Sludge treatment in an Anaerobic BioReactor with external Membranes

Julien Negre, AP/Ecole des Mines d'Albi-Carmaux
R nr 16, september 2007

STOCKHOLM Vatten

ECOLE DES MINES D'ALBI
C A R M A U X

Sludge treatment in an Anaerobic BioReactor with external Membranes

Graduating Internship Report

June 2007

Stockholm Vatten AB
Stockholm (Sweden)

Supervisor, Stockholm Vatten AB : Daniel HELLSTRÖM

Supervisor, Ecole des Mines d'Albi-Carmaux : Patricia ARLABOSSE

NEGRE Julien

Option Eco Industries

IFI 2007

ECOLE DES MINES D'ALBI
C A R M A U X

Sludge treatment in an Anaerobic BioReactor with external Membranes

Graduating Internship Report

June 2007

Stockholm Vatten AB
Stockholm (Sweden)

Supervisor, Stockholm Vatten AB : Daniel HELLSTRÖM

Supervisor, Ecole des Mines d'Albi-Carmaux : Patricia ARLABOSSE

NEGRE Julien

Option Eco Industries

IFI 2007

Acknowledgements

I would like to thank first of all Daniel Hellström, Head of Investment and Planning, and supervisor of my graduating internship.
Thank you for this opportunity at Hammarby Sjöstadsverket, this chance was really important for me. Thank you for directions and advice given during this internship.

I would like to express my gratitude to all the Sjöstadsverket staff, without your help I would not be able to run this pilot unit…
Special thanks to both Mikael Waltner and Lars Bengtsson for your precious advices, for being so cheerful and for all the discussions…

I would like to thank Rasmus Fröhlich for all his advices and his motivation. Thank you for all these weeks when you were my "mentor".

Thanks to Patricia Arlabosse, supervisor of my graduating internship. Thank you for your help and for your advices.

I would like to thank Lars-Erik Olsson, from AnoxKaldnes, for his help and for advice given during this internship.

I would like to express my gratitude to Berndt, Lena, Mitra, Maria, Clara, Klas, Åsa and Thomas, that was really nice to know you and to work with you.

To all of you,

Tack så mycket.

Abstract

This graduating internship has been performed at Sjöstadsverket, 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 carried out to a completely mixed bioreactor where anaerobic degradation process occurs. This reactor is combined with a VSEP membrane unit, ensuring the separation step between permeate and concentrated sludge, led back to the reactor. Temperature in this one was 36°C during all the study.

A period was necessary to make sure the pilot unit could be run properly. During the evaluation period, major troubles came up, disturbing the continuous running 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 to process to be operated in a continuous way. However, these new configurations did not allow running the pilot unit for hours, as it should be. As a consequence, HRT was around 6.5 days during the most significant test, but this was performed typically in two hours instead of four or five hours in a normal running. Other type of problems occurred concerning biogas production measures: the registered flow did not correspond to the expected value. Some investigations have been made, but nothing could really solve this problem.

These troubles resulted in measuring 1.61 up to 27.85 % of the expected methane volume. The gas production range varied from 0.0023 to 0.0898 g CH_4 / g VS_{in}. The degree of VS reduction started at 2.75 % to reach 293.37 %. These unrealistic values are also a consequence of both difficulties to run the pilot unit and inability to register a convenient biogas flow. The pressure and flux for the membranes were evaluated as well. During short periods of satisfying running, the operating pressure was around 4 bar. Due to the variability of permeate flow (from 700 mL/min to 1500 mL/min), the flux through the membranes is in the range 26.42 $L/m^2.h$ to 56.60 $L/m^2.h$. The maximum organic load rate was 5.161 kg VS/week, i.e. 5.27 g VS/L.week. The term “maximum” is meaningless here, as no higher loads were applied to the system and thus no efficiency in producing biogas was estimated. Further experiments should be performed in this way to evaluate the amount of organic material that could be introduced into the anaerobic bioreactor.

Despite these problems, the efficiency concerning biological treatment itself could be considered satisfying, as COD reduction reached at least 98.9 % and TOC reduction at least 96.7 %. However, Nitrogen and Phosphorus monitoring revealed rather high concentrations within outgoing permeate flow, respectively 110 mg/L and 15 mg/L (minimum values).

Table of content

Introduction **1**

Part I : Introduction and project framework **2**

I. Overview of the working environment **2**
I.1 About Henriksdal wastewater treatment plant… 2
I.2… in which Hammarby Sjöstadsverket is settled 2

II. Details on project's objectives **3**

Part II : Theory **5**

I. Anaerobic fermentation and oxidation **5**
I.1 Description of anaerobic process 5
I.1.1 Hydrolysis 5
I.1.2 Fermentation 6
I.1.3 Methanogenesis 6
I.2 Microbiology and bacteria relationships under anaerobic conditions 7
I.3 Stoichiometry in Anaerobic Fermentation and Oxidation 8
I.4 Environmental factors influencing anaerobic process 9
I.5 Toxic and inhibitory substances for anaerobic digestion 10
I.6 Synthesis regarding anaerobic processes running 13

II. Description of the Anaerobic Membrane BioReactor pilot unit (AnMBR) **15**
II.1 Considerations regarding biological reactors including external membranes 15
II.2 VSEP operating principles and properties 16
II.2.1 General description of the membrane filtration unit 16
II.2.2 Details on membrane stack 17
II.2.3 Vibration effects and practical application 18
II.3 Membrane fouling 20
II.3.1 Influence of biomass concentration and structure 22
II.3.2 Influence of organic substances 22
II.3.3 Influence of inorganic substances 23
II.3.4 Reversible and irreversible fouling 23
II.3.5 Observations from the pilot unit 24

Part III : Material and methods **25**

I. Technical description of the Anaerobic Membrane BioReactor unit (AnMBR) **25**
I.1. Storage of primary sludge in the mixer tank 25
I.2 The BioReactor, major component of the pilot unit 26
I.3 Technical considerations regarding the membranes 26
I.4 Other components of the pilot unit 28

II. Different methods and procedures applied to pilot unit running 28
II.1 Several phases during the study 28
II.2 Sample taking and storage 29
II.3 Pilot unit monitoring and analyses 29

III. Troubles that occurred during the evaluation period 31
III.1 The main problem: a low feeding pressure 31
III.2 Trouble related to biogas production measuring system 33
III.3 Difficulties regarding primary sludge transfer 33

Part IV : Results and discussion 35

I. General monitoring of the bioreactor 35
I.1 pH monitoring 35
I.2 Monitoring of VFA 36
I.3 Monitoring of Total Solids (TS) 36

II. Results related to methane production 37
II.1 Potential methanogenic activity and methane produced 37
II.2 Comparison with expected gas production 38
II.3 VS reduction from primary sludge to bioreactor sludge 40
II.4 Biogas production corresponding to VS introduced in the system 41
II.5 The maximum organic load rate 42

III. Results regarding organic issues 42
III.1 COD reduction 42
III.2 TOC reduction 44
III.3 Nitrogen monitoring 44
III.4 Phosphorus monitoring 45

IV. Discussion about the reliability of the results 46

Conclusion 48

References 49

Table of illustrations 51

Appendix 52

Introduction

Urban residual sludge management is a major issue in wastewater treatment processes, as they are most of the time a very wet waste, difficult to handle and to give value to. Nowadays, several ways of valorization are available, and one among them is biogas production. The main interest in promoting biogas production is energy recovery, which can be achieved by recovering methane. This gas can then be used in diverse applications (electricity, gas engine, car and bus fuel, etc.).

The evaluation of biogas production was performed in an Anaerobic Membrane BioReactor pilot unit, at Sjöstadsverket, a research site receiving wastewater from Hammarby Sjöstad neighbourhood. This facility is settled within Henriksdal wastewater treatment plant, managed by Stockholm Vatten AB.

The AnMBR consists of an anaerobic completely mixed reactor followed by a membrane separation stage. The goal of this study was to operate this pilot unit at Hydraulic Retention Time lower than 10 days, at 35 – 37°C. This temperature range corresponds to an optimum for mesophilic micro-organisms. Other operating parameters were considered, Total Solids content for example which limit was set at 2 %. Volatile Fatty Acids critical concentration was set to 500 mg/L and the lowest pH value for the running of the pilot unit was set to 6.8.

The questions related to this pilot unit running were the degree of Volatile Solids reduction, an evaluation of biogas production (more precisely methane production expressed as gCH_4/gVS_{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: description and reasons for them to occur.

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

Part I : Introduction and project framework

I. Overview of the working environment

I.1 About Henriksdal wastewater treatment plant…

Henriksdal wastewater treatment plant is the main facility of Stockholm Vatten in the urban county. It was opened in 1941 and had the capacity for the low-grade treatment of 150 000 m^3 of wastewater per day. Several extensions occurred over years, to include chemical and biological treatments, to reduce nitrogen emissions and to improve phosphorus treatment.

Henriksdal is one of the world's largest underground treatment plant. It covers around 300 000 m^2 and has approximately 18 km of tunnels, with basin blocks dug into the rock. The surface facilities include the main office, mechanical treatment, sludge tanks, upper parts of sludge thickeners, digesters, gas holder, gas collection plant and gas storage. Sludge treatment takes place in a separate facility, two km from Henriksdal[1]. Regarding biogas production for both Henriksdal and Bromma plants, 13 millions m^3 were produced in 2005.

I.2… in which Hammarby Sjöstadsverket is settled

The Hammarby Sjöstad project is a huge urban building project in the Southern part of inner Stockholm, started in 2001. The goal is to turn old local industries and harbour neighbourhood into 9000 flats and into a total activity area of 250 000 m^2, in an environmentally minded way. By the year 2012, about 30 000 people will live and work in this area. The environmental development programme concerns energy, transports, waste and water issues.

A part of this environmentally minded project involves obviously researches in wastewater treatment field, thus concerning Stockholm Vatten AB. In order to perform some studies, several types of treatment lines have been designed, built and run within Henriksdal site to evaluate efficiency of treatment methods (so-called Sjöstadsverket). These four lines model both aerobic and anaerobic processes; a short description is given below. They could be supplied by both Henriksdal and Hammarby Sjöstad area wastewaters.

- **Line 1**: Aerobic treatment with activated sludge, nitrogen and phosphorus biological reduction. This line is a copy of Henriksdal wastewater treatment, completed with phosphorus reduction stage. It basically includes a pre-sedimentation tank, six "biotanks" (5 m^3 each), a post sedimentation tank, a sand filter and a digester.

- **Line 2**: Aerobic treatment with membrane bioreactor and Reverse Osmosis (RO). This line contains a drum filter, a bioreactor with immersed membranes (16.5 m^3) and a RO module (5 m^3).

[1] The Henriksdal Wastewater Treatment Plant, document from Stockholm Vatten AB.

- **Line 3**: Anaerobic treatment with fluidized bed and RO. It includes a pre-sedimentation tank, a fluidized bed (2.8 m^3), a sand filter and a RO module.

- **Line 4**: Anaerobic treatment with UASB reactors and nitrogen reduction. UASB stands for Upflow Anaerobic Sludge Blanket reactors. A biological polishing stage is present in this process, to achieve nitrogen reduction goals. Its volume is 5.1 m^3. The volume for UASB reactors is 2.5 m^3 each.

These are the basic configurations of the lines, but they are submitted to many changes as well, depending on the research needs. The drum filter mentioned in Line 2 provides primary sludge to a mixer tank (considered as the first component of the pilot unit used for this study, see Material and methods).

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 anaerobic digestion in this pilot unit with a Total Solids (TS) content > 5 % in the reactor and a **Hydraulic Retention Time HRT < 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 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 respected some threshold values: the **pH** had to 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 were related to:

- the degree of VS reduction of the primary sludge
- gas production, expressed as g CH_4/g VS_{in}
- the description of the operational problems. Which components were involved and why such troubles occurred ? Details on the provided solutions were also included.
- the pressure and flux for the membranes
- the maximum organic loading rate

The boundaries of the project actually corresponded to the “physical” boundaries of the pilot unit. The project did not include all the maintenance and preparation work required by Line 2 for example. However, every component involved in the pilot unit, starting at the mixer tank, entered into the maintenance requirements of this line.

Part 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 containing micro-organisms, 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, 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 on Figure 1. The starting point on the schematic 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 termed **hydrolysis**. Particulate material is converted to soluble compounds that can be then 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 on Figure 1. Organic substrates serve as both the electron donors and acceptors. The principal products of fermentation are acetate, hydrogen, CO_2, propionate and butyrate. The propionate, the butyrate and a large part of the VFA and of the alcohols (ethanol, glycerol) are assimilated by the autotrophic acetogenic bacteria to also produce hydrogen, CO_2 and acetate. This step is known as the **acetogenesis**. Thus, the final products of fermentation (acetate, hydrogen and CO_2) are the precursors of methane formation (**methanogenesis**).

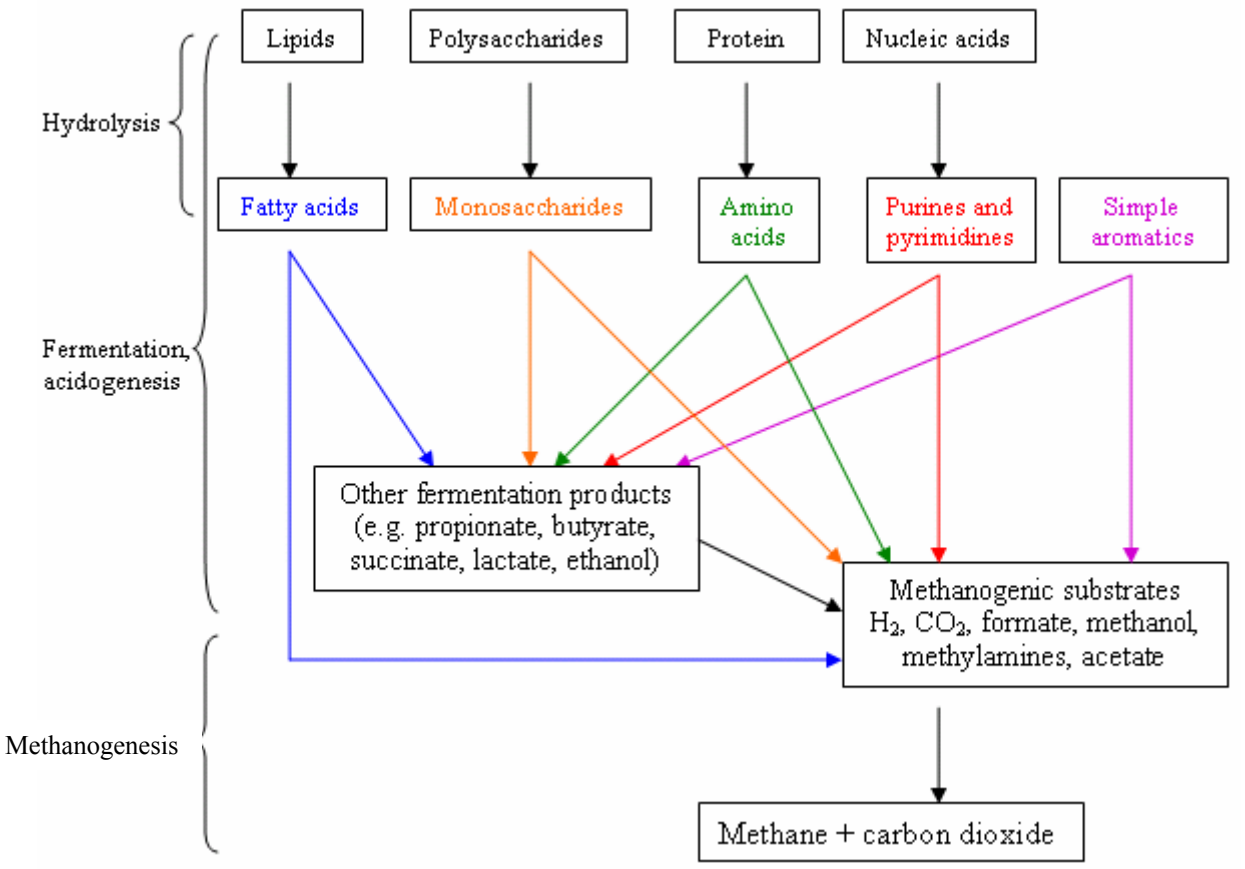


Figure 1: Anaerobic process degradation scheme[1].

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, termed *aceticlastic methanogens*, split acetate into methane and carbon dioxide. The second group, termed hydrogen-utilizing methanogens, uses hydrogen as the electron donor and CO_2 as the electron acceptor to produce methane. Bacteria within anaerobic processes, termed *acetogens*, are also able to use CO_2 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 on Figure 2, about 72 % of the methane produced in anaerobic digestion is from acetate formation. In sludge anaerobic digestion, the limiting step of this biological process is hydrolysis, as kinetics concerning this stage is the slowest[1].

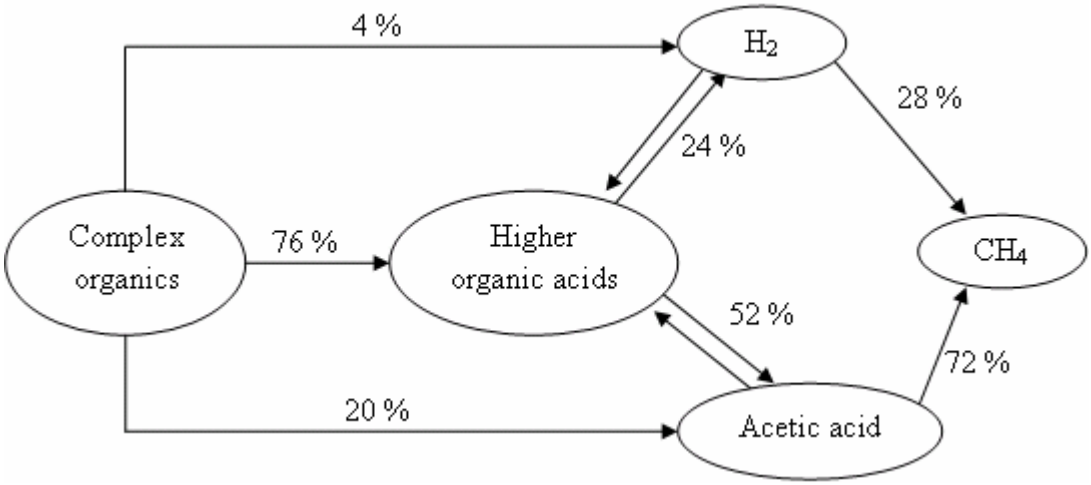


Figure 2: Carbon and hydrogen flow in anaerobic digestion process[2].

I.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 termed *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 H_2, 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 termed interspecies hydrogen transfer.
The methanogenic organisms serve as a hydrogen sink that allows the fermentation reactions to proceed. **If process troubles 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 pH**[3].

[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.

Nuisance organisms in anaerobic processes are the sulphate-reducing bacteria, which can be a problem when the wastewater contains 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 sulphide[1].

I.3 Stoichiometry in Anaerobic Fermentation and Oxidation

A limited number of substrates are used by the methanogenic organisms. The reactions defined as CO_2 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 acetate, respectively:

$4H_2 + CO_2 \rightarrow CH_4 + 2H_2O$

$4HCOO^- + 4H^+ \rightarrow CH_4 + 3CO_2 + 2H_2O$

$4CO + 2H_2O \rightarrow CH_4 + 3CO_2$

$4CH_3OH \rightarrow 3CH_4 + CO_2 + 2H_2O$

$4(CH_3)_3N + H_2O \rightarrow 9CH_4 + 3CO_2 + 6H_2O + 4NH_3$

$CH_3COOH \rightarrow CH_4 + CO_2$

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

$CH_3COO^- + H_2O \rightarrow CH_4 + HCO_3^-$

In the reaction for the acetilastic methanogens (last reaction shown in the list above), the acetate 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.

$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$

Under anaerobic conditions, at 36°C, the volume of methane produced with respect to COD consumed is 0.396 L CH_4/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/m^3. Variable composition of biogas is given in Table 1.

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

Table 1: Biogas composition[1].

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.

I.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 substrate[2].

- 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 in this study. The bioreactor temperature remained constant during all the evaluation period, at 36°C ± 0.3.

[1] GAY (J.), « Lutte contre la pollution des eaux », Techniques de l'ingénieur, G 1455, p 7.
[2] RODRIGUEZ SUSA (M.), « Etude d'un bioréacteur anaérobie à membranes immergées pour le traitement des eaux résiduaires », p 15.

- increase in microbial decay rate, as cellular lysis is increased too
- affinity constant changes (ks)

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 $NH_4(HCO_3)$[1].

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

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

I.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 away from the bioreactor (under its molecular form). The presence of a toxic substance does not mean 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 2.

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

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

Table 2: Toxic and inhibitory organic compounds for anaerobic digestion[1].

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 3, and results from Stockholm Vatten laboratory as well.

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

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^+	1500 – 3000	3000	190 - 250	110 - 220
Sulphide S^{2-}	200	200		
Copper Cu^{2+}		0.5 (soluble) 50 – 70 (total)	3.1 (total)	< 0.02
Chromium Cr(VI)		3 (soluble) 200 – 250 (total)	1.5 (total)	< 0.02
Chromium Cr(III)		180 – 420 (total) 2 (soluble)	1.5 (total)	< 0.02
Nickel Ni^{2+}		30 (total)	0.78 (total)	< 0.02
Zinc Zn^{2+}		1 (soluble)	9200 (mg/kg TS)	< 0.02 (mg/kg TS)
Silver Ag (total)			0.04	< 0.02
Cadmium Cd (total)			0.011	< 0.005
Mercury Hg (total)			0.0057	$< 0.05\ 10^{-3}$
Lead Pb (total)			0.17	< 0.05
Iron Fe (total)			200	1.6

Table 3: Toxic and inhibitory inorganic compounds for anaerobic digestion and results from the pilot unit[1].

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 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 consume organic compounds in the anaerobic reactor and produce hydrogen sulphide (H_2S).

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

Based on the following stoichiometry for H_2S oxidation, 2 moles of oxygen are required per mole of H_2S, just as for methane oxidation.

$$H_2S + 2O_2 \rightarrow H_2SO_4$$

Thus, the amount of H_2S produced per unit COD is the same as for methane (0.40 L H_2S/g COD used at 35°C). Hydrogen sulphide is malodorous and corrosive to metals. Combustion products formed from sulphur oxidation are considered air pollutants. In contrast to methane, H_2S 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 production**[1]. 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 (NH_3), 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 operating conditions and acclimatization time.

I.6 Synthesis regarding anaerobic processes running

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).
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/m^3 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**

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.

[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.

- **Methane production**, a potential energy source and therefore the main interest of anaerobic digestion

- **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**, as anaerobic processes generally have higher volumetric organic loads than aerobic processes.

- **Rapid response to substrate addition** after long period without feeding.

- A very good ability for **treating pollutants** such as PAH (Polycyclic Aromatic Hydrocarbons), PCB (PolyChlorinated Biphenyls) and nitrogenous organic compounds[1].

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

- **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 micro-organisms types, thus optimal conditions may not be reached at the same time.

- **Much more sensitive** to the adverse effect of lower **temperatures** on reaction rates, **pH dependent** and extremely sensitive to **environmental changes**. Micro-organisms population may be more susceptible to troubles due to **toxic substances**.

- **May require alkalinity addition**:
  Alkalinity concentrations of 2000 to 3000 mg/L (as $CaCO_3$) may be needed in anaerobic processes to maintain an acceptable pH with the high CO_2 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, a significant cost may be incurred to purchase alkalinity.

- **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.

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

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

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

II.1 Considerations regarding biological reactors including external membranes

Membranes Biological Reactors (MBRs) consist of a biological reactor (so-called bioreactor) with suspended biomass and solids separation by microfiltration 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 a microfiltration 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 advantages[1]:

- higher volumetric loading rates, so shorter reactor Hydraulic Retention Times (HRT)
- longer Solids Retention Times (SRTs) resulting in less sludge production, as well as a total separation with HRT
- operation at low Demand in 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 detailed (Figure 3).

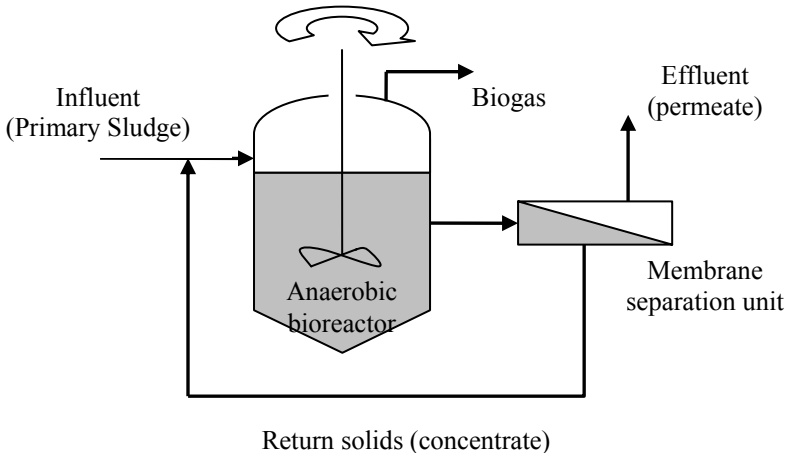


Figure 3 : Anaerobic bioreactor with external membrane separation[2].

[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 processes[1].

Membrane fouling and loss of active cells are critical issues for the proper running 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, consequence of a rise in the pH as the flow passes through the membrane and CO_2 escapes from the liquid. Membrane fouling will be discussed in a further part of this chapter.

To avoid fouling troubles, a "special" type of membrane module has been installed in 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*) was developed by NEW LOGIC Research Inc. since 1987, as an enhanced liquids/solids separation system. The model used at Sjöstadsverket, 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 this configuration.

In the first seconds of running, the pressure has to be built up in the pilot unit and especially within the membrane stack. A minimum pressure of approximately 2.5 bar 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 bar. 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-end 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, 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 running period. The control system automatically records several parameters such as feeding pressure, concentrate pressure, permeate flow, temperature and others that can be read on the operating screen from 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 mass. An AC engine spins this eccentric mass 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 controlling efficiently 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.

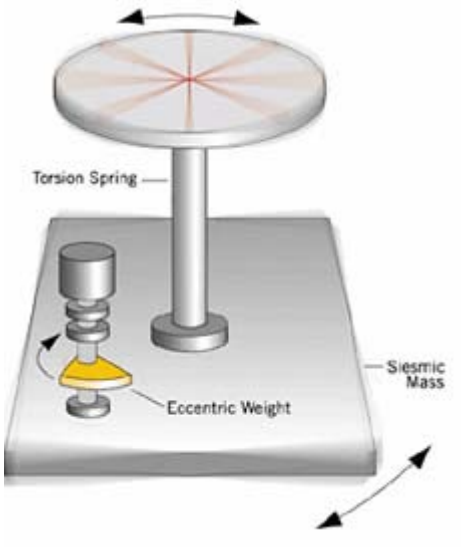


Figure 4 : VSEP resonating drive system[1].

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 split, 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.

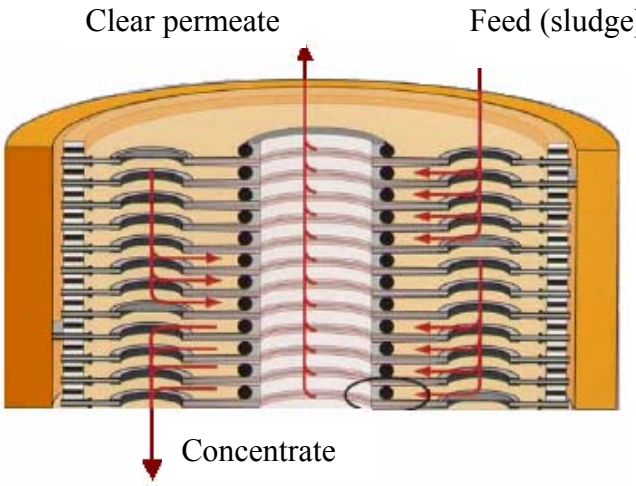


Figure 5 : Flow diagram through the membrane stack[1].

The separation process used in this pilot unit is a microfiltration 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 solutes[2]. Some details and characteristics regarding the membranes themselves are developed in a further part (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 membranes 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 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.

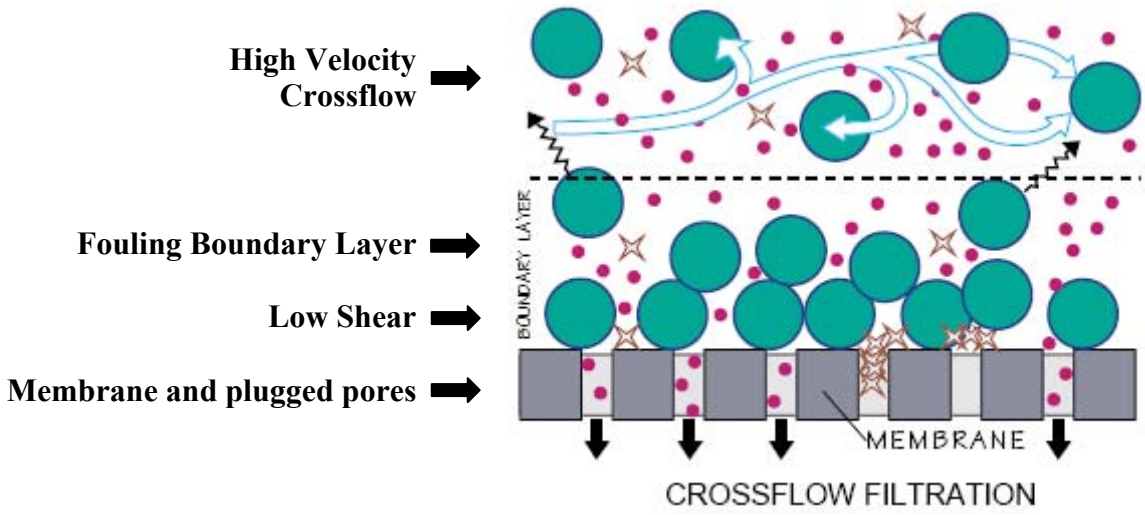


Figure 6 : Illustration of membrane fouling[1].

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 stack[2]. 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.

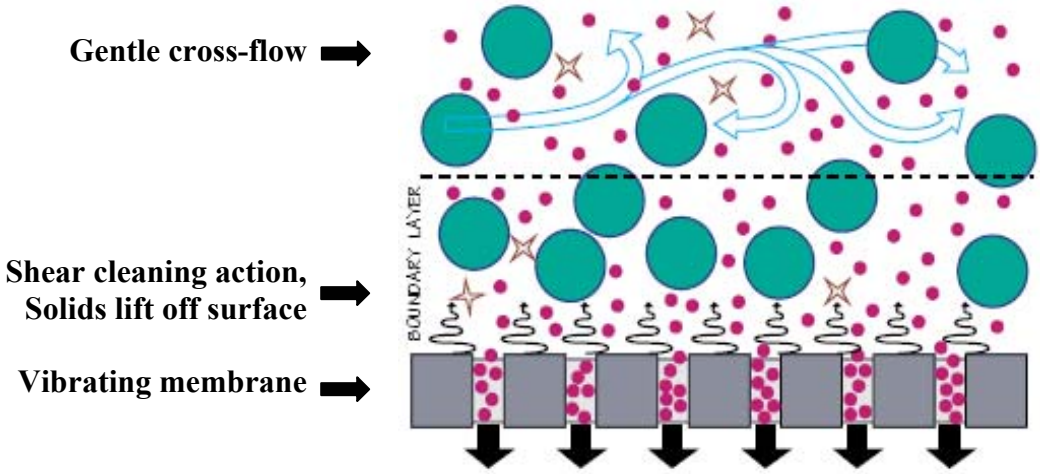


Figure 7 : Effects of shear waves on membrane surface[3].

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: 0.70 – 0.85 inch, 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). This is very important to know the total volume of permeate produced by the membranes for a given running period. 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 of this way of proceeding and this is why a trouble-free running 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 in the element on the feed stream of the membrane. Fouling can be either reversible or irreversible[1]. 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. 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.), 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 4.

Type of membrane fouling	**Fouling** (cake formation sometimes identified as biofilm formation)	**Scaling** (precipitation)	**Damage** to membrane
Responsible constituents	Metal oxides Organic and inorganic colloids Bacteria Microorganisms Concentration, polarization	Calcium sulphate Calcium carbonate Calcium floride Barium sulphate Metal oxide formation Silica	Acids Bases extreme pH values Free chlorine Bacteria Free oxygen

Table 4: Constituents in wastewater responsible for membrane fouling mechanism[2].

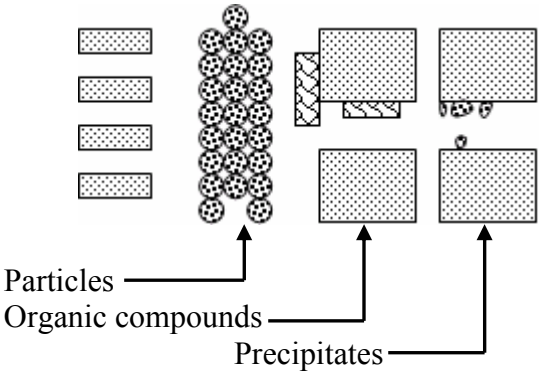
Fouling of the membrane can occur in three general forms:

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

[1] METCALF & EDDY, from Table 11-16, p 1105.
[2] METCALF & EDDY, from Table 11-18, p 1118.

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

$R_T = R_m + R_d + R_a + R_p$



where

R_T is the total resistance to filtration

R_m is the membrane resistance

R_d is surface deposit resistance

R_a is the adsorption resistance

R_p is the resistance to filtration due to internal pore blockade

Figure 8: Serial resistance conceptual model[1].

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 "Wastewater Engineering, Treatment and Reuse" description.

Gel/cake formation may happen when most of the solid matter in the feedwater 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 feedwater 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 SUSA (M.), « Etude d'un bioréacteur anaérobie à membranes immergées pour le traitement des eaux résiduaires », Figure I.9, p 33.

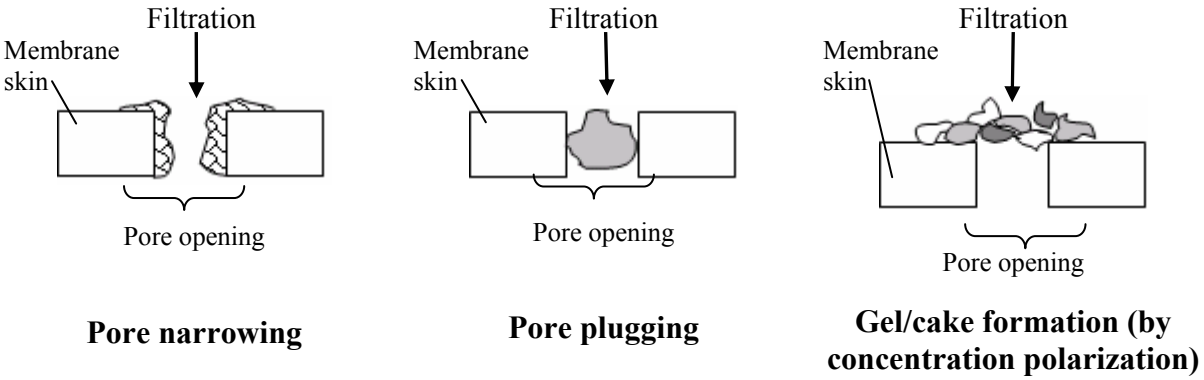


Figure 9: Modes of membrane fouling[1].

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 states that most of the authors have observed a permeate flux decline while micro-organisms concentration increases within the bioreactor. However, these diminution ranges are varying. 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 floc size diminution of anaerobic sludge leads to an increase of filtration resistance. Indeed, a lower particle pore size results in a decrease of porosity in the formed cake; the resistance to filtration is thus raised.

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 (1996, 1998), colloids are responsible for membrane fouling: 83 % of total resistance to filtration is

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

caused by the phase containing colloids, whereas flocculated micro-organisms are responsible for 18 % of total resistance to filtration. Moreover several authors state that 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 ($MgNH_4PO_4 \bullet 6H_2O$); they are one reason of membrane fouling. Others common precipitates responsible for membrane fouling within anaerobic processes are calcium phosphate ($Ca_3(PO_4)_2 \bullet xH_2O$), hydroxyl apatite ($Ca_5(PO_4)_3OH$), newberyite ($MgHPO_4 \bullet 3H_2O$), 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 know (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 biofilm 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 pilot unit running, 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 its running, 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 $L/m^2.h$ at 40°C to 43 $L/m^2.h$ at 47°C. This trend concerning flux improvement due to temperature increase could be related to[1]:

- 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 few minutes running, 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.

Part III : Material and methods

The pilot unit used in this study is described in this part. 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 run this unit, the way samples were taken and stored, the analyses and related calculations are explained as well.
Consequence of this pilot unit running, different troubles 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 m^2 and its volume is 1.5 m^3. 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 rise 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 value for the bioreactor (1.1 %).

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 around 20 cm deep 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 carried 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, anaerobic process occurs, thus producing biogas. It is a 2-meter high cylinder, approximately 1 m in diameter, the total volume is 1.4 m^3 and it is assumed to be completely mixed (continuous agitation with a propeller).

Figure 10: Anaerobic bioreactor[1].

Figure 10 illustrates the previous description. A pre-sedimentation tank can be seen to the right; this where 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 rotating hand valve could be opened or closed to control hot water flow. Therefore, temperature of activated sludge could be set this way.
During this study, temperature within the bioreactor remained stable at **36°C ± 0.3**, right in the optimum range for mesophilic conditions.

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 % corresponds to 1.4 m^3. During the evaluation period, the level was kept more or less constant, around 60 %, i.e. roughly 840 L. In a second phase, the level was increased up to 70 % (about 980 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 troubles occurred in biogas measuring system during the evaluation period; they are detailed in a further part of this chapter.

I.3 Technical considerations regarding the membranes

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

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

themselves, and Polyester for drain clothes. The total area for the membrane stack is 1.59 m^2 (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 bar. 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 changing[2].

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 biofilm 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 running 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 for the membrane stack (1.59 m^2), the values for the flux varied from 26.42 L/m^2.h to 56.60 L/m^2.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 running (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, Sjöstadsverket, 06/08/2007.
[2] Personal picture, Sjöstadsverket, 03/29/2007.

I.4 Other components of the pilot unit

To avoid excess clogging due to activated sludge, two filters are placed in between sludge recirculation loop and the membranes (see **Appendix 2**). The main filter is 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 run 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 rot/min.
The recirculation pump is a little bit more powerful, at 0.86 kW, for a maximum rotation velocity of 1650 rot/min. This model has been installed recently in order to fix troubles related to low feeding pressure.
The centrifugal pump has been manufactured by ABB Motors. At 60 Hz, its power is 0.45 kW and its rotation velocity reaches 3440 rot/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 trouble, 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 1.5 to 8 kgf/cm^2.

II. Different methods and procedures applied to pilot unit running

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 running of the pilot unit.
The next stage concerned membrane substitution, as 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 up to 6.5 days when operational conditions enabled the pilot unit to be run properly. Primary sludge was added to various amounts, from few litres (20 L) to 150 L.

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

II.2 Sample taking and storage

The samples were picked in small plastic containers, 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 main laboratory, 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-03 (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 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. 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 unit running for permeate and concentrate.

- TS and VS parameters

Total Solids (TS) were measured very day for primary sludge and reactor sludge, as a mean of monitoring variations occurring within the mixer tank and the bioreactor. They 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 sludge 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 mass m_t and the pan mass m_p:

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

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, called "GR" (stands for Glödresten, see **Appendix 1**). Therefore, VS fraction is deduced from the GR values:

$$VS\ [\%] = 100 - GR\ [\%]$$

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 known at least a week after sending the samples, so that was also a faster way to get some results confirming a safe running of the process.
These tests concerned COD, Total Phosphorus (PO_4), Ortho Phosphate (PO_4-P), Ammonium-Nitrogen (NH_4-N), Nitrate (NO_3-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 among 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 CH_4-meter, a water trap was built with 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.

[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.

- Membrane cleaning

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 cleaning the membrane, few changes have to be done regarding hose connections: the pilot unit has to be in "recirculation mode" (SP-02 closed), 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 T-13 tank, 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 few minutes. During the whole procedure, feeding pressure must remain stable at 2.5 bars; it could be adjusted with HV-04 valve. The system has to be changed to its initial settings (previous hose connections, opening/closing of some valves).

III. Troubles that occurred during the evaluation period

III.1 The main problem: 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. Therefore, maintaining the feeding pressure above 2.5 bar and around 4 bar for a satisfying running 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 run in a proper way as the system was not able to provide the minimum required pressure. So after 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 gage 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. 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 the provided pressure was before the feeding pump, referring to process sketch (**Appendix 2**).

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

matter 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 bioreactor sludge. So theoretically, it could not explain clogging and pressure drop observed. In practice, bag filter clogging occurred more rapidly since TS content was increased, so there might have 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 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 feeding pressure value 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 bar but the pressure value could not be kept steady. A temporary solution was found: 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 running of the pilot unit was composed of two semi-periods, which was not satisfying.

The problem was the same even by proceeding with two running stages, as described above: the feeding pressure could not be supplied in an efficient way. Moreover, additional troubles 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 running. 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 membranes could drop rapidly. So by adjusting this valve, the pilot unit could run 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 be only 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 remained stable during this period, so running the pilot unit in this situation was far from the suitable operating conditions defined in the research plan.

Due to inability to ensure constant primary sludge incoming flow to the bioreactor, **the pilot unit running was not in a steady state**.

III.2 Trouble related to biogas production measuring system

Monitoring the biogas production was an essential requirement. Obviously, this implies the flow meter had to measure the right biogas volume to indicate reliable results. That was not the case during the whole evaluation period: the measured flow through the flow meter was reduced to 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 run properly due to troubles previously detailed. Therefore, few litres primary sludge was 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 satisfying volume of primary sludge to reach HRT about 10 days: the biogas production measured was really low and far from the expected value. An investigation regarding the entire collection and measuring system was necessary. No leakages were found among the pipes and hoses networks. Researches focused on the flow meter: oil level was adjusted by introducing mineral oil and airtightness was reinforced by adding a plastic gasket around a control bolt. The measured biogas flow was closer to the theoretical value. However, after few days technical troubles occurred again on 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 flow meter. Its unexpected behaviour ("reverse" flow 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 to notice any leakage or perturbation. At the end of the study, an expert for device calibration from JTI[1] inspected the flow meter, finding no dysfunction. He suggested to skip a liquid trap in which biogas passed through before reaching the flow meter, as this trap might be involved in biogas leakage. He also advised to connect a plastic flask prior to the flow meter, to recover possible oil spill.
Finally during the very last days, it seemed that a proper biogas volume was measured after modifying the measuring system as described above. **Due to this lack of accuracy regarding the measured values, the results are unreliable and have to be carefully considered**.

III.3 Difficulties regarding primary sludge transfer

Carrying primary sludge from the mixer tank to the bioreactor was first made with 12-liter 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 P-10 pump (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 around 18 Hz. This incoming flow to

[1] Swedish Institute of Agricultural and Environmental Engineering.

the reactor could balance the permeate flow led off the system, at least at the beginning of the pilot unit running. However, as the permeate flow used to increase after few minutes, the volume removed from the system was higher than the incoming volume of sludge. This situation required to complete the missing volume with sludge buckets. Increasing P-10 pump frequency 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. This implied a dependence on P-10 pump flow and a careful attention to the sludge level within the bioreactor (otherwise the system could have turned off by itself, as a safety measure).

The inability to increase P-10 pump frequency combined with the consequences from the "low feeding pressure" troubles 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.**

Part IV : Results and discussion

I. General monitoring of the bioreactor

I.1 pH monitoring

As previously explained, pH is one of the most important parameter 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.

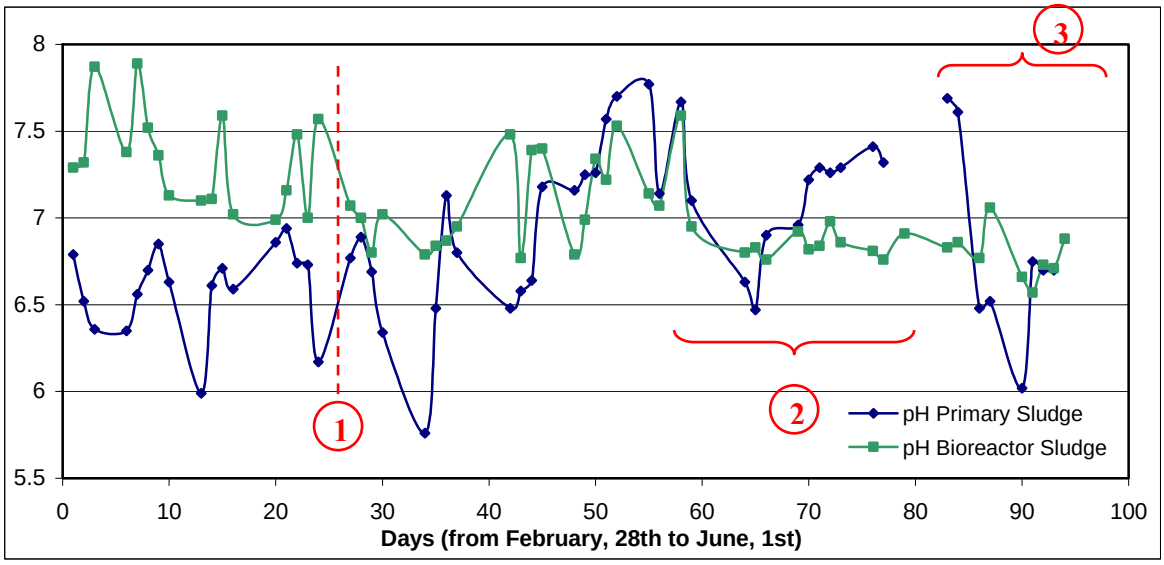


Figure 13: pH in primary and bioreactor sludge over time.

One can notice that pH for bioreactor sludge is in the range 6.6 – 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 always superior to 6.5, lower value for a trouble-free operating system. So inhibition due to pH values was not a problem during all this evaluation, as pH from the bioreactor content was always measured in a satisfying range.

On the diagram, the first red point corresponds to the date of the first primary sludge introduction to the bioreactor (day 27). The second red area covers a period in which any primary sludge at all has been added (day 58 to 82), due to serious technical troubles. One can observe that pH within the bioreactor remains rather stable during these days. The third red period includes trouble-free operating days, with an average HRT of 6.5 days. In between days 30 and 58, a variable amount of primary sludge was introduced in the bioreactor, from 20 L up to 110 L. This irregularity might explain the tendency of the bioreactor pH curve (fluctuations and peaks), even if a quantified correlation has not been found.

I.2 Monitoring of VFA

Monitoring this parameter is an efficient way of checking anaerobic process running. Volatile Fatty Acids are intermediate compounds along 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 anaerobic process at high concentrations (see Theory); this is the second interest in 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.d. above 50 mg/L) during the first weeks of monitoring, from day 1 to day 42. Nevertheless, the concentrations were not continuously detectable during this period, meaning that some days the VFA concentration was below 50 mg/L. PS was added for the first time on day 27, so it is not responsible for changes in VFA concentration prior this day. **The variation range varies from 50 to 162 mg/L**, which is far below the highest tolerable concentration of 500 mg/L. From day 43 till the end of the study, VFA concentration within the bioreactor sludge was not detectable.
By considering these results, one can draw the conclusion that VFA consumption occurred with a suitable rate, meaning that methanogenic stage was satisfactory in the bioreactor.

VFA concentration in the outgoing permeate was also measured every running day of the pilot unit: the values are all lower than 50 mg/L, except for two days during week 21 and week 22. Regarding VFA in the PS, the purpose of daily monitoring was to check that degradation process had not started and that it was possible to add in the bioreactor PS with an appropriate VFA concentration. This one varies from below 50 mg/L to 874 mg/L. The high concentration 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 troubles and so there was no need for mixing the primary sludge in the mixer tank.
A general trend could be noticed: VFA concentration is rather high (some hundreds 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).

I.3 Monitoring of Total Solids (TS)

The goal was to increase TS of bioreactor sludge up to 2 %, referring to the research plan. To have a precise idea of the changes, TS was measured at least twice a week and every day during proper running of the pilot. 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 picked once a week.
Despite the amount of PS added, the TS content of the bioreactor sludge did not reach 2 %; the maximum percentage was 1.1 % during week 16. This is partly due to the rather low TS content of added PS (from 0.5 to 1.6 %). The results are plotted in Figure 14.

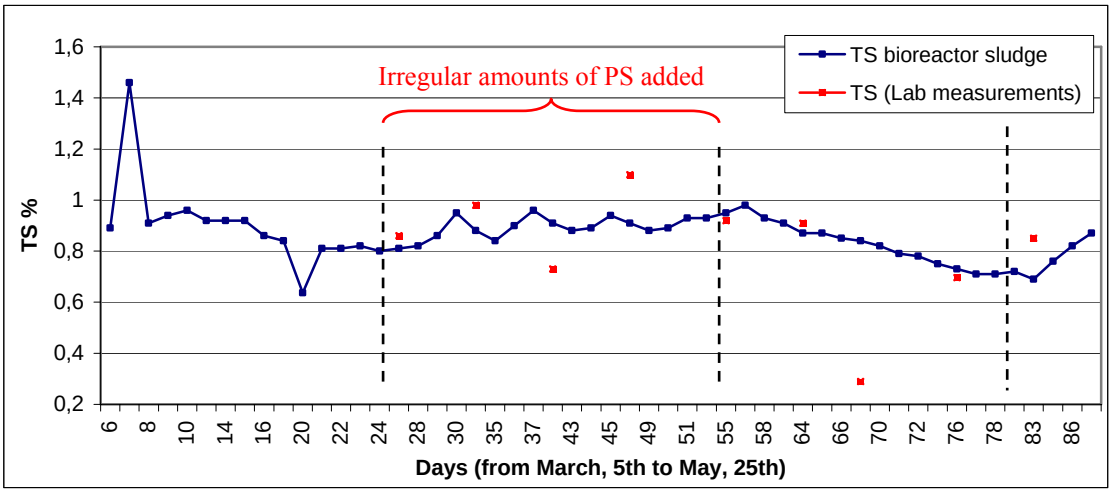


Figure 14: TS content for bioreactor sludge over time.

Temporary amounts of PS were added in between day 27 and day 56: 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. Since day 83, a regular amount of PS was added to decrease the HRT below 10 days. One can notice the increase in TS content starting on this particular date.
The results from the main laboratory are rather close from the daily monitoring performed at Sjöstadsverket in most of the case. However, reliability of measures for the week 19 (around day 70) is not sure. A mistake might have been done in the measure procedure, as the sample taking was performed exactly in the same way during the whole study.

II. Results related to methane production

II.1 Potential methanogenic activity and methane produced

As mentioned in theoretical part, the maximum methane production can generally reach 65 % in volume of the total amount of produced biogas. An activity test has been performed in May to evaluate the potential activity of current bacteria community within the bioreactor sludge. The sample was picked up after a period in which introduction of PS was irregular, although the HRT was around 10 days when adding PS was possible.
The company 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 as good at the test temperature (20°C) and the response as relatively fast (see **Appendix 4**). But this test temperature is not representative of operating temperature within the bioreactor (36°C). Moreover, the pilot unit was not running in a satisfying way when the sample was taken, which means that PS was not introduced in a continuous way. This should be considered as a disturbing element for methanogenic activity, however it does not appear to be so (referring to the conclusions of this activity test).

Regarding the methane production, the measured percentages varied in the range 2 % to 64 % of the total biogas volume. The lowest values are not correlated to any particular troubles 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.
Due to technical troubles detailed in "Material and methods", the measures of biogas flow are not reliable, particularly at the beginning and at the end of the evaluation period (weeks 20 to 23, i.e. from day 76 to the end). The cumulative methane volume and the percentage of methane contained in the biogas flow are drawn in Figure 15, from February, 28th to June, 1st.

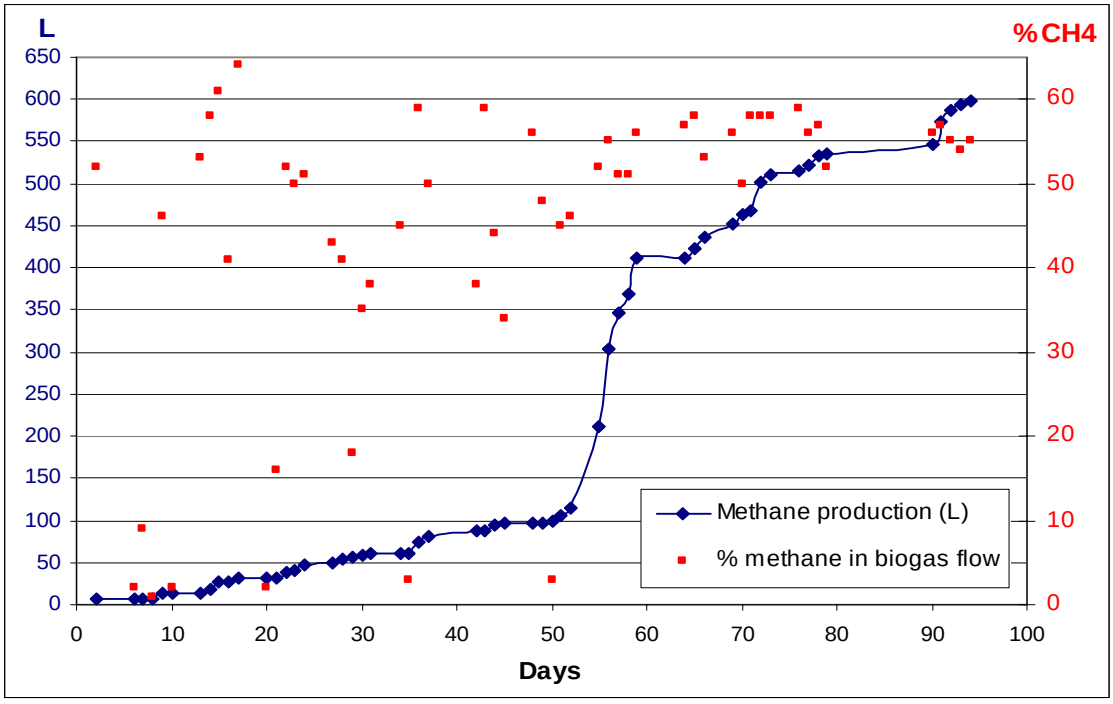


Figure 15: Cumulative methane production and methane content within total biogas flow over time (from February, 28th to June, 1st).

Methane production was clearly increased between day 52 and day 60: during this period, an important amount of PS was added into the bioreactor. Indeed, the values for HRT were in the range 8 to 11 days.
The percentage of methane is higher than 45 % in most of the measures: around one third of these values are below 45 %. The lowest percentages are not correlated to special operating conditions but one can notice that prior 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 methane content in the biogas flow is above or equal to 50 %.

II.2 Comparison with expected gas production

Referring to the maximum percentage for the current bacterial community in the bioreactor, i.e. 58 %, the measures show rather good values, particularly since day 52. Indeed, all the percentages are in between 50 and 58 % from this date. Therefore, by only considering this

percentage of methane among the total biogas flow, the results are satisfying: for the period starting on day 52 until the end (in which high PS volumes have been introduced), **the methane content varied from 86 % to 100 % of the expected methane content**. The reference was the maximal potential methane production determined via AnoxKaldnes activity test (58 % CH_4 as volume in biogas flow).

Despite the satisfying results described above, the volume of produced biogas – and thus of methane – is far away from the expected and theoretical values. For 1 g of COD consumed, 0.396 L of methane should be produced (see Theory).
COD consumed, i.e. resulting is methane production, could be calculated this way:

$$COD_{cons} = COD_{in} - (COD_{acc} + COD_{eff} + COD_{sludge})$$

where COD_{cons} is the COD value used to methane production (mg/L)

COD_{in} is COD concentration in primary sludge (mg/L)

COD_{acc} is accumulated COD concentration within bioreactor (mg/L)

COD_{eff} is COD concentration in permeate (mg/L)

COD_{sludge} is the COD fraction removed with sludge from bag filter cleaning (mg/L)

For week 16, COD concentrations were 15 000 mg/L for primary sludge and 120 mg/L for permeate. One can assume there was no accumulation in between week 15 and week 16, so COD_{acc} = 0 mg/L. VS percentage in mass for disposed sludge is given by:

$$VS\ [\%] = TS \cdot (1 - GR) \cdot 100$$

Thus, for week 16, VS percentage in mass for disposed sludge is $0.018 \cdot (1 - 0.274) = 0.013$.
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 then: $0.013 \cdot 15.84 = 0.206$ kg VS removed. An assessment of COD removed can be made by assuming the ratio COD/VS equals to 1.42, that is to say COD_{sludge} is approximately $0.206 \cdot 1.42 = 0.293$ kg COD removed.

During this period, 270 litres of permeate were removed from the system. The amount of COD consumed is then:

$$COD_{cons} = COD_{in} - (0 + COD_{eff} + 293)$$

$$COD_{cons} = 15.00\ g/L \cdot 270\ L - (0.12\ g/L \cdot 270\ L + 293)$$

$$COD_{cons} = 3724.6\ g$$

The theoretical methane volume is then:

$$V_{methane} = 0.396\ L/\ g\ COD \cdot 3724.6\ g\ COD \approx 1475\ L$$

The measured volume for this week was 113.78 L CH_4. This means that only 7.7 % 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 evaluation period, Table 5 could be built. One has to notice that accumulation is calculated as the variation in COD concentration for reactor sludge times the average volume within the bioreactor for the considered period. Details on calculations can be found in **Appendix 5**.

Week	g COD reduced	Expected CH_4 volume (L)	Measured CH_4 volume (L)	Methane recovered with respect to expected volume (%)
16	3724.6	1475	113.78	7.7
17	2240	720	200.51	27.85
18	1163.6	461	40.45	8.77
19	1861.68	737	63.70	8.64
21	2636.13	758	12.17	1.61
22	5487.58	2173	58	2.67
23	2287.52	906	28.02	3.1

Table 5: Theoretical and recovered methane volumes.

These very low recovering values are due to serious troubles in measuring system (see Material and Methods for details). A leakage could explain this poor volume recovery.

II.3 VS reduction from primary sludge to bioreactor sludge

The degree of reduction is defined by the ratio:

$$VSred = \frac{VSin - VSout - VSacc}{VSin}$$

where VS_{red} is fraction reduced
VS_{in} is the amount of VS introduced (kg)
VS_{out} is the amount of VS removed from the system (kg)
VS_{acc} is the amount of VS accumulated (kg)

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

$$VSin = Qin \cdot TS \cdot (1 - GR)$$

VS_{out} is calculated 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 6.

Week	VSin (kg)	VSout (kg)	VSacc (kg)	VSred · 100 (%)
16	2.7086	0.207	2.4271	2.75
17	1.4078	0.8758	-1.2422	126
18	0.363	0.166	-0.0572	70.03
19	0.4497	0.0971	-0.9667	293.37
21	3.3424	0.9504	1.1866	36.06
22	5.1611	1.6982	-0.0167	67.42
23	3.59	1.0393	-0.3136	79.79

Table 6: VS reduction during evaluation weeks.

Some results are clearly unreliable; they correspond to analyses made during weeks when the pilot unit did not run enough 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 2 to 293 %. Results from the three last weeks seem more reliable, as the pilot unit was running for a sufficient time. The two last percentages are however rather high and do not correspond to the observed biogas production.

II.4 Biogas production corresponding to 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 VS reduction (gCH_4/gVS_{in}). This evaluation could be made from the previous results.

The produced volume of methane is known so the conversion to a mass could be assessed by:

$$m(CH_4) = \frac{P \cdot V}{R \cdot T} \cdot M$$

where P is the pressure (1 atm)
V is the measured volume of gas (L)
R is the universal gas law constant, 0.082057 atm·L/mole·K
T is temperature in K (309.15)
M is the molecular mass of methane (16 $g \cdot mol^{-1}$)

The mass of VS introduced into the bioreactor is given in the first column from Table 6.

Week	V CH_4 (L)	m CH_4 (g)	VSin (g)	g CH_4 / g VSin
16	113.78	71.76	2708.6	0.0265
17	200.51	126.465	1407.8	0.0898
18	40.45	25.513	363	0.0703
19	63.70	40.177	449.7	0.0893
21	12.17	7.676	3342.4	0.0023
22	58	36.582	5161.1	0.0071
23	28.02	17.673	3590	0.0049

Table 7: Methane production with respect to VS introduced in the system.

Two groups of results seem to appear: one for weeks 17, 18 and 19, the other one from week 21 to the end. The low values for this second group could be explained by the major difficulties of registering the right amount of biogas produced, as it has been explained in Material and methods.

II.5 The maximum organic load rate

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 **5.161 kg VS/week**, i.e. **5.27 g VS/L.week** during week 22. It does not mean it is the "maximum" organic load that could be applied to the system; other experiments are necessary to determine this point.

III. Results regarding organic issues

In addition of biogas production efficiency, monitoring of organic parameters has to be performed as well. Analyses were focused on Nitrogen and Phosphorus under various forms, and on Chemical Oxygen Demand (COD), Total Organic Carbon (TOC).

III.1 COD reduction

COD analyses were performed by the main laboratory (SS 028142-2) from weekly mixed samples, and checked directly at Sjöstadsverket once a week. They concerned PS, reactor sludge and permeate, in order to notice changes at different stages of the anaerobic process.

Week	COD_{in} (g)	$COD_{permeate}$ (g)	$COD_{removed}$ (g) [disposed sludge]	CODcons (g) [CH_4 prod]	% reduction
16	4050	32.4	293	287.3	99.2
17	2240	18.2	1244	506.3	99.18
18	480	4.4	263	102.1	99.08
19	660	4.32	138	160.9	99.35
21	5170	56.87	1350	30.7	98.9
22	7003,4	79.42	2412	146.5	98.9
23	4784	40.48	1476	70.8	99.2

Table 8: COD reduction within the whole anaerobic process.

From Table 8 results, one can notice the rather constant and high percentage of reduction, really close to 99 % (and over this value for most of the weeks). Regarding COD reduction, the efficiency of this anaerobic process could be considered as good with more than 99 % reduction in average.

However, the conversion of organic material to produce biogas, and thus methane, may vary over time. This is due to the technical troubles affecting the measuring system and so due to the inability to evaluate the real volume of biogas produced. The percentage of organic matter converted to build methane changes depending on the weeks considered, with respect to initial amount introduced within the bioreactor, as shown on figure 16.

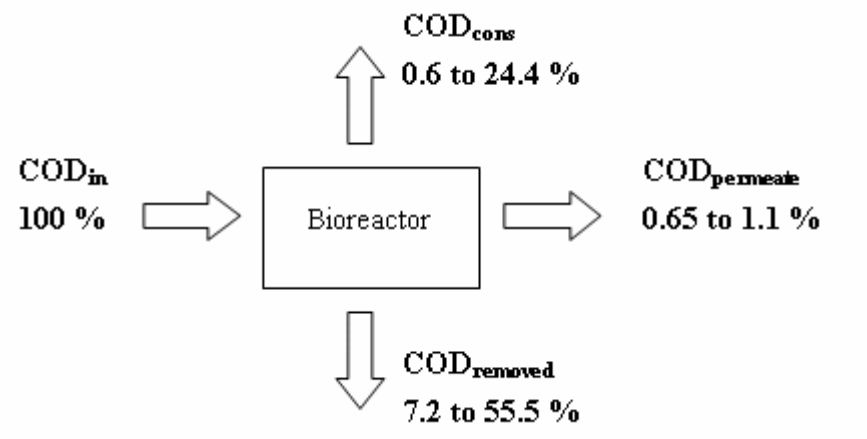


Figure 16: COD dispersion from the bioreactor.

If one considers any single week, the sum of all COD outlets does not reach the amount introduced. Once again, the inability to register accurately the biogas volume produced is mainly responsible for this inconsistency. COD removed with sludge from the bag filter seems to be a major loss of COD, but these highest percentages concern weeks when the pilot unit was not running in a proper way (weeks 17, 18 and 19). Therefore, these high values (up to 55.5 %) could have been expected. COD within permeate is low (maximum 1.1 %), which is rather satisfying for this final effluent.

III.2 TOC reduction

With the same principles than 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 were samples were the same used for COD analyses for instance.

TOC reduction varied from 96.7 % to 99.1 %, always comprised between these two values. This parameter remained constant all the study long. It was also a quite good result: the percentages of reduction themselves are rather satisfying. Figure 17 illustrates TOC reduction in between PS and permeate.

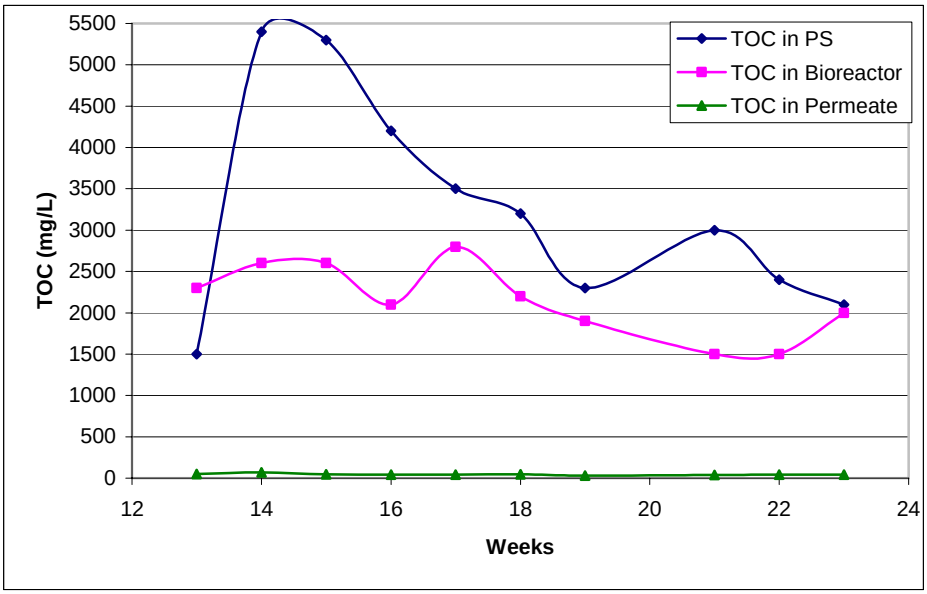


Figure 17: TOC reduction over time.

III.3 Nitrogen monitoring

Nitrogen was analyzed as Kjeldahl Nitrogen (Kjeld-N) [methods AN 300 / AN 3503], nitrates (NO_3-N) [methods SS EN ISO 13395 / AN 5201] for PS, reactor sludge and permeate. An additional analysis was performed for both reactor sludge and permeate: ammonium (NH_4-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, NH_4-N and NO_3-N were checked by carrying out analyses at Sjöstadsverket. These results matched the values given by the main laboratory.

By reviewing the results, one can notice that Tot-N was exactly the same than Kjeld-N. Tot-N was expressed as the sum of Kjeld-N and NO_3-N and due to the low concentration of NO_3-N (below 0.5 mg/L), Kjeld-N was the main component of the Total Nitrogen. Figure 18 illustrates Kjeldahl Nitrogen changes for PS, reactor sludge and permeate. Reduction percentages for this parameter are in the range 8.3 % to 61.7 %, in between PS and permeate. One can observe that concentrations within the bioreactor were always higher than in PS. This situation could come from a possible accumulation, as a low amount of sludge was removed per week (around 50 – 60 kg) while PS was added over time.

Percentages of NH_4-N within Kjeld-N are really different, if reactor sludge and permeate analyses are compared. Indeed, in reactor sludge ammonium represents 32.6 to 48.8 % of Kjeldahl Nitrogen, whereas it is 85.7 to 100 % in permeate flow. This variation could be explained by the ability of the membranes for keeping organic Nitrogen with the sludge: only ammonium ions might be able to pass through the membranes.

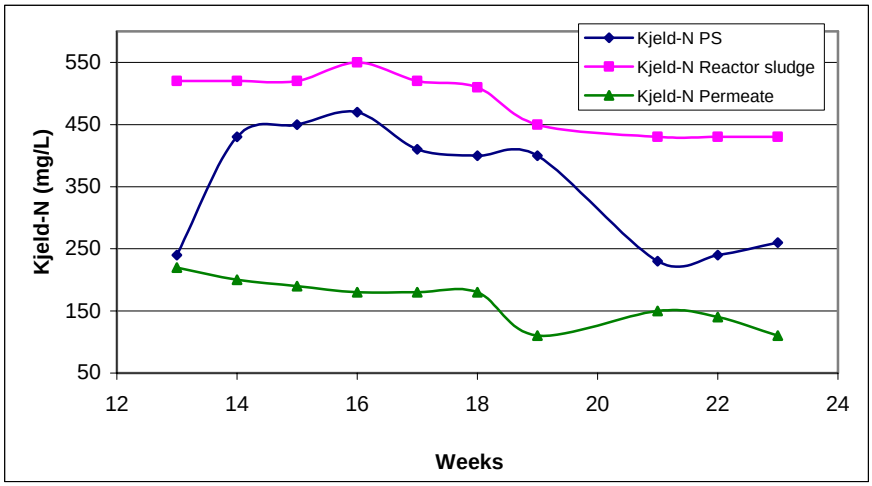


Figure 18: Kjeldahl Nitrogen changes over time.

III.4 Phosphorus monitoring

Phosphorus was analyzed during all this study, from weekly mixed samples. The main laboratory only checked total phosphorus (Tot-P) [tests "Dr Lange"] for PS, bioreactor sludge and permeate. Phosphates concentrations (PO_4-P) were measured from week 18, in order to monitor this particular parameter. Results are illustrated in Figure 19.

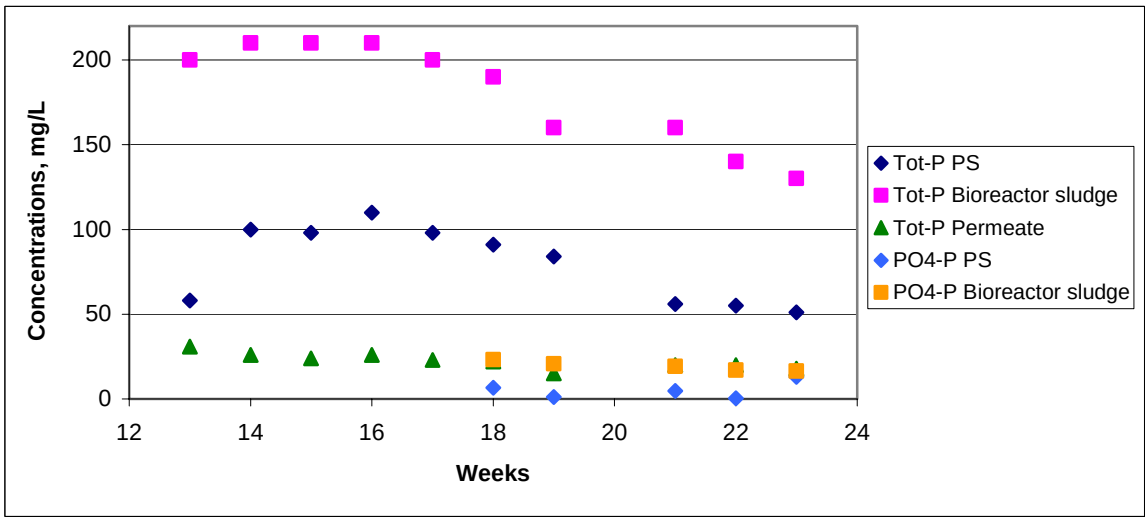


Figure 19: Total Phosphorus and Phosphate concentrations over time.

The concentrations are always higher within bioreactor sludge than in PS, for both Tot-P and PO_4-P. Phosphate ions represent between 0.6 and 25.5 % 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 12 and 13 % of the total amount of phosphorus, within bioreactor. Considering PS and permeate flow, the reduction percentage for Tot-P is in the range 46.5 to 82.1 %, however two groups of values appear: one reduction percentage around 75-76 % (weeks 15, 16, 17 and 18) and the other one around 63-64 % (weeks 21, 22 and 23). 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 as precipitate forms accumulated on membrane surface for example. Comparing the concentrations in the bioreactor and in permeate flow, the membranes are rather efficient during weeks 15 to 18, i.e. they keep around 75-76 % of the incoming phosphorus.

IV. Discussion about the reliability of the results

The first point deals with the way the samples were taken. The pilot unit has been designed to enable the permeate for example to be picked during all the operating time. The final sample is then homogenous 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). The way they are recovered does not match with what they should represent. Some simple actions are made to try to minimize this lack of homogeneity: primary sludge was mixed and agitated all day long in the mixer tank before picking the samples, 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 running time is not sufficient. That was the case during weeks 18 and 19, when only 40 and 60 L primary sludge were added (respectively). Due to the technical troubles previously described, the pilot unit could not operate during a long time, i.e. 20 or 30 minutes. Therefore, the samples recovered in this period did not represent a proper running 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 conserved within acid environment prior to be analyzed. Even if this method is has been proved, damages might have occurred and could partly explain deviated values (VS reduction during week 19).

To perform analyses directly at Sjöstadsverket, fast chemical tests were used. These tests were made to monitor some parameters and to have some values that were not measured by the main laboratory (PO_4-P for instance). The way samples were recovered could be a source of mistakes (samples picking, influence of filtration stage prior analyses…), 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 implied an error on the true volume recovered for example. The same trouble is found while adding the reactants. The consequence is an approximation of the final result, it 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, 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 such low values for the measured methane.

Conclusion

The evaluation of sludge treatment in an Anaerobic Membrane BioReactor with respect to several parameters ended up in mitigated results. The bioreactor wad 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 content as it was stated in the objectives. The mechanical troubles that occurred during the study did not enable the pilot unit to be run in a convenient way.

Regarding the questions to be answered, the degree of VS reduction varied in the range 2.75 % to 293.37 %. The most reliable results seem to correspond to weeks 21 to 23 of the study, with VS reductions of 36.06, 67.42 and 79.79 % respectively. The observed variation in these results could be explained by a lack of homogenous representation of the samples, and eventually by the way the samples were conserved, analyzed.

The gas production, expressed as mass of VS introduced within the bioreactor, varied from 0.0023 to 0.0898 g CH_4 / g VS_{in}. Results from week 21 to week 23 appear to be consistent if they are compared to each other. They could have been the most reliable if serious troubles in the measuring biogas system did not happen. As a consequence, these results are no longer reliable. The activity test from microbial community inside the bioreactor gave satisfying results, with a maximum methane production of 58 % within the entire biogas flow. The critical parameters such as pH and VFA concentration remained in a normal operating range. No excessive concentrations of heavy metals were detected. So these very low values in biogas and thus methane production could be mainly attributed to a measuring system failure.

Concerning organic parameters, rather high percentages of COD and TOC reduction were found, respectively around 99 % and between 96.7 and 99.1 %. The COD mass balance illustrates some failures within the biogas production monitoring. Regarding Kjeldahl Nitrogen, the reduction varied in the range 8.3 % to 61.7 %, between PS and permeate. Moreover, the minimum value for outlet concentrations was 110 mg/L, which is a rather high value. For Total Phosphorus, two groups of reduction percentages appeared: one around 75-76 % and the other one around 63-64 %. The minimum concentration within permeate was 15 mg/L ; this value is also rather high for a final effluent such as permeate.

For the pressure and the flux through the membranes, the results varied from simple to double value. The operating pressure was rather constant, around 4 bar. The permeate flow usually started at 700 mL/min and increased over time to reach 1500 mL/min at the end of the pilot unit running. The corresponding values for the flux were 26.42 $L/m^2.h$ and 56.60 $L/m^2.h$.

The technical troubles 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 parts) are the inability to run the pilot unit in a continuous way, which is not suitable for sample homogeneity for example.

Finally, the “maximum” organic load rate was 5.161 kg VS/week, i.e. 5.27 g VS/L.week. But the adjective “maximum” does not have a real meaning here, as higher loads were not evaluated. It would have required more time, and a safer running of the pilot unit. However, it is a way to investigate in the future.

References

➢ Articles :

- **Choo K.H. and Lee C.H.** (1996a), *Effect of anaerobic digestion broth composition on membrane permeability*, Wat. Sci. Techn. 34 (9), 173-179.

- **Choo K.H. and Lee C.H.** (1996b), *Membrane fouling mechanisms in the membrane-coupled anaerobic bioreactor*, Wat. Res. 30, 1771-1780.

- **Choo K.H. and Lee C.H.** (1998), *Hydrodynamic behaviour of anaerobic solids during crossflow filtration in the anaerobic membrane bioreactor*, Wat. Res. 32 (11), 3387-3397.

- **Gay J.**, *Lutte contre la pollution des eaux*, Techniques de l'ingénieur, 2002, G 1455, 18 p.

- **He Y., Xu P., Li C. and Zhang B.** (2005), *High-concentration food wastewater treatment by an anaerobic membrane bioreactor*, Water Research 39, 4110-4118.

- **Hogetsu A., Ishikawa T., Yoshikawa M., Tanabe T., Yudate S ans Sawada J.** (1992), *High rate anaerobic digestion of wool scouring wastewater in a digester combined with membrane filter*, Wat. Sci. Technol. 25 (7), 341-350.

- **Madigan M. T., Martinko J.M. and Parker J.** (1997), *Brock Biology of Microorganisms*, 8th ed, Prentice-Hall, Upper Saddle River, NJ.

- **Ross W.R., Barnard J.P., Le Roux J. and de Villiers H.A.** (1990), *Application of ultrafiltration membranes for solid-liquid separation in anaerobic digestion systems: the DAUF process*, Water S.A. 16 (2), 85-91.

➢ Reference Books :

- **Metcalf & Eddy, Inc.**, revised by Tchobanoglous G., Burton F.L. and Stensel H.D., *Wastewater Engineering, Treatment and Reuse*, New York, McGraw-Hill, fourth edition, 2003, 1819 p.

➢ Thesis :

- **Carlsson A.**, *Sewage treatment in an anaerobic membrane bioreactor with a VSEP unit*, Master Thesis in Biochemical Technology, Kungliga Tekniska Högskolan, Stockholm, Sweden, 2005, 49 p.

- **Lindblom H.**, *Behandling av svartvatten och matavfall med anaerob MBR och RO – utökade försörk*, Thesis in Civil Engineer Program, Luleå Tekniska Universitet, Stockholm, Sweden, 2007, 45 p.

- **Karczewska K.**, *A rotary drum filter as a pre-treatment for a membrane bioreactor – operation, evaluation and optimization*, Master Thesis in Environmental Engineering and Sustainable Infrastructure Program, Kungliga Tekniska Högskolan, Stockholm, Sweden, 2006, 38 p.

- **Rodriguez Susa M.**, *Etude d'un bioréacteur anaérobie à membranes immergées pour le traitement des eaux résiduaires*, Ph.D. Thesis in Process and Environmental Engineering, Institut National des Sciences Appliquées, Toulouse, France, 2005, 164 p.

➢ Documentation :

- The Henriksdal Wastewater Treatment Plant, document from Stockholm Vatten AB, 2003.

- VSEP Brochure, *A separate revolution*, New Logic Research Inc., 14 p.

- VSEP Technical Manual, New Logic Research Inc., 204 p.

➢ Web sites :

- **Stockholm Vatten AB**, http://www.stockholmvatten.se/

- **New Logic Research Inc.**, *Technology*, http://www.vsep.com/technology/index.html

Table of illustrations

Figure 1: Anaerobic process degradation scheme. 6
Figure 2: Carbon and hydrogen flow in anaerobic digestion process. 7
Figure 3 : Anaerobic bioreactor with external membrane separation. 15
Figure 4 : VSEP resonating drive system. 17
Figure 5 : Flow diagram through the membrane stack. 18
Figure 6 : Illustration of membrane fouling. 19
Figure 7 : Effects of shear waves on membrane surface. 19
Figure 8: Serial resistance 21
Figure 9: Modes of membrane fouling. 22
Figure 10: Anaerobic bioreactor. 26
Figure 11: VSEP unit (membrane stack and electrical engine). 27
Figure 12: Old membranes during changing. 27
Figure 13: pH in primary and bioreactor sludge over time. 35
Figure 14: TS content for bioreactor sludge over time. 37
Figure 15: Cumulative methane production and methane content 38
Figure 16: COD dispersion from the bioreactor. 43
Figure 17: TOC reduction over time. 44
Figure 18: Kjeldahl Nitrogen changes over time. 45
Figure 19: Total Phosphorus and Phosphate concentrations over time. 45

Table 1: Biogas composition. 9
Table 2: Toxic and inhibitory organic compounds for anaerobic digestion. 11
Table 3: Toxic and inhibitory inorganic compounds for anaerobic digestion 12
Table 4: Constituents in wastewater responsible for membrane fouling mechanism. 20
Table 5: Theoretical and recovered methane volumes. 40
Table 6: VS reduction during evaluation weeks. 41
Table 7: Methane production with respect to VS introduced in the system. 42
Table 8: COD reduction within the whole anaerobic process. 43

Appendix

Appendix 1: Results from Stockholm Vatten main laboratory

Appendix 2: Scheme of the pilot unit (made by Rasmus Fröhlich, 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

Miljö och Utveckling 2007-
Vattenvård MV

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

Svarta siffror kontrollerade

Dygn	TS %	GR %	COD mg/L	TOC mg/L	Tot-P mg/L	NO3-N mg/L	Kjeld-N mg/L	S:a Kj + NO3 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	
7/6	1,1	11,2	13000	2100	51	<0,5	260	260	200	

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

* har satts om på osyrat prov

Miljö och Utveckling 2007-
Vattenvård MV

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	
7/6	0,82	27,0	10000	2000	130	<0,5	140	430	430	310	

Metod	SS 028113-1	SS 028113-1	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

* har satts om på syrat prov

Miljö och Utveckling 2007-
Vattenvård MV

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 µg/L ICP-AES Ackred.	B µg/L ICP-AES Ackred.	Cd µg/L ICP-AES Ackred.	Co µg/L ICP-AES Ackred.	Cr µg/L ICP-AES Ackred.	Cu µg/L ICP-AES Ackred.	Fe mg/L ICP-AES Ackred.	Hg µg/L AFS Ackred.	Mn µg/L ICP-AES Ackred.	Mo µg/L ICP-AES Ackred.
D713 (2/4)	40	270	11	40	1500	3100	200	5,7	1700	250
V721 (28/5)										
7/6										

Miljö och Utveckling 2007-
Vattenvård MV

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

Svarta siffror kontrollerade

Dygn	COD mg/L	TOC mg/L	Tot-P mg/L	NO3-N mg/L	NH4-N mg/L	Kjeld-N mg/L	S:a Kj + NO3 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	
7/6	110	44	18	<0,5	100	110	110	110	

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

Miljö och Utveckling 2007-
Vattenvård MV

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

Svarta siffror kontrollerade

Dygn/vecka	Ag µg/L ICP-AES Ackred.	B µg/L ICP-AES Ackred.	Cd µg/L ICP-AES Ackred.	Co µg/L ICP-AES Ackred.	Cr µg/L ICP-AES Ackred.	Cu µg/L ICP-AES Ackred.	Fe mg/L ICP-AES Ackred.	Hg µg/L AFS Ackred.
V713 (2/4)*	<20	100	<5	<20	<20	25	1,6	<0,05
V715 (16/4)	<20	84	<5	<20	<20	<20	1,6	
V721 (28/5)								
7/6								

*** konservarats med H2SO4**

Miljö och Utveckling
Vattenvård

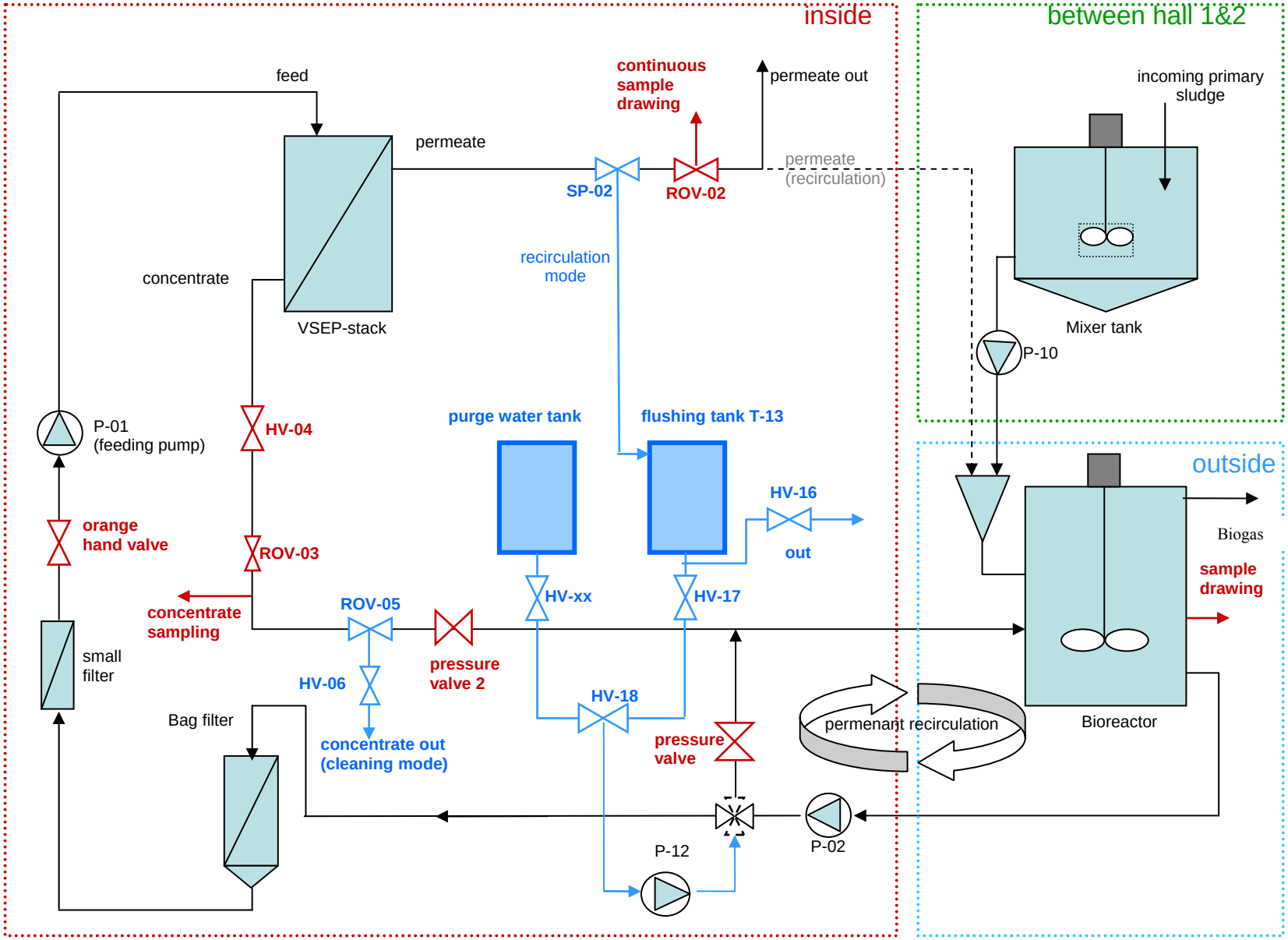
Uppdrag: Analys avloppsvatten Hammarby Sjöstad
Uppdragsgivare: AP
Provets märkning: Hammarby Sjöstad VSEP öslam vecka

Svarta siffror kontrollerade

Dygn	TS %	GR %	Kontrollerade
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	3,2	25,6	
7/6	2,5	24,5	CU

Metod SS 028113-1 SS 028113-1

Appendix 2


inside
between hall 1&2
outside
feed
continuous sample drawing
permeate out
permeate
SP-02
ROV-02
permeate (recirculation)
incoming primary sludge
concentrate
recirculation mode
VSEP-stack
Mixer tank
P-10
P-01 (feeding pump)
HV-04
purge water tank
flushing tank T-13
HV-16
out
orange hand valve
ROV-03
HV-xx
HV-17
Biogas
sample drawing
concentrate sampling
ROV-05
pressure valve 2
small filter
HV-06
HV-18
Bioreactor
Bag filter
concentrate out (cleaning mode)
pressure valve
permenant recirculation
P-12
P-02

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
Total PO_4	LCK 350	6-60	Phosphate ions react with molybdate and antimony ions in an acidic solution to form an antinomyl phosphomolybdate complex, which is reduced by ascorbic acid to phosphomolybdenum blue.	0.4	110
PO_4-P		2-20		0.4	15
NH_4-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
NO_3-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.

Appendix 4

Undersökning av anaerob aktivitet i slamprover från VSEP-reaktorn,

Hammarby Sjöstads Reningsverk

My Carlsson, Lars-Erik Olsson

2007-05-28

AnoxKaldnes

Innehåll

Inledning **2**
Material och metoder **2**
Analyser **2**
Resultat **3**
Slutsatser **4**

Inledning

Ett aktivitetstest har gjorts på slam från VSEP-reaktorn 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 20-21ºC.
Studien utfördes under perioden 070503-070528.

Material och metoder

Slammet till försöken togs ut från VSEP-reaktorn 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 ($NaAc*3H_2O$) 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 $NaAc*3H_2O$ (referens) i de olika lösningar som användes i försöken. Lösningarna späddes med destillerat vatten.

Lösning	Slam	Referens
	g/l	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±1ºC).
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-reaktorn 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.

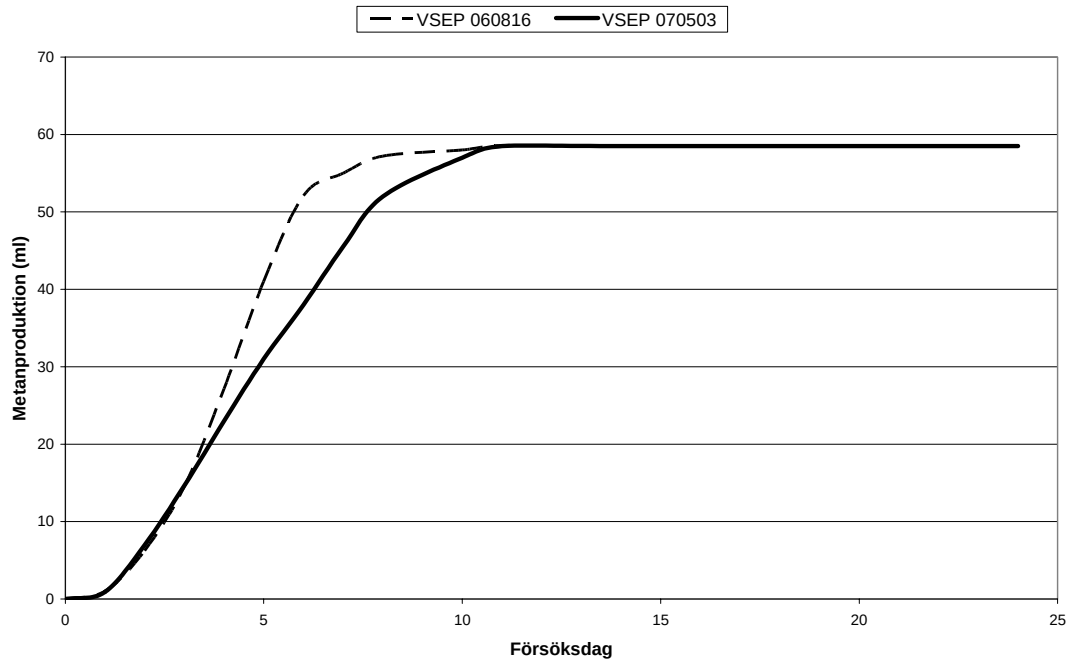


Diagram 1 Resultat från aktivitetstest av slam från VSEP-reaktorn på Hammarby Sjöstads reningsverk hämtat vid två tillfällen. Kurvan visar ackumulerad metanproduktion från referenssubstrat. Kurvorna har korrigerats för ympens bidrag.

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 augus

Appendix 5

Week 17:

- $COD_{in} = 16\,000 \text{ mg/L} \cdot 140 \text{ L} = 2240 \text{ g COD}$
- $COD_{eff} = 130 \text{ mg/L} \cdot 140 \text{ L} = 18.2 \text{ g COD}$
- $COD_{acc} = \Delta COD \cdot V_{react} = -1000 \text{ mg/L} \cdot 840 \text{ L} = -840 \text{ g COD}$
- $COD_{sludge} = 0.019 \cdot (1 - 0.28) \cdot 64.02 \text{ kg} \cdot 1.42 = 1.244 \text{ kg COD}$

$$COD_{cons} = 2240 - (-840 \text{ g} + 18.2 + 1244) \approx 1817.8 \text{ g COD}$$

Theoretical methane volume $V_{methan} = 0.396 \cdot 1817.8 = 720 \text{ L}$

Week 18:

- $COD_{in} = 12\,000 \text{ mg/L} \cdot 40 \text{ L} = 480 \text{ g COD}$
- $COD_{eff} = 110 \text{ mg/L} \cdot 40 \text{ L} = 4.4 \text{ g COD}$
- $COD_{acc} = \Delta COD \cdot V_{react} = -1100 \text{ mg/L} \cdot 840 \text{ L} = -924 \text{ g COD}$
- $COD_{sludge} = 0.014 \cdot (1 - 0.29) \cdot 16.7 \text{ kg} \cdot 1.42 = 0.236 \text{ kg COD}$

$$COD_{cons} = 480 - (-924 \text{ g} + 4.4 + 236) \approx 1163.6 \text{ g COD}$$

Theoretical methane volume $V_{methan} = 0.396 \cdot 1163.6 = 461 \text{ L}$

Week 19:

- $COD_{in} = 11\,000 \text{ mg/L} \cdot 60 \text{ L} = 660 \text{ g COD}$
- $COD_{eff} = 72 \text{ mg/L} \cdot 60 \text{ L} = 4.32 \text{ g COD}$
- $COD_{acc} = \Delta COD \cdot V_{react} = -1600 \text{ mg/L} \cdot 840 \text{ L} = -1344 \text{ g COD}$
- $COD_{sludge} = 0.0046 \cdot (1 - 0.33) \cdot 31.5 \text{ kg} \cdot 1.42 = 0.138 \text{ kg COD}$

$$COD_{cons} = 660 - (-1344 \text{ g} + 4.32 + 138) \approx 1861.68 \text{ g COD}$$

Theoretical methane volume $V_{methan} = 0.396 \cdot 1861.68 = 737 \text{ L}$

Week 21:

- $COD_{in} = 10\,000 \text{ mg/L} \cdot 517 \text{ L} = 5170 \text{ g COD}$
- $COD_{eff} = 110 \text{ mg/L} \cdot 517 \text{ L} = 56.87 \text{ g COD}$
- $COD_{acc} = \Delta COD \cdot V_{react} = +2200 \text{ mg/L} \cdot 840 \text{ L} = 1848 \text{ g COD}$
- $COD_{sludge} = 0.026 \cdot (1 - 0.318) \cdot 53.6 \text{ kg} \cdot 1.42 = 1.3496 \text{ kg COD}$

$$COD_{cons} = 5170 - (1848 \text{ g} + 56.87 + 1350) = 1915.13 \text{ g COD}$$

Theoretical methane volume $V_{methan} = 0.396 \cdot 2636.13 = 758 \text{ L}$

Week 22:

- $COD_{in} = 9\,700 \text{ mg/L} \cdot 722 \text{ L} = 7003.4 \text{ g COD}$
- $COD_{eff} = 110 \text{ mg/L} \cdot 722 \text{ L} = 79.42 \text{ g COD}$
- $COD_{acc} = \Delta COD \cdot V_{react} = -1000 \text{ mg/L} \cdot 980 \text{ L} = -980 \text{ g COD}$

- $COD_{sludge} = 0.032 \cdot (1 - 0.256) \cdot 71.33\ kg \cdot 1.42 = 2.4115\ kg\ COD$

$COD_{cons} = 7003 - (-980\ g + 79.42 + 2416) = 5487.58\ g\ COD$

Theoretical methane volume $V_{methan} = 0.396 \cdot 5487.58 = 2173\ L$

Week 23:

- $COD_{in} = 13\,000\ mg/L \cdot 368\ L = 4784\ g\ COD$
- $COD_{eff} = 110\ mg/L \cdot 368\ L = 40.48\ g\ COD$
- $COD_{acc} = \Delta COD \cdot V_{react} = +1000\ mg/L \cdot 980\ L = 980\ g\ COD$
- $COD_{sludge} = 0.025 \cdot (1 - 0.245) \cdot 55.06\ kg \cdot 1.42 = 1.4757\ kg\ COD$

$COD_{cons} = 4784 - (980\ g + 40.48 + 1476) = 2287.52\ g\ COD$

Theoretical methane volume $V_{methan} = 0.396 \cdot 2287.52 = 906\ L$

Appendix 6

The amount of methane CH_4 produced per unit of COD converted under anaerobic conditions is equal to 0.35 L CH_4/g COD at standard conditions (0°C and 1 atm). The quantity of methane at other than standard conditions is determined by using the universal gas law, to determine the volume of gas occupied by one mole of CH_4 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, 0.082057 atm•L/mole•K
T = temperature, K (273.15 + °C)
P = absolute pressure, atm

Thus, at 36°C, the volume occupied by one mole of CH_4 is

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

Because the COD in one mole of CH_4 is equal to 64 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 L)/(64 g COD/mole CH_4) = 0.396 L CH_4/ g COD

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