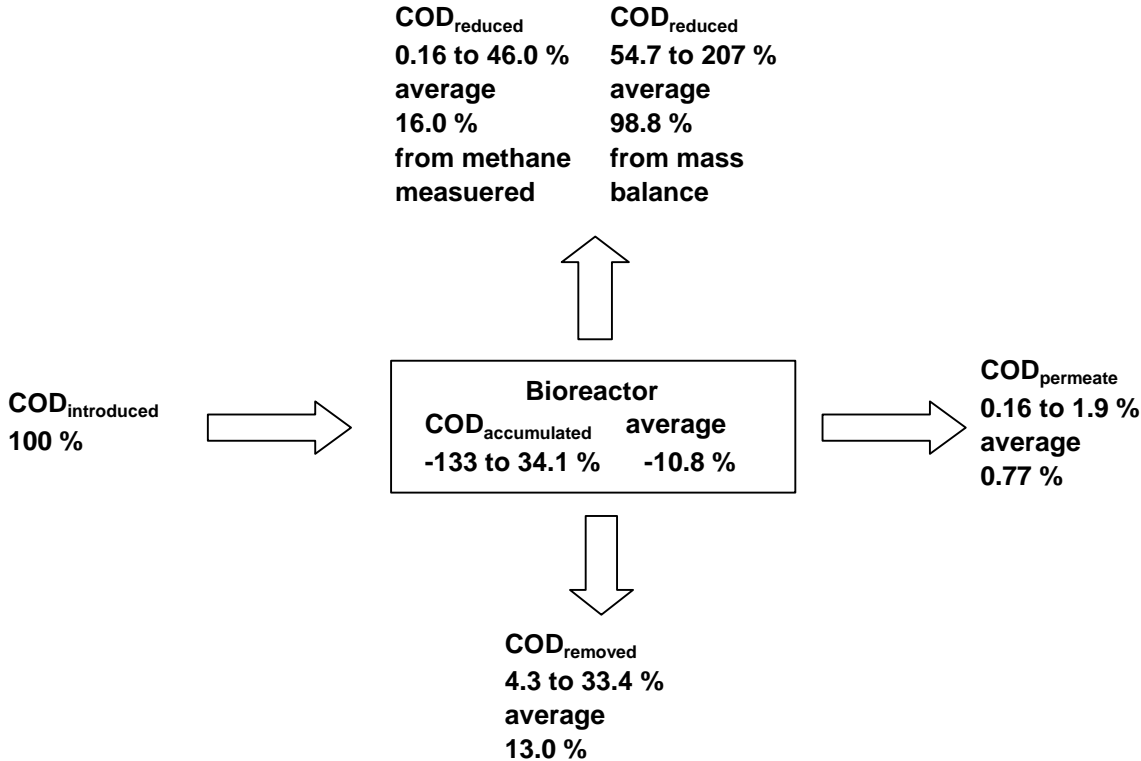


Figure 18: Mass balance of COD over the bioreactor.

COD removed with sludge from the bag filter seems to be a major loss of COD, but the highest percentages concerns weeks when the pilot unit was not operating in a proper way. Therefore, these high values (up to 33.4 % for week 17) could have been expected. The accumulation of COD in the bioreactor was rather high too, with values varying from -133 % (decrease) to 34.1 % (increase) and an average value of -10.8 %. COD within permeate is low (maximum 1.91 %), which is rather satisfying for this final effluent.

III.2 TOC reduction

With the same principles as for COD, TOC was monitored during the entire study. Analyses were also carried out by the main laboratory (method SS-EN 1484-1), from weekly mixed samples. These samples were the same as those used for COD analyses.

The degree of reduction for TOC was calculated according to the formula:

$$\text{Degree of reduction} = \frac{\text{TOC}_{\text{reduced}}}{\text{TOC}_{\text{in}}} = \frac{\text{TOC}_{\text{in}} - \text{TOC}_{\text{permeate}} - \text{TOC}_{\text{sludge}} - \text{TOC}_{\text{accumulated}}}{\text{TOC}_{\text{in}}}$$

Figure 19 illustrates the concentration of TOC for primary sludge, bioreactor sludge, and permeate. As could be seen, the concentration of TOC in the permeate is very low, with a

highest value of 70 mg/L during week 14 corresponding to 0.4 % to 3.6 % of the amount of TOC in influent primary sludge. A mass balance of the amount of TOC is presented in Figure 20. The reduction of TOC varied between -54.8 % and 344 % with an average value of 91.6 %, which suggests a functioning but not stable process. Negative values refer to weeks with a decrease of the amount of TOC within the reactor (negative accumulation).

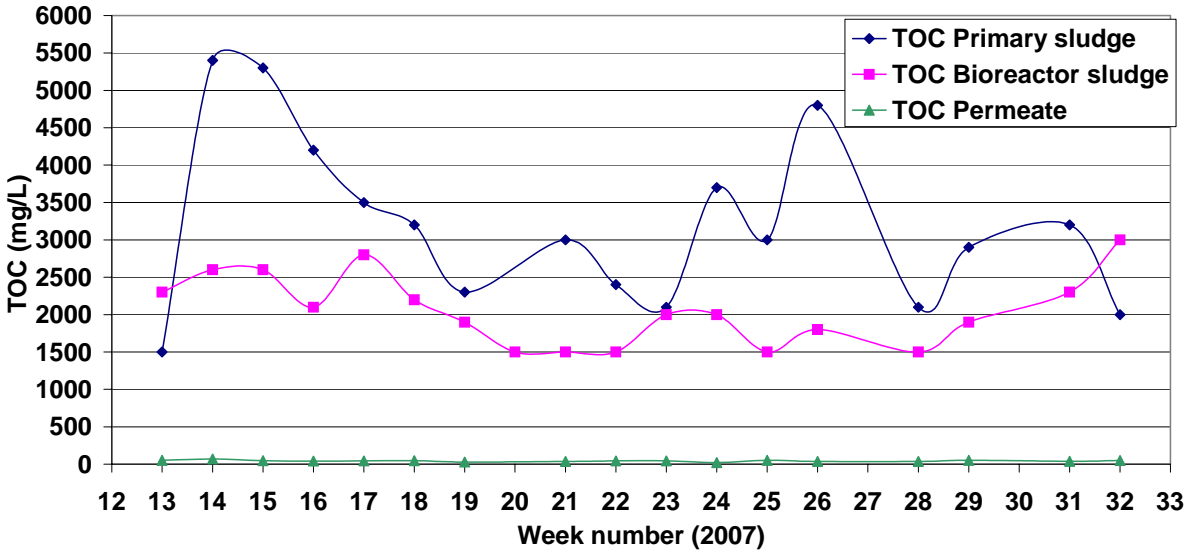


Figure 19: TOC concentration in primary sludge, bioreactor sludge and permeate (from March, 26th, 2007 to August, 12th, 2007).

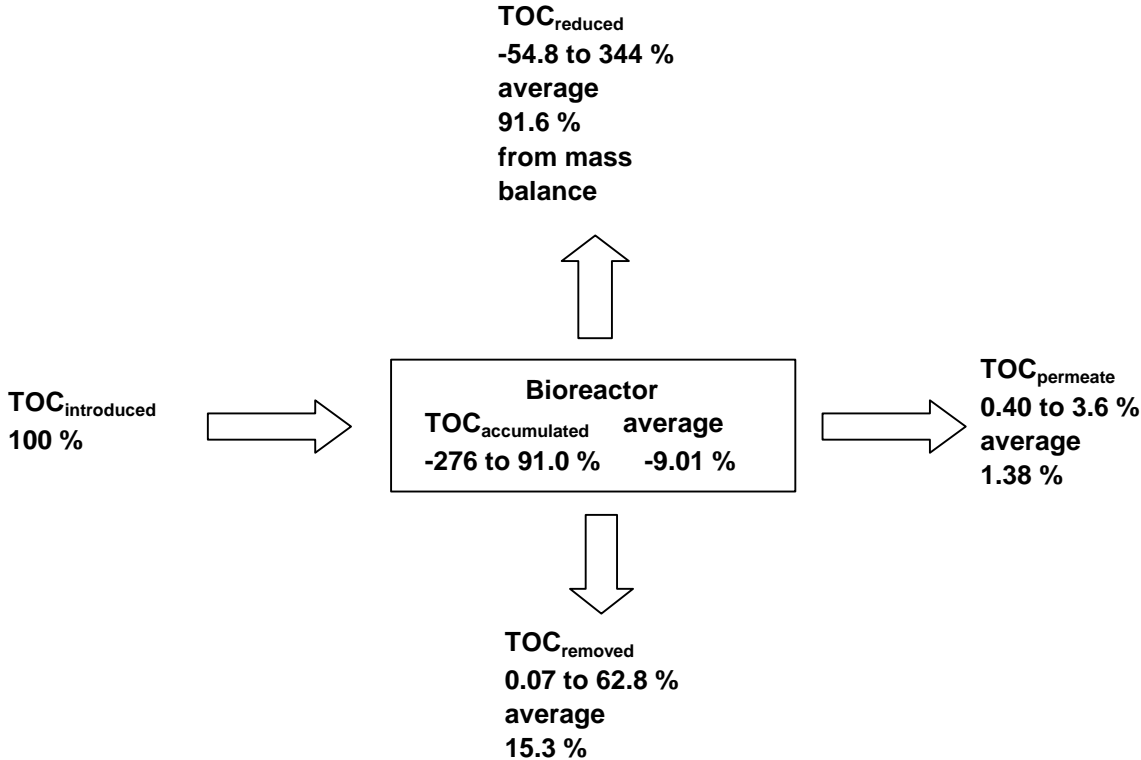


Figure 20: Mass balance of TOC over the bioreactor.

III.3 Nitrogen monitoring

Nitrogen was analyzed as Kjeldahl Nitrogen (Kjeld-N) [methods AN 300 / AN 3503], and as nitrogen nitrate (NO₃-N) [methods SS EN ISO 13395 / AN 5201] for primary sludge, bioreactor sludge and permeate. Additional analyses were performed for both reactor sludge and permeate, for example ammonium nitrogen (NH₄-N) [method AN 300]. Total Nitrogen (Tot-N) was calculated from Kjeld-N, nitrates and nitrites. Concentrations of these parameters were determined by the main laboratory, based on weekly mixed samples. Once a week, NH₄-N and NO₃-N were checked by carrying out analyses at Sjöstadverket on the spectrophotometer Dr.Lange XION 500 and LCK reagents, see Appendix 3. These results matched the values given by the main laboratory.

By reviewing the results, one can notice that Tot-N was exactly the same as Kjeld-N. Tot-N was expressed as the sum of Kjeld-N and NO₃-N, and due to the low concentration of NO₃-N (below 0.5 mg/L), Kjeld-N was the main component of the Total Nitrogen. Figure 21 illustrates Kjeldahl Nitrogen changes for primary sludge, bioreactor sludge and permeate. The percentage of total N in permeate, ($\frac{\text{g total } N_{\text{permeate}}}{\text{g total } N_{\text{primary sludge}}} * 100 \%$), was in the range from 8.7 % to 76.1 % (outlier 98.3 %) with an average value of 42.5 % (39.0 % without outlier). One can observe that concentrations within the bioreactor were nearly always higher than in PS. This situation could come from a possible accumulation, as a low amount of sludge was removed per week (mainly around 15 – 55 kg) while PS was added over time.

Percentages of NH₄-N within Kjeld-N are really different, if reactor sludge and permeate analyses are compared. Indeed, in reactor sludge ammonium represents 28.8 to 48.8 % of Kjeldahl Nitrogen (average value 37.9 %), whereas it is 85.7 to 100 % in permeate flow (average value 97.0 %). This variation could be explained by the ability of the membranes to keep organic Nitrogen within the concentrate. Only ammonium ions might be able to pass through the membranes. In primary sludge, the percentages of NH₄-N within Kjeld-N varies between 2.2 and 21 % (average value 10 %), which means that most of the nitrogen is bound into organic compounds. As could be seen in Figure 22, the concentration of nitrate nitrogen is very low, with values from 0.4 to 1.2 mg NO₃-N/L. The concentrations of ammonium nitrogen in primary sludge lies between 7 and 84 mg NH₄-N/L, in bioreactor sludge between 95 and 250 mg NH₄-N/L, and in permeate between 90 (58 as an outlier) and 220 mg NH₄-N/L. The concentration of ammonium nitrogen was around 50 mg/L lower in the permeate than in the reactor sludge during the study.

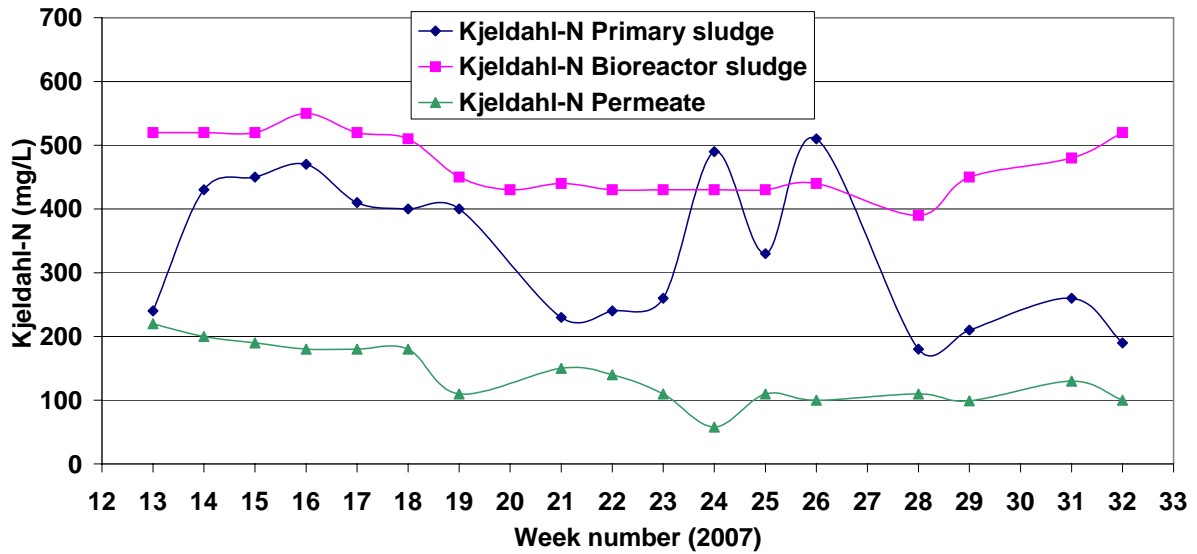


Figure 21: Kjeldahl Nitrogen concentration in primary sludge, bioreactor sludge and permeate (from March, 26th, 2007 to August, 12th, 2007).

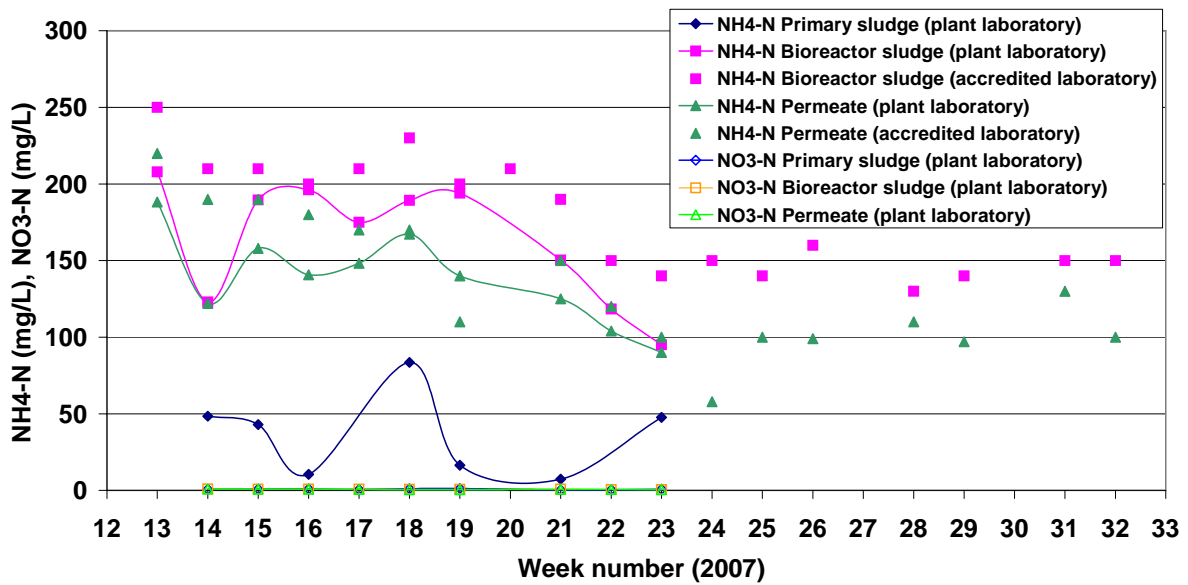


Figure 22: Ammonium Nitrogen and Nitrate Nitrogen concentration in primary sludge, bioreactor sludge and permeate (from March, 26th, 2007 to August, 12th, 2007).

III.4 Phosphorus monitoring

Phosphorus was analyzed during the entire study, from weekly mixed samples. The main laboratory only checked total phosphorus (Tot-P) for primary sludge, bioreactor sludge and permeate. Phosphate concentrations ($\text{PO}_4\text{-P}$) were measured from week 13, in order to monitor this particular parameter. Results are illustrated in Figure 23.

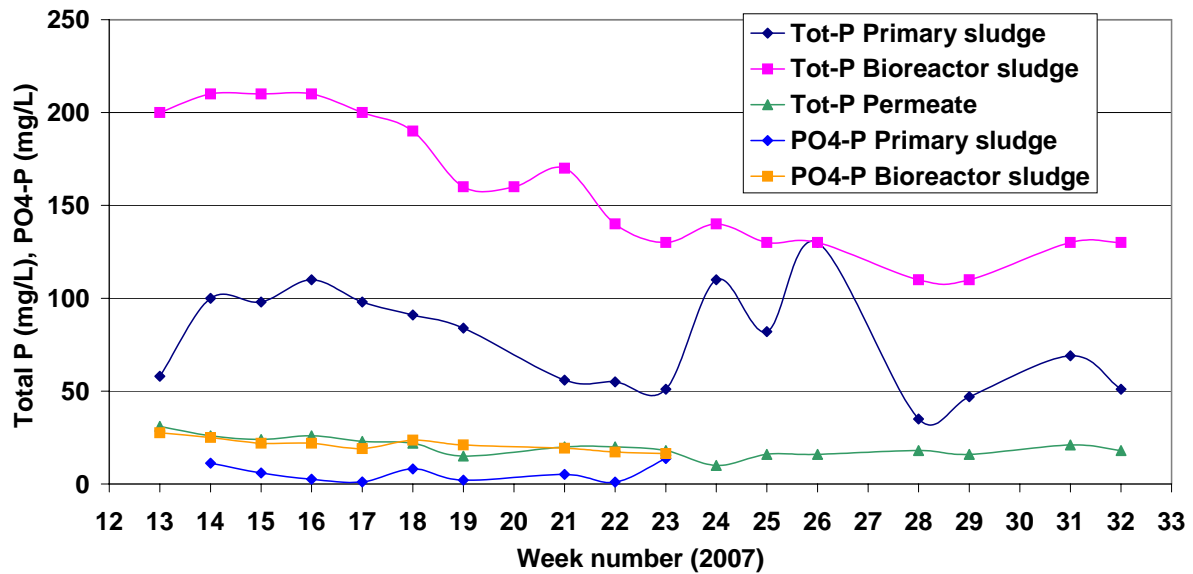


Figure 23: Total phosphorous and phosphate phosphorous concentration in primary sludge, bioreactor sludge and permeate (from March, 26th, 2007 to August, 12th, 2007).

The concentrations are nearly always higher within bioreactor sludge than in PS, for both Tot-P and PO₄-P. Phosphate ions represent between 1.2 and 26.9 % (average value 7.8 %) of Total Phosphorus in PS. One can notice that despite variations in Tot-P concentrations for reactor sludge, phosphate ions remain stable as they represent between 10 and 14 % (average value 12 %) of the total amount of phosphorus within the bioreactor. In the permeate, the concentration of total P nearly equals the concentration of PO₄-P as TS was considered to be 0 mg/L. The percentage of total P in permeate ($\frac{\text{g total P}_{\text{permeate}}}{\text{g total P}_{\text{primary sludge}}} \times 100 \%$) was in the range of 5.7 % to 57.3 % with an average value of 26.9 %. However, several groups of values appear; one with the percentage of 23-25 % (weeks 14, 15, and 16), one of 6-18 % (weeks 17, 18, and 19), one of 30-42 % (weeks 21, 22, and 23), one of 8-17 % (weeks 24, 25, and 26), and one of 31-34 % (weeks 29, 31, and 32). The efficiency of the membranes should be taken into account here, regarding their ability to let a certain amount of phosphorus to pass through. Indeed, phosphorus could be found in the forms of precipitate accumulated on membrane surface for example.

IV. Discussion about the reliability of the results

The first point deals with the way the samples were taken. The pilot unit was designed to enable permeate samples to be taken during the entire period of operation. The final sample is then representative and corresponds to a large volume of permeate taken from the permeate flow. This is not the case for other samples (bioreactor and primary sludge). It was difficult to achieve representative samples. Some simple actions were made to try to minimize this. Primary sludge was mixed and agitated all day long in the mixer tank before the samples were taken, and the sampling point of the bioreactor was emptied from the remaining sludge in the pipe prior to pour sludge in the sampling bottles. But the samples could be unrepresentative anyway, if the time of operation is not sufficient. That was the case during weeks 18, 19, and 20, when only 60, 189, and 68 L primary sludge were added, respectively. Due to the

technical problems previously described, the pilot unit was only in operation sporadically and during short periods during weeks 15 - 33, which covers nearly the entire study. Therefore, the samples recovered in this period did not represent a proper operation of the pilot unit.

Moreover, the analyses carried out by the main laboratory were of course reliable, but the conditions in which some samples were conserved during days or weeks could have damaged their content. This might explain results that were “out of the range”, comparing to other values found. For example, primary and bioreactor sludge samples were preserved with acid prior to be analyzed. Even if this method is approved, damages might have occurred and could partly explain deviated values (VS reduction during weeks 17 and 19 for example).

To perform analyses directly at Sjöstadsverket, fast chemical tests were used. These tests were made to monitor some parameters and to give some values that were not measured by the main laboratory (PO₄-P for instance). The way samples were recovered could be a source of mistakes (sampling, influence of filtration stage prior to analyses and so on), in addition of their real representation problem previously mentioned. Another source of mistakes that cannot be avoided is due to manipulations. Indeed, to use the pipettes, for example, implied an error on the true volume received. The same problem is found while adding the reactants. The consequence is an approximation of the final result, which cannot be considered as an accurate value obtained with an accredited method.

Regarding methane measures, the bacterial community did not seem affected by any disturbance, referring to the Activity Test from AnoxKaldnes. So the low biogas and methane production is mainly due to the measure system failure with leakage of the biogas, as it has been previously stated. However, one can consider a phenomenon that could occur and which has been observed by Carlsson (2005). A part of the produced methane can pass into the permeate phase. According to his conclusions, this phenomenon is not negligible as 41 % of the methane passed through the membranes and ended up in the permeate flow. This mechanism has not been evaluated in this study, but it might be considered to explain the very low values for the measured methane except for the leakage.

Conclusion

A study of sludge treatment in an Anaerobic Membrane BioReactor with respect to several parameters was evaluated. The bioreactor was operated at a temperature of 36°C to promote biogas production at the optimum temperature for mesophilic micro-organisms. This bioreactor was supplied with primary sludge, not or low digested, without reaching 2 % in TS concentration in the reactor as it was stated in the objectives. The mechanical problems that occurred during the study did not enable the pilot unit to be operated in a convenient way.

The methane gas production (calculated from the amount of COD reduced) per mass of organic matter introduced within the bioreactor varied from 0.192 to 0.725 NL CH₄/g COD_{in} with an average value of 0.346, which is 98.8 % of the theoretically maximum value 0.350 NL CH₄/g COD_{in}, which means that 98.8 % of the introduced COD is reduced, and from 0.296 to 0.959 NL CH₄/g VS_{in} with an average value of 0.570, which is 97.7 % of the theoretically maximum value 0.584 NL CH₄/g VS_{in} (calculated from g COD_{primary sludge}/g VS_{primary sludge}). The activity test from microbial community inside the bioreactor gave satisfactory results. The critical parameters such as pH and VFA concentration remained in a normal operating range. No excessive concentrations of heavy metals were detected.

The reduction for methane production of the amount of VS was 75.3 % (median value 81.3 %). In average, for the amount of VS, 0 % was found in the permeate, 3.9 % was accumulated in the bioreactor, and 18.5 % was withdrawn from the system as concentrated sludge. The reduction of the amount of COD was 98.8 %, and of the amount of TOC 91.6 %. Regarding the amount of Kjeldahl Nitrogen, between 8.7 and 98.3 % (average value 42.5 %) was found in the permeate. Moreover, the minimum value for outlet concentrations was 99 mg N/L (outlier 58), which is a rather high value. For the amount of Total Phosphorus, between 5.7 and 57.3 % (average value 26.9 %) was found in the permeate. The minimum concentration within permeate was 15 mg/L (outlier 10), which also is a rather high value.

The degree of degradation of the organic part of the dry solids concentration in the sludge varied between 8 and 70 % (average value 50.9 %, median value 57.5 %). The calculated hydraulic retention time for each week varied between 2 and 105 days (low influent flow that week) (average value 24.6 days, median value 14.5 days).

The operating pressure on the membranes was rather constant, around 4 bars. The permeate flow usually started at 700 mL/min and increased over time to reach 1500 mL/min at the end of a period of operation of the pilot unit. The corresponding values for the flux were 26.42 L/(m²·h) and 56.60 L/(m²·h) with a surface area of 1.59 m² for the membrane stack.

The technical problems faced during this study were mainly related to a low “feeding” pressure to the membrane stack and to difficulties to register biogas production. The consequences of these problems (deeply described in previous chapters) are the inability to operate the pilot unit in a continuous way.

Finally, the “maximum” organic load rate could not be evaluated. It would have required more time, and a continuous and safer operation of the pilot unit. The average value/median value for the entire study was 4.6 / 3.9 kg VS_{in}/week, i.e. 4.9 / 4.1 g VS_{in}/(L · week). This inspires to further investigations in the future.

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Appendix

Appendix 1: Results from Stockholm Vatten's main laboratory

Appendix 2: Scheme of the pilot unit (made by Rasmus Fröhlich, a few changes by Mikael Waltner and Julien Nègre)

Appendix 3: Details on chemical tests used during this study

Appendix 4: Activity test, from AnoxKaldnes

Appendix 5: Calculations related to theoretical methane production

Appendix 6: Calculations related to methane produced with respect to COD consumed

Appendix 1

Uppdrag: Analys avloppsvatten Hammarby Sjöstad

Uppdragsgivare: AP

Provets märkning: Hammarby Sjöstad VSEP primärslam vecka

Svarta siffror kontrollerade

S:a Kj + NO3

| Dygn | TS % | GR % | COD mg/L | TOC mg/L | Tot-P mg/L | NO3-N mg/L | Kjeld-N mg/L | Tot-N mg/L | TNb mg/L | Kontrollerade |
|-------------|---------|---------|-------------|-------------|---------------|---------------|-----------------|---------------|-------------|---------------|
| V713 (2/4) | 0.68 | 19.2 | | 1500 | 58 | <0,5 | 240 | 240 | 160 | CU |
| V714 (10/4) | 1.5 | 12.4 | | 5400 | 100 | <0,5 | 430 | 430 | 350 | CU |
| V715 (16/4) | 1.6 | 13.5 | | 5300 | 98 | <0,5 | 450 | 450 | 360 | CU |
| V716 (23/4) | 1.2 | 16.4 | 15000 | 4200 | 110 | <0,5 | 470 | 470 | 390 | CU |
| V717 (2/5) | 1.2 | 16.2 | 16000 | 3500 | 98 | <0,5 | 410 | 410 | 340 | CU |
| V718 (7/5) | 1.1 | 17.5 | 12000 | 3200 | 91 | <0,5 | 400 | 400 | 300 | CU |
| V719 (14/5) | 0,93* | 19,4* | 11000 | 2300 | 84 | <0,5 | 400 | 400 | 270 | CU |
| V721 (28/5) | 0.75 | 13.8 | 10000 | 3000 | 56 | <0,5 | 230 | 230 | 180 | CU |
| V722 (4/6) | 0.84 | 14.9 | 9700 | 2400 | 55 | <0,5 | 240 | 240 | 180 | CU |
| 7/6 | 1.1 | 11.2 | 13000 | 2100 | 51 | <0,5 | 260 | 260 | 200 | CU |
| V724 (18/6) | 2.2 | 11.1 | 29000 | 3700 | 110 | <0,5 | 490 | 490 | 320 | KM |
| V725 (25/6) | 1.3 | 23.1 | 17000 | 3000 | 82 | <0,5 | 330 | 330 | 270 | KM |
| V726 (2/7) | 2.7 | 27.2 | 30000 | 4800 | 130 | <0,5 | 510 | 510 | 320 | KM |
| | | | | | | | | | | |
| V728 (16/7) | 0.60 | 14.7 | | 2100 | 35 | | 180 | 180 | 130 | KM |
| V729 (23/7) | 0.72 | 17.7 | | 2900 | 47 | | 210 | 210 | 190 | KM |
| | | | | | | | | | | |
| V731 (6/8) | 1.2 | 27.4 | | 3200 | 69 | | 260 | 260 | 200 | KM |
| V732 (13/8) | 0.74 | 26.9 | | 2000 | 51 | | 190 | 190 | 180 | KM |

Metod SS 028113-1 SS 028113-1 SS 028142-2 SS-EN 1484-1 Dr Lange SS EN ISO AN 300/ pr EN 12260
mod 13395 ASN 3503 Ej ackrediterad metod
AN5201

* har satts om på osyrat prov

Uppdrag: Analys avloppsvatten Hammarby Sjöstad

Uppdragsgivare: AP

Provets märkning: Hammarby Sjöstad VSEP reaktorslam dygn/vecka

Svarta siffror kontrollerade

S:a Kj + NO3

| Dygn/vecka | TS % | GR % | COD mg/L | TOC mg/L | Tot-P mg/L | NO3-N mg/L | NH4-N mg/L | Kjeld-N mg/L | Tot-N mg/L | TNb mg/L | Kontrollerade |
|-------------|---------|---------|-------------|-------------|---------------|---------------|---------------|-----------------|---------------|-------------|---------------|
| D713 (2/4) | 0.86 | 36.3 | | 2300 | 200 | <0,5 | 250 | 520 | 520 | 430 | CU |
| D714 (10/4) | 0.98 | 31.9 | | 2600 | 210 | <0,5 | 210 | 520 | 520 | 440 | CU |
| D715 (16/4) | 0.73 | 33.5 | | 2600 | 210 | <0,5 | 210 | 520 | 520 | 450 | CU |
| V716 (23/4) | 1.1 | 29.6 | 12000 | 2100 | 210 | <0,5 | 200 | 550 | 550 | 380 | CU |
| V717 (2/5) | 0.92 | 31.9 | 11000 | 2800 | 200 | <0,5 | 210 | 520 | 520 | 380 | CU |
| V718 (7/5) | 0.91 | 31.9 | 9900 | 2200 | 190 | <0,5 | 230 | 510 | 510 | 390 | CU |
| V719 (14/5) | 0,76* | 33,6* | 8300 | 1900 | 160 | <0,5 | 200 | 450 | 450 | 330 | CU |
| V720 (21/5) | 0.72 | 35.8 | 7800 | 1500 | 160 | <0,5 | 210 | 430 | 430 | 330 | CU |
| V721 (28/5) | 0.85 | 29.0 | 10000 | 1500 | 170 | <0,5 | 190 | 440 | 440 | 320 | CU |
| V722 | 0.85 | 29.2 | 9000 | 1500 | 140 | <0,5 | 150 | 430 | 430 | 260 | CU |
| 7/6 | 0.82 | 27.0 | 10000 | 2000 | 130 | <0,5 | 140 | 430 | 430 | 310 | CU |
| V724 (18/6) | 1.10 | 26.2 | 9400 | 2000 | 140 | <0,5 | 150 | 430 | 430 | 360 | KM |
| V725 (25/6) | 0.89 | 31.4 | 9300 | 1500 | 130 | <0,5 | 140 | 430 | 430 | 300 | KM |
| V726 (2/7) | 0.86 | 32.3 | 9000 | 1800 | 130 | <0,5 | 160 | 440 | 440 | 340 | KM |
| V728 (16/7) | 0.79 | 31.4 | | 1500 | 110 | | 130 | 390 | 390 | 260 | KM |
| V729 (23/7) | 0.91 | 28.1 | | 1900 | 110 | | 140 | 450 | 450 | 320 | KM |
| V731 (6/8) | 0.98 | 29.0 | | 2300 | 130 | | 150 | 480 | 480 | 340 | KM |
| V732 (13/8) | 1.1 | 34.1 | | 3000 | 130 | | 150 | 520 | 520 | 370 | KM |

Metod

SS 028113-1 SS 028113-1 SS 028142-2 SS-EN 1484-1 Dr Lange SS EN ISO AN 300/ pr EN 12260
mod 13395 ASN 3503 Ej ackrediterad metod
AN5201

* har satts om på osyrat prov

Uppdrag: Analys avloppsvatten Hammarby Sjöstad

Uppdragsgivare: AP

Provets märkning: Hammarby Sjöstad VSEP reaktorslam dygn/vecka

Svarta siffror kontrollerade

S:a Kj + NO3

| Dygn/vecka | Ag | B | Cd | Co | Cr | Cu | Fe | Hg | Mn | Mo | Ni | Pb | Zn |
|--------------------|--------------------|--------------------|--------------------|--------------------|--------------------|--------------------|--------------------|----------------|--------------------|--------------------|--------------------|--------------------|--------------------|
| | µg/L | µg/L | µg/L | µg/L | µg/L | µg/L | mg/L | µg/L | µg/L | µg/L | µg/L | µg/L | mg/kg TS |
| | ICP-AES Ackred. | ICP-AES Ackred. | ICP-AES Ackred. | ICP-AES Ackred. | ICP-AES Ackred. | ICP-AES Ackred. | ICP-AES Ackred. | AFS Ackred. | ICP-AES Ackred. | ICP-AES Ackred. | ICP-AES Ackred. | ICP-AES Ackred. | ICP-AES Ackred. |
| D713 (2/4) | 40 | 270 | 11 | 40 | 1500 | 3100 | 200 | 5.7 | 1700 | 250 | 780 | 170 | 9200 |
| V721 (28/5) | 59 | 160 | 10 | 41 | 920 | 3100 | 160 | 18 | 1500 | 140 | 500 | 410 | 7800 |
| 7/6 | 64 | 140 | 9.8 | 39 | 660 | 3100 | 150 | 15 | 1300 | 110 | 360 | 330 | 6700 |
| V732 (13/8) | 85 | 150 | 12 | 67 | 500 | 4500 | 220 | 14 | 2100 | 80 | 300 | 460 | 10000 |
| | | | | | | | | | | | | | |

Uppdrag: Analys avloppsvatten Hammarby Sjöstad
Uppdragsgivare: AP
Provets märkning: Hammarby Sjöstad VSEP permeat vecka

Svarta siffror kontrollerade

S:a Kj + NO3

| Dygn | COD mg/L | TOC mg/L | Tot-P mg/L | NO3-N mg/L | NH4-N mg/L | Kjeld-N mg/L | Tot-N mg/L | TNb mg/L | Kontrollerade |
|--------------|--------------------|--------------|---------------|------------------------------|---------------|---------------------|---------------|--------------------------------------|---------------|
| V713 (2/4) | | 50 | 31 | <0,5 | 220 | 220 | 220 | 240 | CU |
| V714 (10/4) | | 70 | 26 | <0,5 | 190 | 200 | 200 | 210 | CU |
| V715 (16/4) | | 46 | 24 | <0,5 | 190 | 190 | 190 | 180 | CU |
| V716 (23/4) | 120 | 42 | 26 | <0,5 | 180 | 180 | 180 | 190 | CU |
| V717 (2/5) | 130 | 44 | 23 | <0,5 | 170 | 180 | 180 | 170 | CU |
| V718 (7/5) | 110 | 47 | 22 | <0,5 | 170 | 180 | 180 | 180 | CU |
| V719 (14/5) | 72 | 29 | 15 | <0,5 | 110 | 110 | 110 | 110 | CU |
| V721 (28/5) | 110 | 37 | 20 | <0,5 | 150 | 150 | 150 | 130 | CU |
| V722 (4/6) | 110 | 44 | 20 | <0,5 | 120 | 140 | 140 | 120 | CU |
| 7/6 | 110 | 44 | 18 | <0,5 | 100 | 110 | 110 | 110 | CU |
| V724 (18/6) | 52 | 20 | 10 | <0,5 | 58 | 58 | 58 | 59 | KM |
| V725 (25/6) | 140 | 52 | 16 | <0,5 | 100 | 110 | 110 | 100 | KM |
| V726 (2/7) | 100 | 35 | 16 | <0,5 | 99 | 100 | 100 | 100 | KM |
| | | | | | | | | | |
| V728 (16/7) | | 35 | 18 | | 110 | 110 | 110 | 100 | KM |
| V729 (23/7) | | 51 | 16 | | 97 | 99 | 99 | 96 | KM |
| | | | | | | | | | |
| V731 (6/8) | | 38 | 21 | | 130 | 130 | 130 | 120 | KM |
| V732 (13/8) | | 49 | 18 | | 100 | 100 | 100 | 93 | KM |
| | | | | | | | | | |
| | | | | | | | | | |
| Metod | SS 028142-2 mod | SS-EN 1484-1 | Dr Lange | SS EN ISO 13395 AN5201 | AN 300 | AN 300/ ASN 3503 | | pr EN 12260 Ej ackrediterad metod | |

Uppdrag: Analys avloppsvatten Hammarby Sjöstad

Uppdragsgivare: AP

Provets märkning: Hammarby Sjöstad VSEP permeat vecka

Svarta siffror kontrollerade

| Dygn/vecka | Ag | B | Cd | Co | Cr | Cu | Fe | Hg | Mn | Mo | Ni | Pb | Zn |
|-------------|--------------------|--------------------|--------------------|--------------------|--------------------|--------------------|--------------------|----------------|--------------------|--------------------|--------------------|--------------------|--------------------|
| | µg/L | µg/L | µg/L | µg/L | µg/L | µg/L | mg/L | µg/L | µg/L | µg/L | µg/L | µg/L | mg/kg TS |
| | ICP-AES Ackred. | ICP-AES Ackred. | ICP-AES Ackred. | ICP-AES Ackred. | ICP-AES Ackred. | ICP-AES Ackred. | ICP-AES Ackred. | AFS Ackred. | ICP-AES Ackred. | ICP-AES Ackred. | ICP-AES Ackred. | ICP-AES Ackred. | ICP-AES Ackred. |
| V713 (2/4)* | <20 | 100 | <5 | <20 | <20 | 25 | 1.6 | <0,05 | 52 | <20 | 27 | <50 | 20 |
| V715 (16/4) | <20 | 84 | <5 | <20 | <20 | <20 | 1.6 | | 70 | <20 | <20 | <50 | <20 |
| V721 (28/5) | <20 | 53 | <5 | <20 | <20 | <20 | 1.9 | <0,05 | 70 | <20 | <20 | <50 | <20 |
| 7/6 | <20 | 48 | <5 | <20 | <20 | <20 | 2.0 | <0,05 | 97 | <20 | <20 | <50 | <20 |

* konserverats med H₂SO₄

Uppdrag: Analys avloppsvatten Hammarby Sjöstad

Uppdragsgivare: AP

Provets märkning: Hammarby Sjöstad VSEP öslam vecka

Svarta siffror kontrollerade

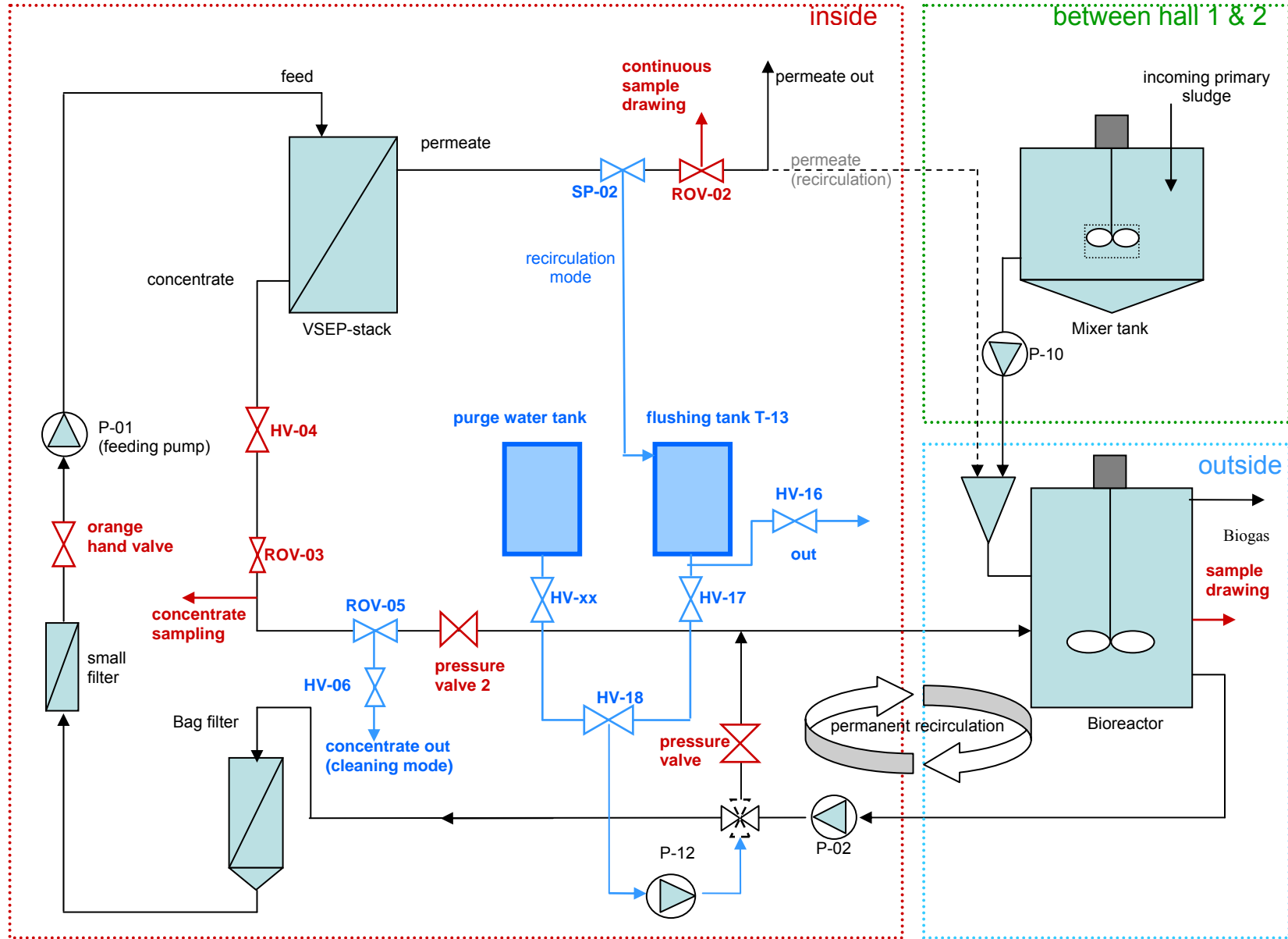
| Dygn | TS % | GR % | <u>Kontrollerade</u> |
|-------------|-----------------|-----------------|----------------------|
| V716 (23/4) | 1.8 | 27.4 | CU |
| V717 (2/5) | 1.9 | 28.0 | CU |
| V718 (7/5) | 1.4 | 29.0 | CU |
| V719 (14/5) | 0.46 | 33.0 | CU |
| V721 (28/5) | 2.6 | 31.8 | CU |
| V722 (4/6) | 3.2 | 25.6 | CU |
| 7/6 | 2.5 | 24.5 | CU |
| V724 (18/6) | 1.7 | 25.5 | KM |
| V725 (25/6) | 2.2 | 25.4 | KM |
| V726 (2/7) | 2.5 | 25.4 | KM |
| | | | |
| V728 | 1.3 | 27.2 | KM |
| V729 | 2.7 | 24.4 | KM |
| V731 (6/8) | 3.0 | 24.7 | KM |
| V732 (13/8) | 3.4 | 27.9 | KM |
| | | | |
| | | | |

Metod

SS 028113-1

SS 028113-1

Appendix 2



Appendix 3

The pipettes used for carrying out these tests were manufactured by BIOHIT (ranges: 20-200 μL [m200], 100-1000 μL [m1000], and 500-5000 μL [m5000]).

| | Name | Range (mg/L) | Principle | Sample volume required (mL) | Approx. time needed (min) |
|------------------------|---------|--------------|---|-----------------------------|---------------------------|
| COD | LCK 314 | 15-150 | Oxidizable substances react with sulphuric acid-potassium dichromate solution in the presence of silver sulphate as a catalyst. Chloride is masked by mercury sulphate. The reduction in the yellow coloration of Cr^{6+} is evaluated (LCK 314). The green coloration of Cr^{3+} is evaluated (LCK 514). | 2 | 180 |
| | LCK 514 | 100-2000 | | 2 | 180 |
| $\text{PO}_4\text{-P}$ | LCK 350 | 2-20 | Phosphate ions react with molybdate and antimony ions in an acidic solution to form an antimonyl phosphomolybdate complex, which is reduced by ascorbic acid to phosphomolybdenum blue. | 0.4 | 15 |
| $\text{NH}_4\text{-N}$ | LCK 302 | 47-130 | Ammonium ions react at pH 12.6 with hypochlorite ions and salicylate ions in the presence of sodium nitroprusside as a catalyst to form indophenol blue | 0.2 | 20 |
| | LCK 303 | 2-47 | | 0.2 | 20 |
| $\text{NO}_3\text{-N}$ | LCK 339 | 0.23-13.5 | Nitrate ions in solutions containing sulphuric and phosphoric acids react with 2,6-dimethylphenol to form 4-nitro-2,6-dimethylphenol | 0.2 | 20 |
| VFA | LCK 365 | 50-2500 | Fatty acids react with diols in an acidic environment, forming fatty acid esters. These are reduced by iron(III) salts to form red coloured complexes, which are evaluated photometrically | 0.4 | 50 |

Standard method names used for analyses performed by the main laboratory are available in Appendix 1, below the columns. For the analysis of total P, Dr Lange refers to the instrument Dr Lange Ganimed-P with the analysis SS EN 1189-1.

Appendix 4



Undersökning av anaerob aktivitet i slamprover från VSEP-reaktorn, Hammarby Sjöstads Reningsverk

My Carlsson, Lars-Erik Olsson
2007-05-28



74

AnoxKaldnes

Innehåll

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Inledning

Ett aktivitetstest har gjorts på slam från VSEP-reaktor på Hammarby Sjöstads reningsverk. Syftet med detta test var att bestämma anaerob aktivitet i provet. Testet visar vilken aktivitet ett slam har under optimala anaeroba förhållanden, vid 20-21°C. Studien utfördes under perioden 070503-070528.

Material och metoder

Slammet till försöken togs ut från VSEP-reaktor 070416. Två olika lösningar bereddes till försöket enligt Tabell 1. Den ena lösningen innehöll endast slam spätt med destillerat vatten, för att kontrollera hur mycket som fanns kvar att bryta ner i cellinnehållet. Den andra lösningen innehöll även natriumacetat-trihydrat ($\text{NaAc} \cdot 3\text{H}_2\text{O}$) som substrat för att se vilken aktivitet som kunde erhållas med ett lättnedbrytbart substrat under optimala förhållanden. En mycket låg belastning (0,5 g COD/g VS) valdes för att garantera att aktiviteten inte hämmades av överbelastning.

Tabell 1 Koncentrationer av slam respektive $\text{NaAc} \cdot 3\text{H}_2\text{O}$ (referens) i de olika lösningar som användes i försöken. Lösningarna späddes med destillerat vatten.

| Lösning | Slam g/l | Referens g/l |
|----------|-------------|-----------------|
| Blank | 620 | - |
| Referens | 620 | 3,96 |

Vid försökets början mättes pH samt TSS/VSS i lösningarna. De olika lösningarna sattes som triplikat om 100 ml i 155 ml gastäta testflaskor (minirötkammare). Testflaskorna förvarades under hela försöksperioden i rumstemperatur ($20 \pm 1^\circ\text{C}$). Under försöksperioden togs gasprover regelbundet ur flaskorna för att beräkna och mäta gasproduktion och metanhalt.

Analyser

Tabell 2 redovisar metoderna som använts för att utföra analyserna som presenteras i denna rapport.

Tabell 2 Metoder och standarder som använts för analyserna i denna rapport.

| Analys | Metod/standard |
|--------------------|----------------|
| Gas-sammansättning | GC-TCD |
| pH | SS 028122-2 |
| TSS/VSS | SS 028113-1 |

Resultat

Resultaten från TSS/VSS-analyser redovisas i Tabell 3.

Tabell 3 Resultat från TSS/VSS-analyser av slam.

| | TSS (g/kg slam) | VSS (g/kg slam) |
|-------------|-----------------------|-----------------------|
| Slam | 8,2 | 6,0 |
| Testlösning | 5,1 | 3,7 |

Resultaten från aktivitetstestet av slam från VSEP-reaktor redovisas i Diagram 1 tillsammans med motsvarande kurva för slam hämtat i augusti 2006. Kurvan visar ackumulerad mängd metangas som produceras från tillsatsen av referenssubstrat. Teoretiskt kan ca 65 ml metan produceras. Detta test visar hur snabbt slammet reagerar. Vid test med ett rötslam med god aktivitet börjar gasproduktionen inom ett par dagar och avslutas inom 10 dagar.

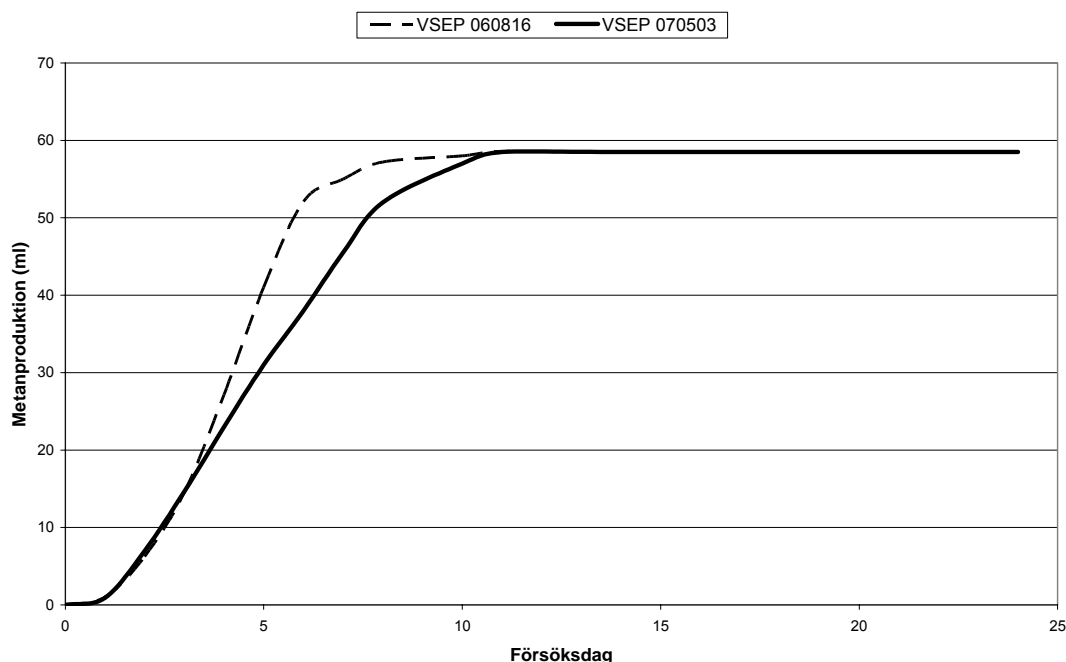


Diagram 1 Resultat från aktivitetstest av slam från VSEP-reaktor på Hammarby Sjöstads reningsverk hämtat vid två tillfällen. Kurvan visar ackumulerad metanproduktion från referenssubstrat. Kurvorna har korrigerats för ympens bidrag.

Kurvan visar att metanproduktionen kommer igång nästan omedelbart och avslutas inom 10-11 dagar. Aktiviteten är något lägre än den aktivitet som uppmättes i slammet hämtat i februari.

Slutsatser

- Metanproduktionen kommer igång nästan omedelbart och avslutas relativt snabbt.
- Aktivitetstestet visar att slammet från reningsanläggningen har godkänd anaerob aktivitet för den aktuella temperaturen.
- Aktiviteten i slammet är något lägre än den som uppmättes i augusti 2006.

Appendix 5

Week 8:

$$\text{COD}_{\text{in}} = \text{no value available mg/L} \cdot 624.97 \text{ L} = ? \text{ g COD}$$

$$\text{COD}_{\text{eff}} = \text{no value available mg/L} \cdot 551.25 \text{ L} = ? \text{ g COD}$$

$$\text{COD}_{\text{sludge}} = ? \text{ kg TS/kg} \cdot ? \text{ kg VS/kg TS} \cdot 0 \text{ kg} \cdot 1086.4 \text{ g COD/kg VS} = 0 \text{ g COD}$$

$$\text{COD}_{\text{acc}} = \text{COD}_{\text{w2}} \cdot V_{\text{w2,react}} - \text{COD}_{\text{w1}} \cdot V_{\text{w1,react}} =$$

$$? \text{ mg/L} \cdot 883 \text{ L} - ? \text{ mg/L} \cdot 809 \text{ L} = ? \text{ g COD}$$

$$\text{COD}_{\text{red}} = ? - (? + 0 + ?) = ? \text{ g COD}$$

$$\text{Theoretical methane volume, } 0^\circ\text{C and 1 atm, } V_{\text{methane}} = 0.350 \cdot ? = ? \text{ NL}$$

Week 9:

$$\text{COD}_{\text{in}} = \text{no value available mg/L} \cdot 2496.23 \text{ L} = ? \text{ g COD}$$

$$\text{COD}_{\text{eff}} = \text{no value available mg/L} \cdot 2526 \text{ L} = ? \text{ g COD}$$

$$\text{COD}_{\text{sludge}} = ? \text{ kg TS/kg} \cdot ? \text{ kg VS/kg TS} \cdot 0 \text{ kg} \cdot 1086.4 \text{ g COD/kg VS} = 0 \text{ g COD}$$

$$\text{COD}_{\text{acc}} = \text{COD}_{\text{w2}} \cdot V_{\text{w2,react}} - \text{COD}_{\text{w1}} \cdot V_{\text{w1,react}} =$$

$$? \text{ mg/L} \cdot 853 \text{ L} - ? \text{ mg/L} \cdot 883 \text{ L} = ? \text{ g COD}$$

$$\text{COD}_{\text{red}} = ? - (? + 0 + ?) = ? \text{ g COD}$$

$$\text{Theoretical methane volume, } 0^\circ\text{C and 1 atm, } V_{\text{methane}} = 0.350 \cdot ? = ? \text{ NL}$$

Week 10:

$$\text{COD}_{\text{in}} = \text{no value available mg/L} \cdot 932.39 \text{ L} = ? \text{ g COD}$$

$$\text{COD}_{\text{eff}} = \text{no value available mg/L} \cdot 965 \text{ L} = ? \text{ g COD}$$

$$\text{COD}_{\text{sludge}} = ? \text{ kg TS/kg} \cdot ? \text{ kg VS/kg TS} \cdot 0 \text{ kg} \cdot 1086.4 \text{ g COD/kg VS} = 0 \text{ g COD}$$

$$\text{COD}_{\text{acc}} = \text{COD}_{\text{w2}} \cdot V_{\text{w2,react}} - \text{COD}_{\text{w1}} \cdot V_{\text{w1,react}} =$$

$$? \text{ mg/L} \cdot 821 \text{ L} - ? \text{ mg/L} \cdot 853 \text{ L} = ? \text{ g COD}$$

$$\text{COD}_{\text{red}} = ? - (? + 0 + ?) = ? \text{ g COD}$$

$$\text{Theoretical methane volume, } 0^\circ\text{C and 1 atm, } V_{\text{methane}} = 0.350 \cdot ? = ? \text{ NL}$$

Week 11:

$$\text{COD}_{\text{in}} = \text{no value available mg/L} \cdot 485.66 \text{ L} = ? \text{ g COD}$$

$$\text{COD}_{\text{eff}} = \text{no value available mg/L} \cdot 368 \text{ L} = ? \text{ g COD}$$

$$\text{COD}_{\text{sludge}} = ? \text{ kg TS/kg} \cdot ? \text{ kg VS/kg TS} \cdot 0 \text{ kg} \cdot 1086.4 \text{ g COD/kg VS} = 0 \text{ g COD}$$

$$\text{COD}_{\text{acc}} = \text{COD}_{\text{w2}} \cdot V_{\text{w2,react}} - \text{COD}_{\text{w1}} \cdot V_{\text{w1,react}} =$$

$$? \text{ mg/L} \cdot 938 \text{ L} - ? \text{ mg/L} \cdot 821 \text{ L} = ? \text{ g COD}$$

$$\text{COD}_{\text{red}} = ? - (? + 0 + ?) = ? \text{ g COD}$$

$$\text{Theoretical methane volume, } 0^\circ\text{C and 1 atm, } V_{\text{methane}} = 0.350 \cdot ? = ? \text{ NL}$$

Week 12:

$$\text{COD}_{\text{in}} = \text{no value available mg/L} \cdot 1\,329.57 \text{ L} = ? \text{ g COD}$$

$$\text{COD}_{\text{eff}} = \text{no value available mg/L} \cdot 1\,329 \text{ L} = ? \text{ g COD}$$

$$\text{COD}_{\text{sludge}} = \text{no value available kg TS/kg} \cdot \text{no value available kg VS/kg TS} \cdot 0.57 \text{ kg} \cdot 1086.4 \text{ g COD/kg VS} = ? \text{ g COD}$$

$$\text{COD}_{\text{acc}} = \text{COD}_{\text{w2}} \cdot V_{\text{w2,react}} - \text{COD}_{\text{w1}} \cdot V_{\text{w1,react}} =$$

$$? \text{ mg/L} \cdot 938 \text{ L} - ? \text{ mg/L} \cdot 938 \text{ L} = ? \text{ g COD}$$

$$\text{COD}_{\text{red}} = ? - (? + ? + ?) = ? \text{ g COD}$$

$$\text{Theoretical methane volume, } 0^\circ\text{C and 1 atm, } V_{\text{methane}} = 0.350 \cdot ? = ? \text{ NL}$$

Week 13:

$$\text{COD}_{\text{in}} = 7\,499.32 \text{ mg/L} \cdot 429.87 \text{ L} = 3224 \text{ g COD}$$

$$\text{COD}_{\text{eff}} = 133.79 \text{ mg/L} \cdot 461 \text{ L} = 61.7 \text{ g COD}$$

$$\text{COD}_{\text{sludge}} = \text{no value available kg TS/kg} \cdot \text{no value available kg VS/kg TS} \cdot 1.52 \text{ kg} \cdot 1086.4 \text{ g COD/kg VS} = ? \text{ g COD}$$

$$\text{COD}_{\text{acc}} = \text{COD}_{\text{w2}} \cdot V_{\text{w2,react}} - \text{COD}_{\text{w1}} \cdot V_{\text{w1,react}} =$$

$$11\,976.30 \text{ mg/L} \cdot 904 \text{ L} - ? \text{ mg/L} \cdot 938 \text{ L} = ? \text{ g COD}$$

$$\text{COD}_{\text{red}} = 3224 - (61.7 + ? + ?) \approx 3162.08 \text{ g COD}$$

$$\text{Theoretical methane volume, } 0^\circ\text{C and 1 atm, } V_{\text{methane}} = 0.350 \cdot 3162.08 \approx 1107 \text{ NL}$$

Week 14:

$$\text{COD}_{\text{in}} = 26\,997.54 \text{ mg/L} \cdot 1\,270.84 \text{ L} = 34310 \text{ g COD}$$

$$\text{COD}_{\text{eff}} = 187.30 \text{ mg/L} \cdot 1238 \text{ L} = 232 \text{ g COD}$$

$$\text{COD}_{\text{sludge}} = \text{no value available kg TS/kg} \cdot \text{no value available kg VS/kg TS} \cdot 1.34 \text{ kg} \cdot 1086.4 \text{ g COD/kg VS} = ? \text{ g COD}$$

$$\text{COD}_{\text{acc}} = \text{COD}_{\text{w2}} \cdot V_{\text{w2,react}} - \text{COD}_{\text{w1}} \cdot V_{\text{w1,react}} =$$

$$13\,538.42 \text{ mg/L} \cdot 924 \text{ L} - 11\,976.30 \text{ mg/L} \cdot 904 \text{ L} = 1682 \text{ g COD}$$

$$\text{COD}_{\text{red}} = 34310 - (232 + ? + 1682) \approx 32396 \text{ g COD}$$

$$\text{Theoretical methane volume, } 0^\circ\text{C and 1 atm, } V_{\text{methane}} = 0.350 \cdot 32396 \approx 11346 \text{ NL}$$

Week 15:

$$\text{COD}_{\text{in}} = 26\,497.59 \text{ mg/L} \cdot 372.16 \text{ L} = 9861 \text{ g COD}$$

$$\text{COD}_{\text{eff}} = 123.08 \text{ mg/L} \cdot 359.1 \text{ L} = 44.2 \text{ g COD}$$

$$\text{COD}_{\text{sludge}} = \text{no value available kg TS/kg} \cdot \text{no value available kg VS/kg TS} \cdot 1.00 \text{ kg} \cdot 1086.4 \text{ g COD/kg VS} = ? \text{ g COD}$$

$$\text{COD}_{\text{acc}} = \text{COD}_{\text{w2}} \cdot V_{\text{w2,react}} - \text{COD}_{\text{w1}} \cdot V_{\text{w1,react}} =$$

$$13\,538.42 \text{ mg/L} \cdot 933 \text{ L} - 13\,538.42 \text{ mg/L} \cdot 924 \text{ L} = 115 \text{ g COD}$$

$$\text{COD}_{\text{red}} = 9861 - (44.2 + ? + 115) \approx 9702.01 \text{ g COD}$$

$$\text{Theoretical methane volume, } 0^\circ\text{C and 1 atm, } V_{\text{methane}} = 0.350 \cdot 9702.01 \approx 3398 \text{ NL}$$

Week 16:

$$\text{COD}_{\text{in}} = 15\,000 \text{ mg/L} \cdot 273.13 \text{ L} = 4097 \text{ g COD}$$

$$\text{COD}_{\text{eff}} = 120 \text{ mg/L} \cdot 270 \text{ L} = 32.4 \text{ g COD}$$

$$\text{COD}_{\text{sludge}} = 0.018 \text{ kg TS/kg} \cdot (1 - 0.274) \text{ kg VS/kg TS} \cdot 15.84 \text{ kg} \cdot 1086.4 \text{ g COD/kg VS} = 225 \text{ g COD}$$

$$\text{COD}_{\text{acc}} = \text{COD}_{\text{w2}} \cdot V_{\text{w2,react}} - \text{COD}_{\text{w1}} \cdot V_{\text{w1,react}} = 12\,000 \text{ mg/L} \cdot 919 \text{ L} - 13\,538.42 \text{ mg/L} \cdot 933 \text{ L} = -1605 \text{ g COD}$$

$$\text{COD}_{\text{red}} = 4097 - (32.4 + 225 - 1605) = 5444.77 \text{ g COD}$$

$$\text{Theoretical methane volume, } 0^\circ\text{C and 1 atm, } V_{\text{methane}} = 0.350 \cdot 5444.77 = 1907 \text{ NL}$$

Week 17:

$$\text{COD}_{\text{in}} = 16\,000 \text{ mg/L} \cdot 178.14 \text{ L} = 2850 \text{ g COD}$$

$$\text{COD}_{\text{eff}} = 130 \text{ mg/L} \cdot 140 \text{ L} = 18.2 \text{ g COD}$$

$$\text{COD}_{\text{sludge}} = 0.019 \text{ kg TS/kg} \cdot (1 - 0.280) \text{ kg VS/kg TS} \cdot 64.02 \text{ kg} \cdot 1086.4 \text{ g COD/kg VS} = 951 \text{ g COD}$$

$$\text{COD}_{\text{acc}} = \text{COD}_{\text{w2}} \cdot V_{\text{w2,react}} - \text{COD}_{\text{w1}} \cdot V_{\text{w1,react}} = 11\,000 \text{ mg/L} \cdot 892 \text{ L} - 12\,000 \text{ mg/L} \cdot 919 \text{ L} = -1215 \text{ g COD}$$

$$\text{COD}_{\text{red}} = 2850 - (18.2 + 951 - 1215) = 3095.45 \text{ g COD}$$

$$\text{Theoretical methane volume, } 0^\circ\text{C and 1 atm, } V_{\text{methane}} = 0.350 \cdot 3095.45 = 1084 \text{ NL}$$

Week 18:

$$\text{COD}_{\text{in}} = 12\,000 \text{ mg/L} \cdot 59.83 \text{ L} = 718.0 \text{ g COD}$$

$$\text{COD}_{\text{eff}} = 110 \text{ mg/L} \cdot 40 \text{ L} = 4.4 \text{ g COD}$$

$$\text{COD}_{\text{sludge}} = 0.014 \text{ kg TS/kg} \cdot (1 - 0.290) \text{ kg VS/kg TS} \cdot 16.70 \text{ kg} \cdot 1086.4 \text{ g COD/kg VS} = 180 \text{ g COD}$$

$$\text{COD}_{\text{acc}} = \text{COD}_{\text{w2}} \cdot V_{\text{w2,react}} - \text{COD}_{\text{w1}} \cdot V_{\text{w1,react}} = 9\,900 \text{ mg/L} \cdot 895 \text{ L} - 11\,000 \text{ mg/L} \cdot 892 \text{ L} = -953 \text{ g COD}$$

$$\text{COD}_{\text{red}} = 718.0 - (4.4 + 180 - 953) = 1486.05 \text{ g COD}$$

$$\text{Theoretical methane volume, } 0^\circ\text{C and 1 atm, } V_{\text{methane}} = 0.350 \cdot 1486.05 = 520 \text{ NL}$$

Week 19:

$$\text{COD}_{\text{in}} = 11\,000 \text{ mg/L} \cdot 188.64 \text{ L} = 2075 \text{ g COD}$$

$$\text{COD}_{\text{eff}} = 72 \text{ mg/L} \cdot 60 \text{ L} = 4.3 \text{ g COD}$$

$$\text{COD}_{\text{sludge}} = 0.0046 \text{ kg TS/kg} \cdot (1 - 0.330) \text{ kg VS/kg TS} \cdot 31.50 \text{ kg} \cdot 1086.4 \text{ g COD/kg VS} = 105 \text{ g COD}$$

$$\text{COD}_{\text{acc}} = \text{COD}_{\text{w2}} \cdot V_{\text{w2,react}} - \text{COD}_{\text{w1}} \cdot V_{\text{w1,react}} = 8\,300 \text{ mg/L} \cdot 991 \text{ L} - 9\,900 \text{ mg/L} \cdot 895 \text{ L} = -631 \text{ g COD}$$

$$\text{COD}_{\text{red}} = 2075 - (4.3 + 105 - 631) = 2596.40 \text{ g COD}$$

$$\text{Theoretical methane volume, } 0^\circ\text{C and 1 atm, } V_{\text{methane}} = 0.350 \cdot 2596.40 = 909 \text{ NL}$$

Week 20:

$$\text{COD}_{\text{in}} = \text{no value available mg/L} \cdot 68.20 \text{ L} = ? \text{ g COD}$$

$$\text{COD}_{\text{eff}} = \text{no value available mg/L} \cdot 55.44 \text{ L} = ? \text{ g COD}$$

$$\text{COD}_{\text{sludge}} = ? \text{ kg TS/kg} \cdot ? \text{ kg VS/kg TS} \cdot 0 \text{ kg} \cdot 1086.4 \text{ g COD/kg VS} = 0 \text{ g COD}$$

$$\begin{aligned} \text{COD}_{\text{acc}} &= \text{COD}_{\text{w2}} \cdot V_{\text{w2,react}} - \text{COD}_{\text{w1}} \cdot V_{\text{w1,react}} = \\ 7\,800 \text{ mg/L} \cdot 1004 \text{ L} - 8\,300 \text{ mg/L} \cdot 991 \text{ L} &= -396 \text{ g COD} \end{aligned}$$

$$\text{COD}_{\text{red}} = ? - (? + 0 - 396) = ? \text{ g COD}$$

$$\text{Theoretical methane volume, } 0^\circ\text{C and 1 atm, } V_{\text{methane}} = 0.350 \cdot ? = ? \text{ NL}$$

Week 21:

$$\text{COD}_{\text{in}} = 10\,000 \text{ mg/L} \cdot 443.34 \text{ L} = 4433 \text{ g COD}$$

$$\text{COD}_{\text{eff}} = 110 \text{ mg/L} \cdot 517 \text{ L} = 56.9 \text{ g COD}$$

$$\begin{aligned} \text{COD}_{\text{sludge}} &= 0.026 \text{ kg TS/kg} \cdot (1 - 0.318) \text{ kg VS/kg TS} \cdot 53.60 \text{ kg} \cdot 1086.4 \text{ g COD/kg} \\ \text{VS} &= 1033 \text{ g COD} \end{aligned}$$

$$\begin{aligned} \text{COD}_{\text{acc}} &= \text{COD}_{\text{w2}} \cdot V_{\text{w2,react}} - \text{COD}_{\text{w1}} \cdot V_{\text{w1,react}} = \\ 10\,000 \text{ mg/L} \cdot 875 \text{ L} - 7\,800 \text{ mg/L} \cdot 1004 \text{ L} &= 918 \text{ g COD} \end{aligned}$$

$$\text{COD}_{\text{red}} = 4433 - (56.9 + 1033 + 918) = 2425.88 \text{ g COD}$$

$$\text{Theoretical methane volume, } 0^\circ\text{C and 1 atm, } V_{\text{methane}} = 0.350 \cdot 2425.88 = 850 \text{ NL}$$

Week 22:

$$\text{COD}_{\text{in}} = 9\,700 \text{ mg/L} \cdot 887.71 \text{ L} = 8611 \text{ g COD}$$

$$\text{COD}_{\text{eff}} = 110 \text{ mg/L} \cdot 722 \text{ L} = 79.4 \text{ g COD}$$

$$\begin{aligned} \text{COD}_{\text{sludge}} &= 0.032 \text{ kg TS/kg} \cdot (1 - 0.256) \text{ kg VS/kg TS} \cdot 71.33 \text{ kg} \cdot 1086.4 \text{ g COD/kg} \\ \text{VS} &= 1845 \text{ g COD} \end{aligned}$$

$$\begin{aligned} \text{COD}_{\text{acc}} &= \text{COD}_{\text{w2}} \cdot V_{\text{w2,react}} - \text{COD}_{\text{w1}} \cdot V_{\text{w1,react}} = \\ 9\,000 \text{ mg/L} \cdot 965 \text{ L} - 10\,000 \text{ mg/L} \cdot 875 \text{ L} &= -58.1 \text{ g COD} \end{aligned}$$

$$\text{COD}_{\text{red}} = 8611 - (79.4 + 1845 - 58.1) = 6744.55 \text{ g COD}$$

$$\text{Theoretical methane volume, } 0^\circ\text{C and 1 atm, } V_{\text{methane}} = 0.350 \cdot 6744.55 = 2362 \text{ NL}$$

Week 23:

$$\text{COD}_{\text{in}} = 13\,000 \text{ mg/L} \cdot 383.00 \text{ L} = 4979 \text{ g COD}$$

$$\text{COD}_{\text{eff}} = 110 \text{ mg/L} \cdot 368 \text{ L} = 40.5 \text{ g COD}$$

$$\begin{aligned} \text{COD}_{\text{sludge}} &= 0.025 \text{ kg TS/kg} \cdot (1 - 0.245) \text{ kg VS/kg TS} \cdot 55.06 \text{ kg} \cdot 1086.4 \text{ g COD/kg} \\ \text{VS} &= 1129 \text{ g COD} \end{aligned}$$

$$\begin{aligned} \text{COD}_{\text{acc}} &= \text{COD}_{\text{w2}} \cdot V_{\text{w2,react}} - \text{COD}_{\text{w1}} \cdot V_{\text{w1,react}} = \\ 10\,000 \text{ mg/L} \cdot 923 \text{ L} - 9\,000 \text{ mg/L} \cdot 965 \text{ L} &= 540 \text{ g COD} \end{aligned}$$

$$\text{COD}_{\text{red}} = 4979 - (40.5 + 1129 + 540) = 3269.30 \text{ g COD}$$

$$\text{Theoretical methane volume, } 0^\circ\text{C and 1 atm, } V_{\text{methane}} = 0.350 \cdot 3269.30 = 1145 \text{ NL}$$

Week 24:

$$\text{COD}_{\text{in}} = 29\,000 \text{ mg/L} \cdot 97.99 \text{ L} = 2842 \text{ g COD}$$

$$\text{COD}_{\text{eff}} = 52 \text{ mg/L} \cdot 85.65 \text{ L} = 4.5 \text{ g COD}$$

$$\text{COD}_{\text{sludge}} = 0.017 \text{ kg TS/kg} \cdot (1 - 0.255) \text{ kg VS/kg TS} \cdot 15.35 \text{ kg} \cdot 1086.4 \text{ g COD/kg VS} = 211 \text{ g COD}$$

$$\text{COD}_{\text{acc}} = \text{COD}_{\text{w2}} \cdot V_{\text{w2,react}} - \text{COD}_{\text{w1}} \cdot V_{\text{w1,react}} = 9\,400 \text{ mg/L} \cdot 919 \text{ L} - 10\,000 \text{ mg/L} \cdot 923 \text{ L} = -594 \text{ g COD}$$

$$\text{COD}_{\text{red}} = 2842 - (4.5 + 211 - 594) = 3219.75 \text{ g COD}$$

$$\text{Theoretical methane volume, } 0^\circ\text{C and 1 atm, } V_{\text{methane}} = 0.350 \cdot 3219.75 = 1128 \text{ NL}$$

Week 25:

$$\text{COD}_{\text{in}} = 17\,000 \text{ mg/L} \cdot 861.78 \text{ L} = 14650 \text{ g COD}$$

$$\text{COD}_{\text{eff}} = 140 \text{ mg/L} \cdot 730.62 \text{ L} = 102 \text{ g COD}$$

$$\text{COD}_{\text{sludge}} = 0.022 \text{ kg TS/kg} \cdot (1 - 0.254) \text{ kg VS/kg TS} \cdot 55.90 \text{ kg} \cdot 1086.4 \text{ g COD/kg VS} = 997 \text{ g COD}$$

$$\text{COD}_{\text{acc}} = \text{COD}_{\text{w2}} \cdot V_{\text{w2,react}} - \text{COD}_{\text{w1}} \cdot V_{\text{w1,react}} = 9\,300 \text{ mg/L} \cdot 991 \text{ L} - 9\,400 \text{ mg/L} \cdot 919 \text{ L} = 581 \text{ g COD}$$

$$\text{COD}_{\text{red}} = 14650 - (102 + 997 + 581) = 12970.8 \text{ g COD}$$

$$\text{Theoretical methane volume, } 0^\circ\text{C and 1 atm, } V_{\text{methane}} = 0.350 \cdot 12970.8 = 4543 \text{ NL}$$

Week 26:

$$\text{COD}_{\text{in}} = 30\,000 \text{ mg/L} \cdot 263.48 \text{ L} = 7904 \text{ g COD}$$

$$\text{COD}_{\text{eff}} = 100 \text{ mg/L} \cdot 252.91 \text{ L} = 25.3 \text{ g COD}$$

$$\text{COD}_{\text{sludge}} = 0.025 \text{ kg TS/kg} \cdot (1 - 0.254) \text{ kg VS/kg TS} \cdot 25.04 \text{ kg} \cdot 1086.4 \text{ g COD/kg VS} = 507 \text{ g COD}$$

$$\text{COD}_{\text{acc}} = \text{COD}_{\text{w2}} \cdot V_{\text{w2,react}} - \text{COD}_{\text{w1}} \cdot V_{\text{w1,react}} = 9\,000 \text{ mg/L} \cdot 975 \text{ L} - 9\,300 \text{ mg/L} \cdot 991 \text{ L} = -438 \text{ g COD}$$

$$\text{COD}_{\text{red}} = 7904 - (25.3 + 507 - 438) = 7809.43 \text{ g COD}$$

$$\text{Theoretical methane volume, } 0^\circ\text{C and 1 atm, } V_{\text{methane}} = 0.350 \cdot 7809.43 = 2735 \text{ NL}$$

Week 27:

$$\text{COD}_{\text{in}} = \text{no value available mg/L} \cdot 0 \text{ L} = 0 \text{ g COD}$$

$$\text{COD}_{\text{eff}} = \text{no value available mg/L} \cdot \text{no value available L} = 0 \text{ g COD}$$

$$\text{COD}_{\text{sludge}} = ? \text{ kg TS/kg} \cdot ? \text{ kg VS/kg TS} \cdot 0 \text{ kg} \cdot 1086.4 \text{ g COD/kg VS} = 0 \text{ g COD}$$

$$\text{COD}_{\text{acc}} = \text{COD}_{\text{w2}} \cdot V_{\text{w2,react}} - \text{COD}_{\text{w1}} \cdot V_{\text{w1,react}} = ? \text{ mg/L} \cdot 975 \text{ L} - 9\,000 \text{ mg/L} \cdot 975 \text{ L} \approx 0 \text{ g COD}$$

$$\text{COD}_{\text{red}} = 0 - (0 + 0 + 0) \approx 0 \text{ g COD}$$

$$\text{Theoretical methane volume } V_{\text{methane}} = 0.350 \cdot 0 \approx 0 \text{ NL}$$

Week 28:

$$\text{COD}_{\text{in}} = 10\,499.04 \text{ mg/L} \cdot 1014.86 \text{ L} = 10655 \text{ g COD}$$

$$\text{COD}_{\text{eff}} = 93.65 \text{ mg/L} \cdot 955.78 \text{ L} = 89.5 \text{ g COD}$$

$$\text{COD}_{\text{sludge}} = 0.013 \text{ kg TS/kg} \cdot (1 - 0.272) \text{ kg VS/kg TS} \cdot 44.50 \text{ kg} \cdot 1086.4 \text{ g COD/kg VS} = 458 \text{ g COD}$$

$$\text{COD}_{\text{acc}} = \text{COD}_{\text{w2}} \cdot V_{\text{w2,react}} - \text{COD}_{\text{w1}} \cdot V_{\text{w1,react}} = 7\,810.63 \text{ mg/L} \cdot 987 \text{ L} - ? \text{ mg/L} \cdot 975 \text{ L} \approx -1071 \text{ g COD}$$

$$\text{COD}_{\text{red}} = 10655 - (89.5 + 458 - 1071) \approx 11179.5 \text{ g COD}$$

$$\text{Theoretical methane volume, } 0^\circ\text{C and 1 atm, } V_{\text{methane}} = 0.350 \cdot 11179.5 \approx 3915 \text{ NL}$$

Week 29:

$$\text{COD}_{\text{in}} = 14\,498.68 \text{ mg/L} \cdot 812.81 \text{ L} = 11785 \text{ g COD}$$

$$\text{COD}_{\text{eff}} = 136.46 \text{ mg/L} \cdot 782.56 \text{ L} = 107 \text{ g COD}$$

$$\text{COD}_{\text{sludge}} = 0.027 \text{ kg TS/kg} \cdot (1 - 0.244) \text{ kg VS/kg TS} \cdot 43.68 \text{ kg} \cdot 1086.4 \text{ g COD/kg VS} = 969 \text{ g COD}$$

$$\text{COD}_{\text{acc}} = \text{COD}_{\text{w2}} \cdot V_{\text{w2,react}} - \text{COD}_{\text{w1}} \cdot V_{\text{w1,react}} = 9\,893.46 \text{ mg/L} \cdot 971 \text{ L} - 7\,810.63 \text{ mg/L} \cdot 987 \text{ L} = 1901 \text{ g COD}$$

$$\text{COD}_{\text{red}} = 11785 - (107 + 969 + 1901) = 8808.47 \text{ g COD}$$

$$\text{Theoretical methane volume, } 0^\circ\text{C and 1 atm, } V_{\text{methane}} = 0.350 \cdot 8808.47 = 3085 \text{ NL}$$

Week 30:

$$\text{COD}_{\text{in}} = \text{no value available mg/L} \cdot 173.69 \text{ L} = ? \text{ g COD}$$

$$\text{COD}_{\text{eff}} = \text{no value available mg/L} \cdot 166.44 \text{ L} = ? \text{ g COD}$$

$$\text{COD}_{\text{sludge}} = ? \text{ kg TS/kg} \cdot ? \text{ kg VS/kg TS} \cdot 12.92 \text{ kg} \cdot 1086.4 \text{ g COD/kg VS} = ? \text{ g COD}$$

COD

$$\text{COD}_{\text{acc}} = \text{COD}_{\text{w2}} \cdot V_{\text{w2,react}} - \text{COD}_{\text{w1}} \cdot V_{\text{w1,react}} = ? \text{ mg/L} \cdot 965 \text{ L} - 9\,893.46 \text{ mg/L} \cdot 971 \text{ L} \approx 400 \text{ g COD}$$

$$\text{COD}_{\text{red}} = ? - (? + ? + 400) = ? \text{ g COD}$$

$$\text{Theoretical methane volume, } 0^\circ\text{C and 1 atm, } V_{\text{methane}} = 0.350 \cdot ? = ? \text{ NL}$$

Week 31:

$$\text{COD}_{\text{in}} = 15\,998.54 \text{ mg/L} \cdot 446.13 \text{ L} = 7138 \text{ g COD}$$

$$\text{COD}_{\text{eff}} = 101.68 \text{ mg/L} \cdot 459 \text{ L} = 46.7 \text{ g COD}$$

$$\text{COD}_{\text{sludge}} = 0.030 \text{ kg TS/kg} \cdot (1 - 0.247) \text{ kg VS/kg TS} \cdot 16.61 \text{ kg} \cdot 1086.4 \text{ g COD/kg VS} = 408 \text{ g COD}$$

$$\text{COD}_{\text{acc}} = \text{COD}_{\text{w2}} \cdot V_{\text{w2,react}} - \text{COD}_{\text{w1}} \cdot V_{\text{w1,react}} = 11\,976.30 \text{ mg/L} \cdot 936 \text{ L} - ? \text{ mg/L} \cdot 965 \text{ L} \approx 1199 \text{ g COD}$$

$$\text{COD}_{\text{red}} = 7138 - (46.7 + 408 + 1199) \approx 5484.58 \text{ g COD}$$

$$\text{Theoretical methane volume, } 0^\circ\text{C and 1 atm, } V_{\text{methane}} = 0.350 \cdot 5484.58 \approx 1921 \text{ NL}$$

Week 32:

$$\text{COD}_{\text{in}} = 9\,999.09 \text{ mg/L} \cdot 1033.10 \text{ L} = 10330 \text{ g COD}$$

$$\text{COD}_{\text{eff}} = 131.11 \text{ mg/L} \cdot 998.5 \text{ L} = 131 \text{ g COD}$$

$$\text{COD}_{\text{sludge}} = 0.034 \text{ kg TS/kg} \cdot (1 - 0.279) \text{ kg VS/kg TS} \cdot 25.90 \text{ kg} \cdot 1086.4 \text{ g COD/kg}$$

$$\text{VS} = 690 \text{ g COD}$$

$$\text{COD}_{\text{acc}} = \text{COD}_{\text{w2}} \cdot V_{\text{w2,react}} - \text{COD}_{\text{w1}} \cdot V_{\text{w1,react}} =$$

$$15\,621.26 \text{ mg/L} \cdot 943 \text{ L} - 11\,976.30 \text{ mg/L} \cdot 936 \text{ L} = 3521 \text{ g COD}$$

$$\text{COD}_{\text{red}} = 10330 - (131 + 690 + 3521) = 5988.29 \text{ g COD}$$

$$\text{Theoretical methane volume, } 0^\circ\text{C and } 1 \text{ atm, } V_{\text{methane}} = 0.350 \cdot 5988.29 = 2097 \text{ NL}$$

Week 33:

$$\text{COD}_{\text{in}} = \text{no value available mg/L} \cdot 0 \text{ L} = 0 \text{ g COD}$$

$$\text{COD}_{\text{eff}} = \text{no value available mg/L} \cdot \text{no value available L} = ? \text{ g COD}$$

$$\text{COD}_{\text{sludge}} = ? \text{ kg TS/kg} \cdot ? \text{ kg VS/kg TS} \cdot 0 \text{ kg} \cdot 1086.4 \text{ g COD/kg VS} = 0 \text{ g COD}$$

$$\text{COD}_{\text{acc}} = \text{COD}_{\text{w2}} \cdot V_{\text{w2,react}} - \text{COD}_{\text{w1}} \cdot V_{\text{w1,react}} =$$

$$? \text{ mg/L} \cdot 938 \text{ L} - 15\,621.26 \text{ mg/L} \cdot 943 \text{ L} = ? \text{ g COD}$$

$$\text{COD}_{\text{red}} = 0 - (? + 0 + ?) \approx 0 \text{ g COD}$$

$$\text{Theoretical methane volume, } 0^\circ\text{C and } 1 \text{ atm, } V_{\text{methane}} = 0.350 \cdot 0 \approx 0 \text{ NL}$$

Appendix 6

The amount of methane, CH₄, produced per unit of COD converted under anaerobic conditions is equal to 0.350 NL CH₄/g COD at normal conditions (0°C and 1 atm), where NL stands for normal litres. The quantity of methane at other conditions than standard is determined by using the universal gas law, to determine the volume of gas occupied by one mole of CH₄ at the temperature in question.

$$V = \frac{nRT}{P}$$

where V = volume occupied by the gas, L

n = moles of gas, mole

R = universal gas law constant, 0.0820562 (atm·L)/(mole·K)

T = temperature, K (273.15 + °C)

P = absolute pressure, atm

Thus, at 36°C for example, the volume occupied by one mole of CH₄ is

$$V = \frac{(1 \text{ mole})(0.082057 \text{ atm}\cdot\text{L} / \text{mole}\cdot\text{K})(273.15 + 36)\text{K}}{1.0 \text{ atm}} = 25.368 \text{ L}$$

Because the COD in one mole of CH₄ is equal to 63.9976 g, the amount of methane produced per unit of COD converted under anaerobic conditions at 36°C is equal to 0.396 L, as it is shown below:

$$(25.368 \text{ L CH}_4/\text{mole CH}_4)/(63.9976 \text{ g COD/mole CH}_4) = 0.396 \text{ L CH}_4/\text{g COD}_{\text{reduced}}$$

Gases are, however, generally presented in normal litres i.e. the volume of the gas at 0 °C and 1 atm. This gives a volume of

$$V_{\text{normal}} = \frac{(1 \text{ mole}) \cdot (0.082057 \text{ (atm}\cdot\text{L)/(mole}\cdot\text{K)}) \cdot (273.15 \text{ K})}{(1.0 \text{ atm})} = 22.41 \text{ NL}$$

One mole of CH₄ is still equal to 63.9976 g COD, which gives 0.350 L CH₄/g COD according to

$$(22.41 \text{ NL CH}_4/\text{mole CH}_4)/(63.9976 \text{ g COD/mole CH}_4) = 0.350 \text{ NL CH}_4/\text{g COD}_{\text{reduced}}$$

from Metcalf & Eddy (2003), *10-2 General Design Considerations for Anaerobic Treatment Processes*, p 992-993.