Master in Chemical Engineering

Decreasing Caustic Soda Use in Biological Gas Desulfurization

A Master's Dissertation

Of

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Abstract

Biogas is one of the most promising sources of renewable energy that can be used as an alternative to fossil fuels. Before use, however, biogas requires pretreatment to remove hydrogen sulfide (H_2S) since this compound is toxic and corrosive. For the removal of H_2S various desulfurization processes have been developed. One of those processes is Sulfurex®BR, commercialized by DMT Environmental Technology. This system consists of a gas absorber, a biological reactor and a settler. In the bioreactor, H_2S is primarily oxidized into non-toxic elemental sulfur (S^0) by sulfide-oxidizing microorganisms (SOM). However, depending on the conditions, sulfate (SO_4^{2-}) can also be formed by biological reaction and thiosulfate ($S_2O_3^{2-}$) by chemical reaction. The main operational expense of this biological desulfurization process is caustic soda (NaHO) use. Caustic soda use depends on selectivity for elemental sulfur and bicarbonate concentration. Consumption of NaHO can be reduced by operating at high electric conductivity as this leads to less addition of make-up water and therefore less acidification of the reaction medium. The goal of the present study was to demonstrate whether sulfide-oxidizing microorganisms (SOM) can oxidize hydrogen sulfide into primarily elemental sulfur at high electric conductivities. Operating such desulfurization process at conductivities higher than 75 $mS \cdot cm^{-1}$ would substantially decrease caustic soda usage and thus operational costs. On that regard, a continuous lab-scale bioreactor experiment was carried for more than 150 days. Results show that SOM are able to grow and produce SO_4^{2-} at high conductivities (91.68 ± 0.98 $mS \cdot cm^{-1}$). Within S^0 production conditions, the maximum S^0 selectivity (85.99 ± 3.05 %) was achieved at high conductivity (94.67 ± 1.26 $mS \cdot cm^{-1}$) while thiosulfate selectivity was insignificant (2.75 ± 5.42 %). It is possible to reduce caustic soda use by 2.32 $kg_{NaHO} \cdot kg_S^{-1}$, which corresponds to a saving of 1.14 $€ \cdot kg_S^{-1}$, by applying this conductivity to the full-scale system. Higher conductivities could not be tested in the lab as saturation point would be reached and precipitation of salts could occur, leading to operational problems. Alongside, a different nutrient mixture from Celtic Chemicals was also tested for possible future Sulfurex®BR plants in Europe. These results show that SOM were able to consume hydrogen sulfide with almost no thiosulfate formation. Thus, Celtic Chemicals is a possible future nutrient supplier.

Keywords: biogas desulfurization, biotechnological conversion process, sulfide-oxidizing microorganisms, haloalkaline conditions, caustic soda consumption, conductivity

Resumo

O biogás é uma das fontes mais promissoras de energia renovável que pode ser usada como uma alternativa para os combustíveis fósseis. Contudo, antes do seu uso, o biogás requer um pré-tratamento para remover o sulfureto de hidrogénio (H_2S), já que este composto é tóxico e corrosivo. Para a remoção de H_2S, vários processos de dessulfurização foram desenvolvidos. Um deles é o Sulfurex®BR, comercializado pela DMT Environmental Technology. Este sistema consiste num absorvedor de gás, um bioreator e um sedimentador. No bioreator, o H_2S é oxidado maioritariamente a enxofre elementar não tóxico (S^0) por microrganismos oxidantes de sulfureto (MOS). No entanto, dependendo das condições, também se podem formar sulfato (SO_4^{2-}) por reação biológica e tiossulfato ($S_2O_3^{2-}$) por reação química. O principal custo operacional deste processo de dessulfurização biológico é o uso de cáustica (NaHO). O uso cáustica depende da seletividade para enxofre elementar e da concentração de bicarbonato. O consumo de NaHO pode ser reduzido operando a elevada condutividade elétrica, visto que isso leva a um menor consumo de água de reposição e, consequentemente, menor acidificação do meio reacional. O objetivo do presente estudo foi investigar se os MOS poderiam oxidar o H_2S maioritariamente em enxofre elementar a condutividades elétricas elevadas. Operar este processo de dessulfurização com condutividades superiores a 75 $mS \cdot cm^{-1}$ reduziria substancialmente o uso de cáustica e, consequentemente, os custos operacionais. Assim, realizou-se uma experiência num biorreator contínuo em escala laboratorial durante mais de 150 dias. Os resultados mostram que os MOS são capazes de crescer e produzir SO_4^{2-} a condutividade elevada (91.68 ± 0.98 $mS \cdot cm^{-1}$). Nas condições de produção de S^0, a seletividade máxima alcançada para S^0 (85.99 ± 3.05 %) foi alcançada a condutividade elevada (94.67 ± 1.26 $mS \cdot cm^{-1}$), enquanto a seletividade para tiossulfato foi insignificante (2.75 ± 5.42 %). É possível reduzir o uso de cáustica em 2.32 kg de $NaHO \cdot kg_S^{-1}$, o que corresponde a uma diminuição de custos de 1.14 €$\cdot kg_S^{-1}$, aplicando esta condutividade ao sistema de larga escala. Condutividades superiores não poderiam ser testadas no laboratório, uma vez que o ponto de saturação seria atingido e poderia ocorrer precipitação de sais, levando a problemas operacionais. Paralelamente, uma mistura diferente de nutrientes fornecida pela Celtic Chemicals também foi testada para possíveis futuras plantas Sulfurex®BR na Europa. Os resultados mostram que os MOS foram capazes de consumir sulfureto com quase nenhuma formação de tiossulfato. Assim, a Celtic Chemicals é um possível futuro fornecedor de nutrientes.

Palavras-chave: dessulfurização de biogás, processo de conversão biotecnológico, microrganismos oxidantes de sulfureto, condições haloalcalinas, consumo de cáustica, condutividade

Declaration

I hereby declare, on my word of honor, that this work is original and that all non-original contributions were properly referenced with source identification.

28th June 2019

Joana Pereira Campos

Index

List of Figures

List of Tables

Notation and Glossary

S_P	Selectivity for product *P*	mol_S %
$S_{SO_4^{2-}}$	Selectivity for sulfate	mol_S %
$S_{S_2O_3^{2-}}$	Selectivity for thiosulfate	mol_S %
S_{S^0}	Selectivity for elemental sulfur	mol_S %
$n_{S,P}$	moles of sulfur per mole of product	$mol_S \cdot mol_P^{-1}$
n_{S,HS^-}	moles of sulfur per mole of bisulfide	$mol_S \cdot (mol_{HS^-})^{-1}$
$[P]_{inf}$	concentration of product in the influent	$g \cdot L^{-1}$
$[P]_{out}$	concentration of product in the outlet stream	$g \cdot L^{-1}$
$[HS^-]_{inf}$	concentration of bisulfide in the influent	$g \cdot L^{-1}$
$[HS^-]_{out}$	concentration of bisulfide in the outlet stream	$g \cdot L^{-1}$
Q_{inf}	flow rates of the influent	$L \cdot d^{-1}$
Q_{out}	flow rates of the outlet stream	$L \cdot d^{-1}$
MM_P	molar mass of the product (*P*)	$g \cdot mol^{-1}$
MM_{HS^-}	molar mass of bisulfide	$g \cdot mol^{-1}$
TSS	total suspended solids	$g \cdot L^{-1}$
$W_{filter+solids}$	mass of the dried filter with the solids	g
W_{filter}	mass of the dried filter	g
V_{sample}	sample volume	L

List of Acronyms

DMT	Dirkse Milieutechniek
WAC	Water Application Centre
ORP	Oxidation-Reduction Potential
SOM	Sulfide-Oxidizing Microorganisms
TSS	Total Suspended Solids
DO	Dissolved Oxygen
HRT	Hydraulic Retention Time
USA	United States of America
UK	United Kingdom

1 Introduction

1.1 Framing and presentation of the work

1.1.1 The Problem of Anthropogenic Activities and Combustion of Fossil Fuels

Combustion of fossil fuels to obtain energy is one of the major causes of air pollution, resulting in emissions of toxic gases to the atmosphere, namely carbon dioxide (CO_2), carbon monoxide (CO), nitrogen oxides (NO_x), sulfur dioxide (SO_2) and volatile organic compounds (VOC) (Najjar, 2011).

These gases can have different impacts both for human health and for the environment, which are summarized in Table 1.

Table 1 - Various pollutants and their effect on human health and on the environment (Bhandarkar, 2013 ; Ismail & Hameed, 2013).

Pollutants	Negative Impacts on human health and/or the environment
CO_2	Greenhouse gas associated with global warming.
CO	Can affect the cardiovascular system; may affect fetuses, sickle cell anemic and young children; can affect the central nervous system, impairing physical coordination, vision and judgment, creating nausea and headaches.
NO_x	Nitrogen dioxide (NO_2) can affect the respiratory system; nitrogen monoxide (NO) and nitrogen dioxide (NO_2) may contribute indirectly to increased susceptibility to infections, pulmonary disease, impairment of lung function and eye, nose and thread irritations. NO and NO_2 can contribute significantly to acid deposition damaging aquatic ecosystems and other ecosystems such as forests.
SO_2	Can affect lung function. Can contribute significantly to acid deposition impairing aquatic and forest ecosystems.
VOC	Can have effects on human health such as tiredness, dizziness, confusion, nausea; may cause diseases like anemia, liver damage, dysfunction of the central nervous system and cancer, specifically leukemia. VOCs react with stratospheric ozone, leading to the depletion of the ozone layer which increases exposure to dangerous ultraviolet rays.

Decreasing the consumption of fossil fuels and searching for renewable energy sources has therefore been a major concern of society.

Biogas, more specifically, methane obtained from biogas upgrading is one of the most promising sources of green energy that can be used as an alternative for fossil fuels.

1.1.2 Biogas

Biogas is a gas mixture obtained by anaerobic digestion of organic matter. It is primarily composed of methane (CH_4) and carbon dioxide (CO_2), with small portions of hydrogen sulfide (H_2S). It can also contain small amounts of other compounds such as nitrogen (N_2). The proportions of these components depend on the source of the biogas (Environnement, 2009).

This gas mixture is considered one of the cleanest forms of renewable energy nowadays, and it is produced by fermentation of organic waste. However, biogas contains toxic products as contaminations, particularly, the hydrogen sulfide (H_2S), which make it impossible to use it directly for this purpose. H_2S is not only a toxic compound associated with health and safety risks, but it also causes corrosion, as well as environmental problems. Thus, this compound needs to be removed before biogas upgrading and/or its use (DMT Environmental Technology, 2019).

The present work is focused on further developing a biogas desulfurization process, Sulfurex®BR, commercialized by DMT Environmental Technology.

1.2 DMT Environmental Technology

DMT (Dirkse MilieuTechniek) Environmental Technology was founded in 1987 by Rob Dirkse and in 2001, when he retired, his son Erwin Dirkse assumed his position. DMT is now a leading company in biogas upgrading using membrane technology. The company commercializes technologies and products for biogas upgrading (Carborex®MS), gas desulfurization (Sulfurex®CR, Sulfurex®BF, Sulfurex®BR), wastewater treatment and resource recovery (TurboTec®, NutriTec®) to contribute to the sustainability of the environment. Today DMT Environmental Technology employs around 50 employees, has 20 international sales managers, maintains extensive relationships with knowledge institutes, and provides 24/7 productions and services worldwide (DMT Environmental Technology, 2019).

1.3 Contributions of the Work

The internship had a duration of 5 months and the experimental work was conducted in the Water Application Centre (WAC) facilities, in Leeuwarden. During this period, I was responsible

for the operation of a continuous lab-scale reactor simulating the full-scale Sulfurex®BR process. This work involved the following tasks:

- Repair and solve problems in the reactor (*e.g.*, clogging issues, issues with air valve, air sparger and pumps);
- Determine the consumption flow rates of influent, nutrients and HCl fed to the reactor;
- Clean and validate or calibrate pH/conductivity/ORP sensors regularly;
- Analyze reactor samples every day: measure pH and conductivity, prepare samples for HPLC analysis, perform Hach Lang cuvette tests (SO_4^{2-}, S^{2-} and Total Nitrogen) as well as TSS and sludge settleability procedures;
- Analyze influent samples one time/week: measure pH and conductivity, prepare samples for HPLC analysis and perform S^{2-} Hach Lange cuvette test;
- Prepare influent medium, nutrients mixture and 5M HCl when needed;
- Manage inventory to assure there were always enough resources;
- Perform simple maintenance in the system when needed (*e.g.*, pipes);
- Keep the workplace clean, tidy and safe.

1.4 Organization of the thesis

This report is organized in 7 chapters. **Chapter 2** briefly describes the evolution of desulfurization processes and explores Sulfurex®BR in detail. It also presents the main goal of this project. In **Chapter 3**, the experimental set-up in WAC is fully described, as well as all the procedures applied during the study, including materials and equipment that were used for each method. **Chapter 4** provides the main results obtained from the laboratory experiments. In **Chapter 5,** these results and the implications they have at the full-scale system are discussed. **Chapter 6** is an overview of the study performed. It presents the conclusions of the project, based on the obtained results. Finally, **Chapter 7** provides an overall assessment of the work performed, including all the limitations to the project and suggestions for future work development.

2 Context and State of the art

2.1 Evolution of desulfurization processes

Desulfurization of biogas started with physicochemical processes which were relatively expensive due to high temperatures and pressures applied as well as high chemical use and often high residual concentrations. Biological desulfurization is presented as an alternative for the previous processes, using microorganisms that are capable of oxidizing sulfide under ambient temperature and atmospheric pressure, consuming lower amount of chemicals (Jensen & Webb, 1995).

In the 1980s and 1990s, the concept of a full-scale biodesulfurization installation was developed at Wageningen University and the Delft University of Technology, in the Netherlands. This concept was then further developed into a process for biogas treatment by Paques B.V. and the first biogas desulfurization unit was built in 1993. Besides from purifying biogas, it can also be applied to treat high-pressure natural gas and oil refinery gasses (Buisman, Geraats, Ijspeert, & Lettinga, 1990; Janssen, Meijer, Bontsema, & Lettinga, 1998; Paqell BV, 2012).

As mentioned before, DMT Environmental Technology is already commercializing three types of processes for desulfurization, but this study only concerns the Sulfurex®BR, which is briefly described below.

2.2 Sulfurex®BR

Sulfurex®BR is a process that combines a chemical absorber and a biological desulfurization unit. The system consists of a gas absorber, a biological reactor and a settler (decanter). It is based on the Thiopaq process commercialized by Paques. An overview of Thiopaq is presented in Figure 1.

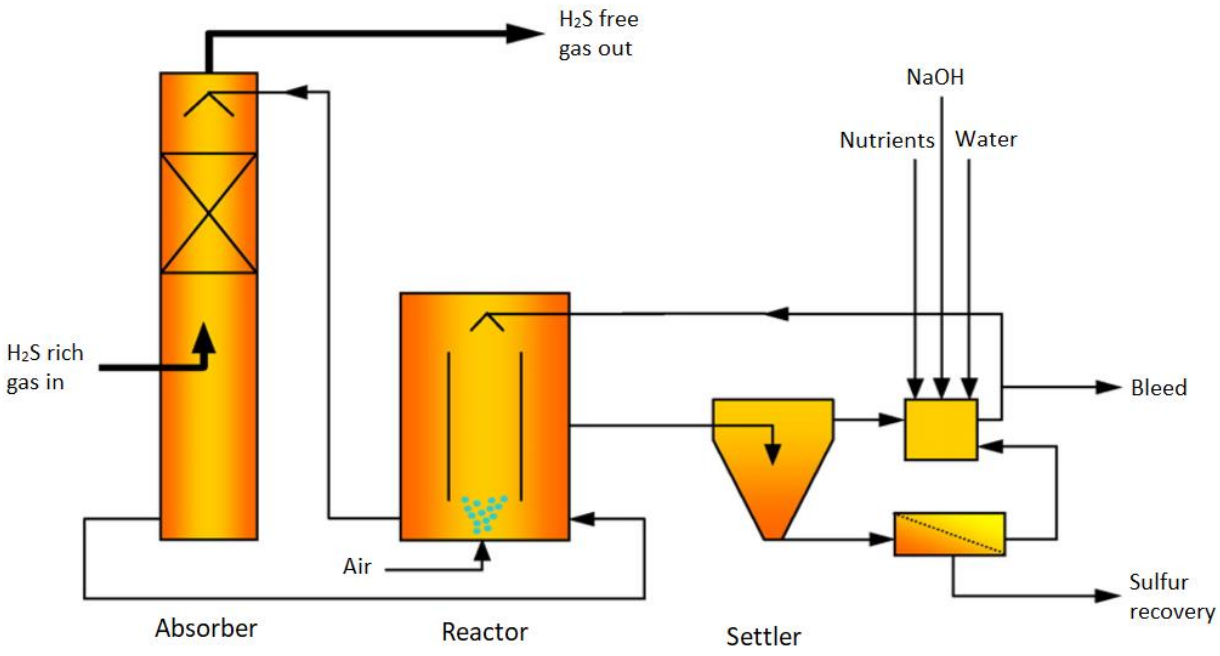

Figure 1 - Flow scheme of the Thiopaq process for biogas desulfurization (Janssen, et al., 2009).

Absorber (Packed Column)

Sour gas (biogas with H_2S) is directed to the Sulfurex®BR absorber, flows upwards through the packing material and leaves at the top almost free of H_2S ("sweet" gas). The treated biogas is then further polished by activated carbon filters to remove residual amounts of H_2S. An alkaline solution (i.e., solvent) is sprayed on top of the absorber and falls through the packing material. As such, the absorber is operated in counter-current mode, which allows greater driving-forces during the process. The packing material inside the column ensures proper contact between hydrogen sulfide (H_2S) and the solvent for a maximum mass transfer. While the biogas flows through the packed column, H_2S is absorbed in the solvent (Equation 2.1), thereby consuming caustic soda (Equation 2.2):

$$H_2S(g) \rightleftharpoons H_2S\ (l) \qquad 2.1$$

$$H_2S\ (l) + HO^-\ (aq) \rightleftharpoons HS^-\ (aq) + H_2O\ (l) \qquad 2.2$$

After absorption in the solvent, the dissolved sulfide (HS^-) is collected at the bottom of the absorber and flows under gravity to the bioreactor (DMT Environmental Technology, 2019; Klok J., 2015).

Bioreactor

In the bioreactor, under low ORP (Oxidation-Reduction Potential), *i.e.*, low oxygen (O_2) concentrations, sulfide-oxidizing microorganisms (SOM) oxidize bisulfide (HS^-) to elemental sulfur (S^0) and simultaneously regenerate the caustic soda to be used in another washing step in the absorber (see Equation 2.3). These microorganisms operate in a halo-alkaline medium, which means double extreme conditions - high pH and high alkalinity. Earlier microbiological work isolated a *Thioalkalivibrio* strain from a full-scale bioreactor removing H_2S from biogas under alkaline conditions (Sorokin, Muntyan, & Panteleeva, 2012).

$$HS^- (aq) + \frac{1}{2} O_2 (g) \longrightarrow S^0 (s) + HO^- (aq) \qquad 2.3$$

A relatively small fraction of the sulfide (typically less than 10 % mol) is oxidized by SOM to sulfate (SO_4^{2-}) ions (see Equation 2.4) (Janssen et al., 1995). Because of the considerable change in the Gibbs free energy, bacteria prefer to oxidize sulfide to sulfate (Buisman, Geraats, Ijspeert, & Lettinga, 1990). However, when sulfide levels are high and/or oxygen levels are becoming limiting, elemental sulfur is formed (Janssen, Ma, Lens, & Lettinga, 1996).

$$HS^- (aq) + 2O_2 (g) \longrightarrow SO_4^{2-} (aq) + H^+ (aq) \qquad 2.4$$

Besides biological oxidation, undesirable chemical oxidation reactions can occur during the desulfurization process. The selectivity for product formation depends on the reactor conditions such as substrate levels, ORP, temperature and pH. Thiosulfate ($S_2O_3^{2-}$) is the main abiotically formed intermediate from the oxidation of sulfide and polysulfide (see Equations 2.5 - 2.7) (O'Brien & Birkner, 1977; E.Kleinjan, Keizer, & Janssen, 2005):

$$2HS^- (aq) + 2O_2 (g) \rightarrow {S_2O_3}^{2-} (aq) + H_2O (l) \qquad 2.5$$

$$HS^- (aq) + (x-1)\, S^0 (s) \rightleftharpoons S_x^{2-} (aq) + H^+ (aq) \qquad 2.6$$

$$S_x^{2-} (aq) + 1\frac{1}{2} O_2 (g) \longrightarrow S_2O_3^{2-} (aq) + (x-2)\ S^0 (s) \qquad 2.7$$

Formation of elemental sulfur is preferred for several reasons. Firstly, sulfate and thiosulfate production leads to the formation of protons and acidification of the medium. Therefore, the addition of caustic soda is required to maintain the optimal pH value. Second, elemental sulfur can be applied for agricultural purposes. Furthermore, the biological conversion of sulfide into elemental sulfur regenerates caustic soda (see Equation 2.3), resulting in lower caustic soda use comparing to thiosulfate/sulfate formation reactions. Formation of sulfate and thiosulfate can be

prevented by operating at low oxygen levels (low ORP) (Alcántara et al., 2004; Janssen, Meijer, Bontsema, & Lettinga, 1998) and at pH values between 8.0 and 9.0 (van den Bosch, Sorokin, Buisman, & Janssen, 2008).

Settler

Part of the reactor effluent is recirculated over to the absorption column for H_2S removal and a smaller flow is directed to a gravity settler, in which elemental sulfur is separated from the process liquid. The overflowing process liquid flows back to the bioreactor. Sulfur sludge is removed from the bottom of the settler with a high dry matter content of 5-10 % mass. This sulfur sludge can then be dewatered in a decanter centrifuge or filter press and used as a high-quality fertilizer. The purity of the recovered sulfur is 95 to 98 wt.% and the remainder consists of biomass and salts (DMT Environmental Technology, 2019; Cline, Hoksberg, Abry, & Janssen, 2003).

Automatic Control Loops in Sulfurex®BR

The optimal operational conditions for Sulfurex®BR bioreactor during the production phase were determined and are presented in Table 2. To maintain these conditions, the reactor has various proportional–integral–derivative (PID) control systems (Table 2). However, there is no PID control over some parameters, for example, the Total Suspended Solids (TSS). TSS in the reactor depends only on the sludge discharge from the settler. When the settler is full of solids, some sludge can be removed manually. Also, nutrients and antifoam are supplied by dosing pumps at a fixed rate and frequency and do not depend on PID control.

pH is controlled at pH 8.3 by addition of a solution of 30 % caustic soda. The system is also equipped with a heat exchanger to maintain temperature at 35 ℃. Electric conductivity is controlled at 75 $mS \cdot cm^{-1}$ by addition of make-up water, which dilutes the reaction medium when the concentration of ions is too high. Addition of make-up water also occurs when the fluid level inside the reactor decreases. On the opposite, if the liquid level increases, part of the liquid will be discharged as bleed stream. This bleed stream is harmless and can generally be discharged without any form of post-treatment. The oxygen concentration was controlled by the Oxidation-Reduction Potential (ORP); the higher the ORP the higher the oxygen concentration. This means that, if the ORP value is below the setpoint, the system starts aerating. Otherwise, there is no air supply. The ORP setpoint value depends on whether the reactor is at the start-up phase or the production phase. During the start-up phase, an operational regime to promote biomass growth should be applied. Since microorganisms need more oxygen to grow, the ORP setpoint is higher during the start-up phase. On the contrary, under limiting concentrations of oxygen, SOM have a better performance

converting the H_2S to S^0. Thus, the ORP setpoint is lower during the production phase. Figure 2 presents the difference between these two operational regimes.

Table 2 – Controlled parameters, corresponding setpoint values and control mechanisms.

	Parameter	Control Mechanism	Setpoint Value
With PID control	pH	Caustic soda addition (↑)	8.3
	Temperature	Heat exchanger (↑)	35 °C
	Electric conductivity	Make-up water addition (↓)	75 $mS \cdot cm^{-1}$
	Liquid level	Make-up water addition (↑) Bleed (↓)	-
	Redox	Air addition (↑)	-300 mV (start-up phase) ≈ -360 mV (production phase)
Without PID control	TSS	Sludge discharge from settler (↓)	8 $g_{TSS} \cdot L^{-1}$
	Nutrients supply	Nutrient dosing pump	83 $mL \cdot kg_S^{-1}$ (River Bend Lab)
	Antifoam supply	Antifoam dosing pump	-

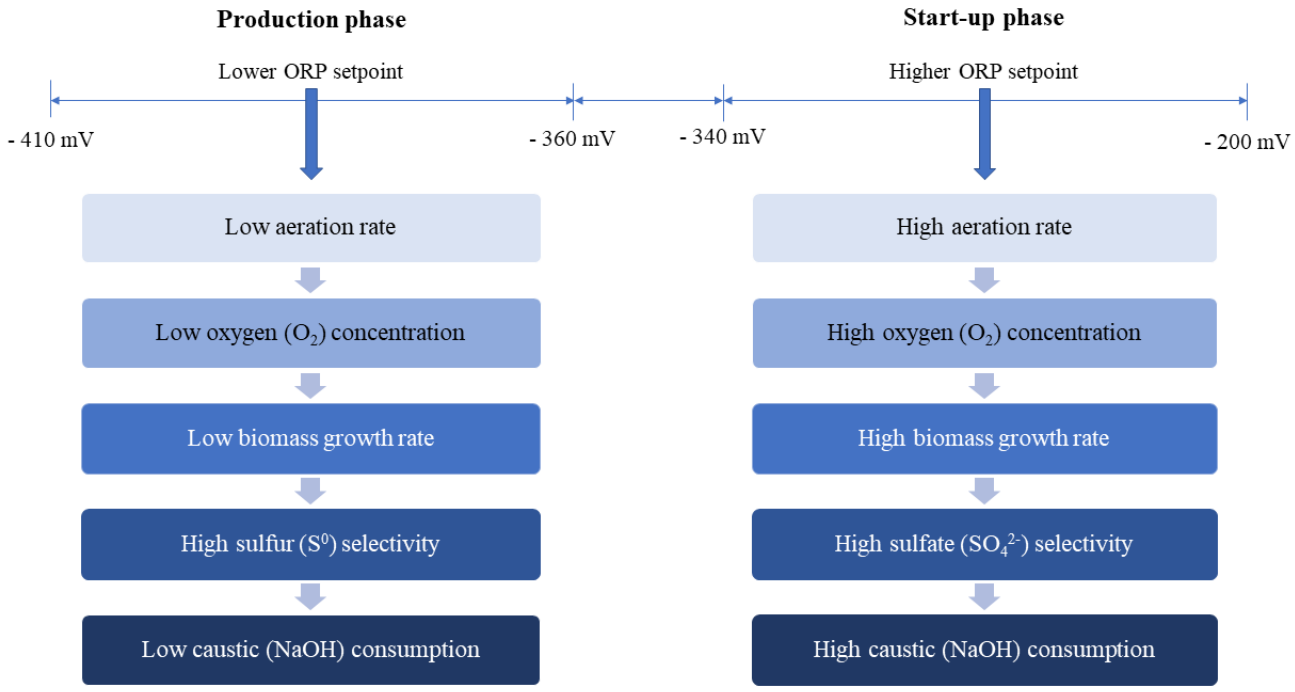

Figure 2 - Main differences between the operational regimes of Sulfurex®BR reactor.

2.3 Decreasing Caustic Soda Use

The main operational cost of Sulfurex®BR process is the caustic soda (NaHO) consumption. Thus, the main goal of this project is to further develop the Sulfurex®BR process by optimizing caustic soda use and therefore costs.

As mentioned before, NaHO is used to absorb H_2S in the packed column (Equation 2.2). As it enables the regeneration of caustic soda through the biological conversion of sulfide into elemental sulfur (Equation 2.3), Sulfurex®BR has a clear advantage when compared to other DMT desulfurization processes. Despite that, NaHO is still consumed in different reactions, for instance, to compensate for biological sulfate formation (Equation 2.4) and bicarbonate loss in the bleed stream (Equation 2.8). Hence, it is of the utmost importance that a solution of caustic soda is regularly added to the system. This also means that caustic soda use depends on selectivity for elemental sulfur and bicarbonate concentration.

$$CO_2\,(g) + OH^-\,(aq) \rightarrow HCO_3^-\,(aq) \qquad 2.8$$

When there is addition of caustic soda to the system, the electric conductivity of the reactor medium increases, leading to addition of make-up water (dilution water). When that happens, the CO_2/HCO_3^- equilibrium changes and more CO_2 is dissolved, consuming caustic soda (see Equation 2.8), which causes a decrease in pH. Sulfate production reaction also acidifies the reaction medium (see Equation 2.4). To reset the desirable pH, there is more caustic soda addition in the system, resulting in a vicious cycle (see Figure 3). If the system is operated at a higher conductivity setpoint, less make-up water is needed when caustic soda is added to the system resulting in a lower decrease in pH and therefore less caustic soda addition is needed. This implies that it is possible to save on caustic soda when operating at a higher conductivity setpoint, which means higher salt concentration in the reactor (NaHO is the main component contributing to conductivity). Thus, this study aims to demonstrate high elemental sulfur selectivity (> 80 %) at a conductivity higher than 75 $mS \cdot cm^{-1}$ (current value applied in the full-scale system). However, it is not possible to limitless increase the conductivity. It is necessary to take into consideration the saturation point of the salt so that precipitation does not occur, which can cause clogging problems through scaling. It could also inhibit microbiological activity, thereby enhancing thiosulfate formation by chemical reaction.

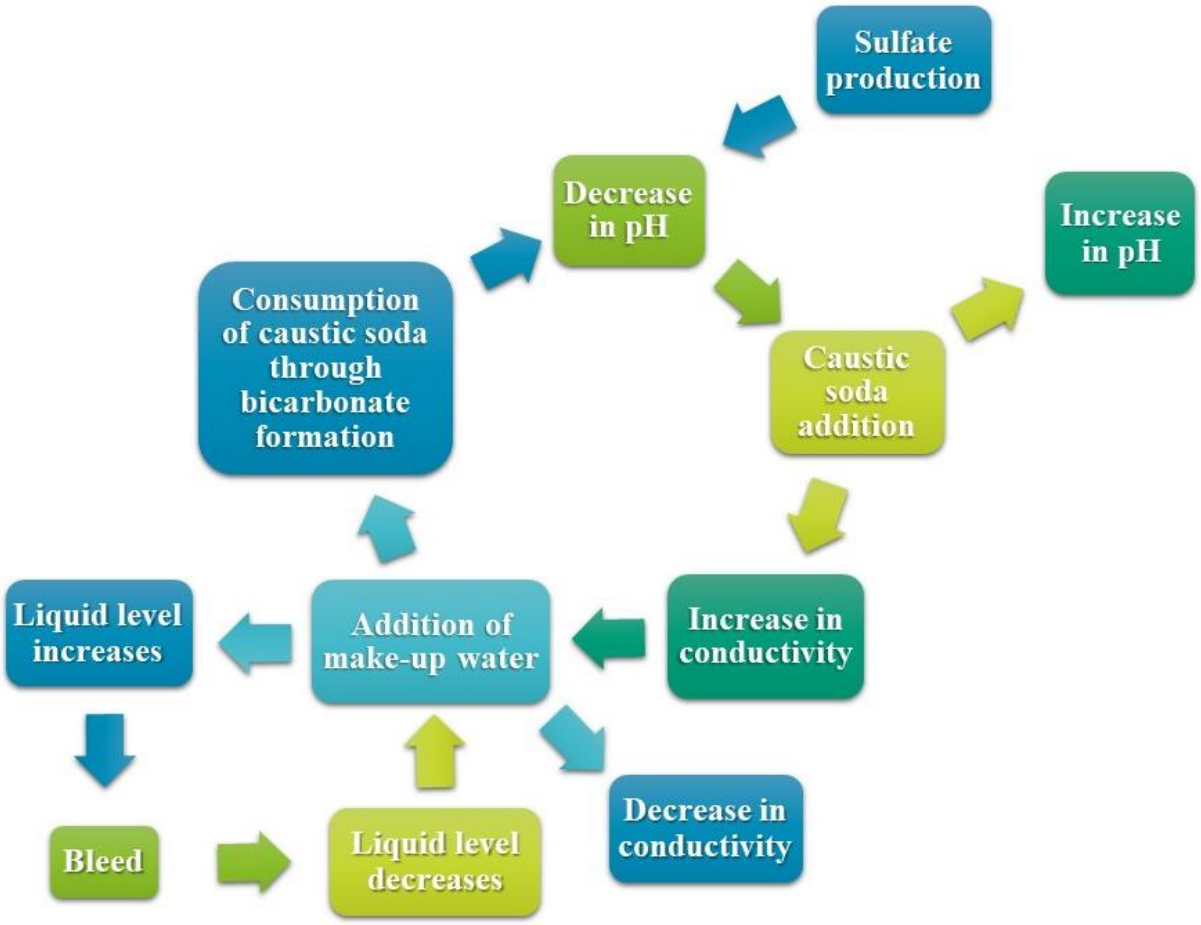

Figure 3 – Automatic control loops in Sulfurex BR.

3 Materials and Methods

3.1 Experimental Set-Up

The experimental set-up consisted of a five-liter up-flow aerobic bioreactor, a settler and additional equipment, such as pumps and a controller (see Figure 4 and Figure 5). Reactor content was recirculated (287 $L \cdot d^{-1}$) using a MASTERFLEX® L/S pump (Model 77200-60, USA). Temperature inside the reactor was controlled at 35 °C by a water jacket connected to a thermostat bath (Stephan, Germany). pH of the reactor content was controlled at 8.3 by supplying a 5M hydrochloric acid (HCl) solution and it was monitored using a pH probe (Orbisint CPS11D, Endress+Hausser, Germany) connected to a controller (Liquiline CM448, Endress+Hauser, Germany). HCl was fed to the reactor by a peristaltic pump (SIMDOS 10, KNF, Switzerland). Safety data of HCl 37 % can be found in Table 4 of Appendix 1. The oxidation-reduction potential (ORP) was controlled by supplying air to the reactor through an air sparger and it was monitored using a SE 564 ORP Sensor (M4 Knick, Ohio), connected to the controller. Reactor was continuously fed (3.25 $L \cdot d^{-1}$) with a synthetic medium consisting of $Na_2S \cdot 9H_2O$ and $NaHCO_3$ (Section 3.4.) by a Watson-Marlow 101 U/R (England) pump. A liquid nutrient mixture was also fed to the reactor (141 $mL \cdot d^{-1}$) by a dosing pump (SIMDOS 10, KNF, Switzerland), to have a specific nitrogen loading rate of 19.97 $g_N \cdot kg_S^{-1}$ (Section 3.3). Liquid samples were taken for analysis from one sampling point, located in the middle of the reactor.

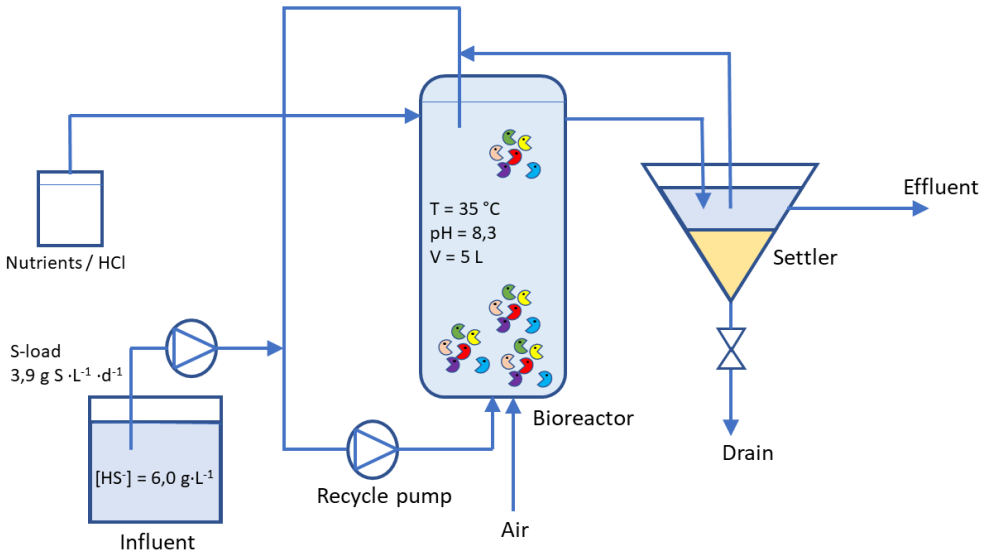

Figure 4 - Flow scheme of the experimental set-up in WAC.

Figure 5 - Set-up in Water Application Centre.

3.2 Inoculum

An open mixed microbial culture was used in the bioreactor as sulfur-oxidizing microorganisms. The inoculum originates from a full-scale desulfurization system at Eerbeek Industriewater, the Netherlands.

3.3 Nutrients preparation

The liquid nutrient mixture was prepared by diluting 20-times the concentrated nutrients supplied by River Bend Labs (US) with tap water for a total amount of approximately four liters. To prevent microbial growth in the medium, acidification was performed in the fume hoot using hydrochloric acid (HCl) until pH was approximately 1.0.

Later on this study, nutrients from another supplier (Celtic Chemicals) were tested, as it will be described in Chapter 4. Since nitrogen (N) concentration in these nutrients was different from the others, the flow rate was adjusted to 219 $mL \cdot d^{-1}$ to have the same specific N loading rate as before (19.97 $g_N \cdot kg_S^{-1}$).

3.4 Influent preparation

That lab set-up had some differences compared to the full-scale Sulfurex®BR. For instance, unlike the full-scale system, it did not include an absorption column, since it was not the major concern of this study, nor a biogas inlet stream. For safety reasons, instead of the absorber treating hydrogen sulfide (H_2S) containing biogas, it was decided to operate with a chemical influent prepared with a sulfide salt - sodium sulfide nonahydrate ($Na_2S \cdot 9H_2O$) - so that sulfide was already in a dissolved form (HS^-). Safety data from this compound can be found in Table 4 of Appendix 1. Apart from that, biogas also contains carbon dioxide (CO_2) as an impurity. In Sulfurex®BR full-scale system, this CO_2 dissociates in the reactor, resulting in bicarbonate ions (HCO_3^-) which increase alkalinity in the reactor and contribute to the buffer effect. In addition, CO_2 (or HCO_3^-) is also essential for the microorganisms as it is their carbon source (they cannot use carbon from organic matter). Since there was no biogas entering this bioreactor and therefore no CO_2, sodium bicarbonate ($NaHCO_3$) was added to the influent for the same purposes. Because $NaHCO_3$ was already an alkaline substance, it was also used as an alternative to caustic soda (NaHO), the solvent applied in Sulfurex®BR absorber. In addition to these salts, one drop of antifoam (Burst® FC 180, BASF, Germany) was added per liter of influent to prevent foaming.

The influent was prepared with deoxygenized water and the mentioned salts so that the final concentration of sulfide (HS^-) was always 6.0 $g \cdot L^{-1}$. This corresponds to a sulfur load similar to the one applied in the full-scale system (3.9 $g_S \cdot L^{-1} \cdot d^{-1}$). On the contrary, to have different conductivity setpoints in the reactor, different concentrations of $NaHCO_3$ were applied during the study depending on the total sodium (Na^+) concentration required. Initially, 25 grams of Na^+ per liter of influent was used. Since the goal of this study was to demonstrate the reactor performance with higher conductivities, this concentration was later increased to 28 $g_{Na+} \cdot L^{-1}$ (leading to a conductivity of approximately 90 $mS \cdot cm^{-1}$). Finally, 30 grams of Na^+ per liter of influent were used to further increase conductivity to almost 95 $mS \cdot cm^{-1}$.

Experimental conditions were changed after a steady-state was observed. The reactor was in steady-state when sulfate concentrations were similar (maximum standard deviation of 30 %) over a period of at least five days. Thiosulfate concentrations were excluded from this criterion since it was produced in insignificant selectivities (< 6.39 %).

3.5 Chemical Selectivity

Chemical selectivity (S_P) is defined as the product produced relative to substrates consumed on a mol-S basis. It can be calculated as the volumetric production rate of the product (SO_4^{2-},

$S_2O_3^{2-}$) divided by total substrate (HS^-) consumption rate (Grootscholten, Strik, Steinbusch, Buisman, & Hamelers, 2014), through equation 3.1:

$$S_P\ (\%) = \frac{product\ formation\ rate\ [mol{\cdot}L^{-1}{\cdot}d^{-1}]}{HS^-\ consumption\ rate\ [mol{\cdot}L^{-1}{\cdot}d^{-1}]} \cdot 100 = \frac{n_{S,P} \cdot \frac{[P]_{out} - [P]_{inf}}{MM_P} \cdot Q_{out}}{n_{S,HS^-} \cdot \frac{[HS^-]_{out} - [HS^-]_{inf}}{MM_{HS^-}} \cdot Q_{inf}} \cdot 100 \qquad 3.1$$

where $n_{S,P}$ are moles of sulfur per mole of product and n_{S,HS^-} are moles of sulfur per mole of sulfide;

$[P]_{inf}$ and $[P]_{out}$ are the product concentrations entering the reactor (in the influent) and leaving the reactor (in the outlet stream), respectively, in g·L^{-1};

$[HS^-]_{inf}$ and $[HS^-]_{out}$ are the concentrations of bisulfide (reactant) entering the reactor (in the influent/inlet stream) and leaving the reactor (in the outlet stream), respectively, in g·L^{-1};

Q_{inf} and Q_{out} are the volumetric flow rates of the influent (inlet stream) and of the outlet stream, respectively, in L/d;

MM_P and MM_{HS^-} are the molar masses of the product (P) and the bisulfide (HS^-), in g·mol^{-1}.

To calculate selectivity for SO_4^{2-} and $S_2O_3^{2-}$, the concentrations of each product, either in the influent or in the reactor (equivalent to the outlet stream), were determined by HPLC (analysis is described in Section 3.7.1). Additionally, concentrations of HS^- in the reactor were measured with sulfide Hach Lange cuvette tests (analysis described in Section 3.7.1) and HS^- concentration in the influent was always 6.0 g·L^{-1}. The influent and the outlet stream flow rates were also determined, as it is described in Section 3.6. With these values, it was possible to calculate selectivities for SO_4^{2-} and $S_2O_3^{2-}$, according to Equation 3.1. However, elemental sulfur concentrations could not be directly quantified, since it is a solid, which means it is not in a dissolved form in the reaction medium like SO_4^{2-} and $S_2O_3^{2-}$. Instead, it forms deposits on equipment walls and pipes. Therefore, selectivity for S^0, S_{S^0}, was calculated by subtracting SO_4^{2-} selectivity, $S_{SO_4^{2-}}$, and $S_2O_3^{2-}$ selectivity, $S_{S_2O_3^{2-}}$, from 100% (Equation 3.2):

$$S_{S^0}\ (\%) = 100\ \% - S_{SO_4^{2-}}\ (\%) - S_{S_2O_3^{2-}}\ (\%) \qquad 3.2$$

3.6 Calculation of influent, nutrients and hydrochloric acid flow rates

The influent, the nutrients and the hydrochloric acid tanks were weighed daily in order to estimate the consumption mass flow rates of each. The corresponding volumetric flow rates, in liters per day, were also calculated using the densities for each fluid. These densities were determined by weighing a sample of known volume. Finally, the flow rate of the outlet stream equals the sum of the flow rates of all inlet streams (see Equation 3.3.).

$$Q_{out} = Q_{inf} + Q_{nutrients} + Q_{HCl} \quad 3.3.$$

where $Q_{nutrients}$ and Q_{HCl} are the flow rates of nutrients and HCl, respectively.

3.7 Analytical Procedures

Some procedures were applied to analyze the system behavior over time, particularly the reactor medium and the influent.

3.7.1 Reactor Sample Analysis

For the reactor sample analysis, the following procedures were performed daily:

- **pH and Conductivity**

External pH was measured using a pH meter (SevenCompact pH/Ion S220, Meter Toledo, Canada) previously validated and calibrated when needed with the suitable calibration solutions. Conductivity was estimated with a conductivity probe (HQ40d multimeter, Hach), also previously validated and calibrated when required with a standard conductivity solution (1000 $\mu S \cdot cm^{-1}$, NaCl, 50 mL, Hach).

- **Sample preparation for HPLC (High-Performance Liquid Chromatography) Analysis**

The HPLC was the most important analysis procedure since it allowed to determine the sulfate (SO_4^{2-}) and thiosulfate ($S_2O_3^{2-}$) concentrations in the reactor with accuracy. To prepare the HPLC vial for the analysis, the reactor sample was first filtered with a syringe and a 0.2 µm filter and then diluted 80-times with the HPLC solvent which is a solution prepared with 1.7 mM $NaHCO_3$ and 1.8 mM Na_2CO_3.

- **HPLC analysis**

Sulfate and thiosulfate were analyzed by HPLC (Agilent 1260 infinity). Compounds were separated on a Metrosep A supp 16 column. The eluent contained 1.7 mM $NaHCO_3$ and 1.8 mM Na_2CO_3. Detection of the anions was achieved with a Metrohm 896 Professional Detector.

- **Hach Lange™ Cuvette Tests (LCK 353, LCK 653, LCK 238)**

Although more accurate, HPLC analysis is a slow process and results cannot be obtained immediately. For quick but less accurate results, Hach Lange™ (Germany) cuvette tests were used to determine the sulfate, bisulfide and nitrogen concentrations in the reactor (see Figure 6-A). The analysis with these test kits is relatively simple since it is only necessary to follow the protocol of each package. After that, the cuvettes were analyzed in a DR3900 VIS spectrophotometer with

RFID Technology from Hach that measures and displays the corresponding concentration (see Figure 6-B).

For the sulfate test (LCK 353), the samples from the reactor were filtered with a syringe and a 0.2 µm filter and then diluted 10-times with deionized (Milli-Q®) water; otherwise the concentration would be above the measuring range. On the contrary, no dilution was performed for the sulfide test (LCK 653), which measures total sulfides (H_2S, HS^- and S^{2-}), since the reactor should not contain significant amounts of these compounds.

The total nitrogen (total N) Hach Lange cuvette test (LCK 238) was applied to have an insight into the biomass content. For each reactor sample, two nitrogen tests were performed: one with non-filtered medium, which contains biomass and other forms of inorganic nitrogen, *e.g.*, ammonium (NH_3) and one with filtered medium (using a syringe and a 0.2 µm filter) that should not contain biomass, but only inorganic nitrogen. Thus, the difference between the filtered and non-filtered samples indicates the total amount of N present in the biomass, which is directly proportional to biomass content.

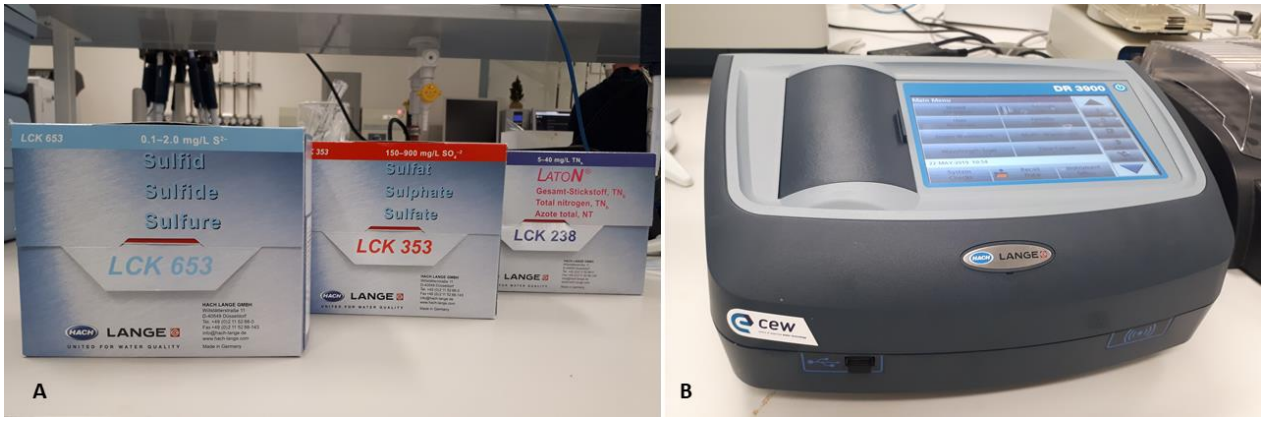

Figure 6 – A) Hach Lange test kits; B) Hach spectrophotometer used for the measurements.

- **Total Suspended Solids (TSS) Analysis**

Total Suspended Solids (TSS) is an analytical method to quantify suspended solid-phase material concentration. For this type of analysis, a filtration apparatus was needed (see Figure 7): filtration flask, Buchner funnel, vacuum pump and filter paper (Whatman 589/3 was used in these experiments). All used filters were previously washed with demineralized water, dried overnight at 105 ℃ and then weighed in an analytical balance. The procedure started by placing a clean and dried filter onto the filtration apparatus and then applying the vacuum. After rinsing it with demineralized water, 30 mL of the reactor sample was poured carefully. To remove salts in the filter and the remaining solids of the sample, the filter was then rinsed again with demineralized water. Finally, the filter with the solids was placed in an aluminum sheet into an oven set to 45 °C

overnight. The next day, the dried filter with solids was weighed in the analytical balance (A200S, Sartorius, Germany). TSS value, in grams per liter, was then estimated by the following expression:

$$TSS = \frac{W_{filter+solids} - W_{filter}}{V_{sample}} \quad 3.4$$

where $W_{filter+solids}$ is the mass of the dried filter with the solids, in grams, W_{filter} is the mass of the dried filter (before the procedure), also in grams and V_{sample} is the sample volume, in liters (Water Testing and Environmental Analysis, 2007).

Figure 7 - Filtration apparatus used for TSS analysis.

- **Settleable matter**

Settleable matter test was applied to determine the settled sludge (biomass) volume of a one-liter reactor sample. The sludge settleability test is useful to observe the settling characteristics of the biomass and determine the sludge flow rate. To perform this test, a conical settleometer (Imhoff cone) was filled with one liter of the reactor sample. After 45 minutes, the cone was twisted to release solid particles of the walls and 15 minutes later (total time of one hour) the result, in milliliters of solids per liter of reactor sample per hour ($mL \cdot L^{-1} \cdot h^{-1}$), was read in the settleometer. This procedure is shown in Figure 8 below.

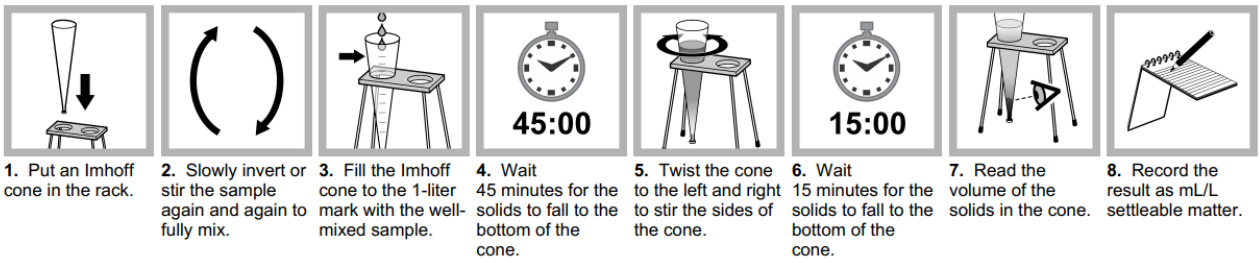

Figure 8 - Test procedure for settleable matter.

3.7.2 Influent Analysis

The prepared influent was also analyzed regularly to determine the pH and conductivity and to estimate the bisulfide, sulfate and thiosulfate concentrations.

- **pH and Conductivity**

pH and conductivity of each influent tank were always measured two times - at the beginning of a new tank and at the end (the moment of changing influents) – in the same way as the reactor samples.

- **Sulfide Hach Lange™ Cuvette Tests (LCK 653)**

Since the influent is the primary source of bisulfide (HS^-), it was useful to analyze the concentration of this compound to guarantee that the HS^- load was in the expected range. These sulfide tests were carried out once a week for a total of four times for each influent tank. Unlike the reaction medium, the influent contained large amounts of sulfide so, in this case, it was necessary to perform a 5000-times dilution so that the concentration was in the measurement range ($0.1 – 2.0\ mg \cdot L^{-1}$) of the Hach Lange™ test.

- **HPLC sample preparation**

HPLC analyzes of the influent were also performed once a week (total of four times for each tank) to determine the sulfate and thiosulfate concentrations with accuracy. For the HPLC vial preparation, the influent sample was first diluted two-times with a zinc acetate solution in order to precipitate the sulfide. After filtering it with a syringe and a 0.2 µm filter, the sample was then diluted five-times (in total, a ten-times dilution) with the HPLC buffer (1.7 mM $NaHCO_3$ and 1.8 mM Na_2CO_3).

4 Results

4.1 Reactor performance at different ORP setpoints and different conductivities

A sulfide-rich synthetic medium was fed to an aerobic up-flow bioreactor with SOM, resulting in production of sulfate (SO_4^{2-}), thiosulfate ($S_2O_3^{2-}$) and elemental sulfur (S^0). Results from this study are summarized in Figure 9, in which sulfate and thiosulfate concentrations (obtained by HPLC) *vs.* time are plotted. Calculated selectivities for each product over time is shown in Figure 10. Operational conditions (ORP, Na^+ concentration in the influent, pH and conductivity in the reactor) of each steady state, as well as the corresponding main results (product concentrations obtained by HPLC, selectivities, TSS, and sludge settlement results), are summarized in Table 3.

Consumption flow rates of influent, nutrients and HCl over time can be consulted in Appendix 2. Influent measurements and Total nitrogen concentrations corresponding to biomass for each steady-state are presented in Appendix 3 and Appendix 4, respectively.

The first steady-state was reached on day 54. In this steady-state (day 54-58), the reactor was operated at high ORP (-280 mV) so that more oxygen was available for biomass growth. The conductivity in the reactor was 91.68 ± 0.98 $mS \cdot cm^{-1}$. In this growth phase, sulfate was produced at a high concentration (11.69 ± 0.78 $g \cdot L^{-1}$) while thiosulfate was produced at insignificant concentrations (0.14 ± 0.19 $g \cdot L^{-1}$). Since the reactor was operating with growth conditions, selectivity for elemental sulfur was low (19.20 ± 6.91 %) while sulfate selectivity was high (80.80 ± 6.91 %). TSS (1.68 ± 0.51 $g \cdot L^{-1}$) was also low in this phase, which is in accordance with the low selectivity for elemental sulfur. The same applies to the result from the sludge settlement test, which was 16.75 ± 3.89 $mL \cdot L^{-1} \cdot h^{-1}$. Results from this first steady-state show that SOM are able to grow and produce SO_4^{2-} at high conductivities.

After the first phase, the ORP setpoint was lowered to -360 mV to improve elemental sulfur production. A second steady-state was then observed (day 61-65). Although the Na^+ concentration in the influent was the same, there was a decrease in conductivity to 86.20 ± 3.75 $mS \cdot cm^{-1}$. This can be explained by the lower sulfate concentration in the reactor (6.86 ± 0.69 $g \cdot L^{-1}$), which also contributes to conductivity. SO_4^{2-} selectivity also decreased (47.35 ± 4.69 %), whereas selectivities for $S_2O_3^{2-}$ (6.39 ± 3.00 %) and for S^0 (46.25 ± 3.59 %) increased compared to the first stage. TSS (2.23 ± 0.52 $g \cdot L^{-1}$) and sludge settleability (22.10 ± 9.70 $mL \cdot L^{-1} \cdot h^{-1}$) results were also higher

compared to the previous steady-state. Results from this second stage show that SOM are able to produce elemental sulfur at substantial selectivity at high conductivities.

After the second phase, the ORP setpoint was further lowered to -385 mV to improve elemental sulfur selectivity once more. This ORP corresponds to the production regime, *i.e.*, favorable conditions to produce elemental sulfur. Na^+ concentration in the influent was increased to 28 $g \cdot L^{-1}$ to have higher conductivity in the reactor again, which was 91.18 ± 1.30 $mS \cdot cm^{-1}$. A third steady-state was then reached on day 86 to 92. SO_4^{2-} concentration (3.06 ± 0.81 $g \cdot L^{-1}$) and SO_4^{2-} selectivity (21.01 ± 5.67 %) decreased once more, comparing to the previous steady-state. $S_2O_3^{2-}$ concentration (0.60 ± 0.04 $g \cdot L^{-1}$) also decreased leading to a $S_2O_3^{2-}$ selectivity of approximately zero percentage points. Selectivity for elemental sulfur increased to 78.94 ± 5.75 % and reached 84.59 % at day 89. TSS and sludge settlement results also increased to 4.88 ± 1.69 $g \cdot L^{-1}$ and 52.60 ± 18.78 $mL \cdot L^{-1} \cdot h^{-1}$, respectively, because of higher amounts of S^0 in the system. Results from this steady-state show that more than 80 % of selectivity for elemental sulfur can be achieved at conductivities higher than 90 $mS \cdot cm^{-1}$ in the reactor.

Finally, at the same ORP setpoint (-385 mV) as the previous stage, Na^+ concentration in the influent was further increased to 30 $g \cdot L^{-1}$. The fourth and last steady-state was reached during day 103 to 117 with the highest conductivity setpoint, which was 94.67 ± 1.26 $mS \cdot cm^{-1}$. In this phase, SO_4^{2-} concentration (1.67 ± 0.43 $g \cdot L^{-1}$) and SO_4^{2-} selectivity (11.26 ± 3.14 %) were the lowest compared to the other steady-states. On the opposite, S^0 selectivity (85.99 ± 3.05 %) was the highest, reaching a maximum of 88.87 % on day 113. As expected, TSS (8.94 ± 4.34 $g \cdot L^{-1}$) and sludge settlement values (80.86 ± 43.46 $mL \cdot L^{-1} \cdot h^{-1}$) were also the highest, since the reactor was full of elemental sulfur during this steady-state. Results from this final steady-state prove that elemental sulfur selectivity may even increase at higher conductivities, achieving nearly 90 % at a conductivity of approximately 95 $mS \cdot cm^{-1}$ in the reactor.

SO_4^{2-} concentrations determined by Hach Lange cuvette tests were not used in calculations since those values are less accurate than the ones obtained by HPLC, as mentioned in Section 3.7.1. However, Hach Lange cuvette tests are the only method used by the clients to calculate concentrations on-site. Thus, it is essential to evaluate the difference between SO_4^{2-} concentrations determined by these tests and SO_4^{2-} concentrations obtained by HPLC. A graphical comparison of these concentrations is shown in Figure 11. This graph shows that results obtained by Hach Lange test and HPLC are similar for SO_4^{2-} concentrations below 6.00 $g \cdot L^{-1}$. However, above 6.00 $g \cdot L^{-1}$, the Hach Lange test seems to underestimate the concentrations.

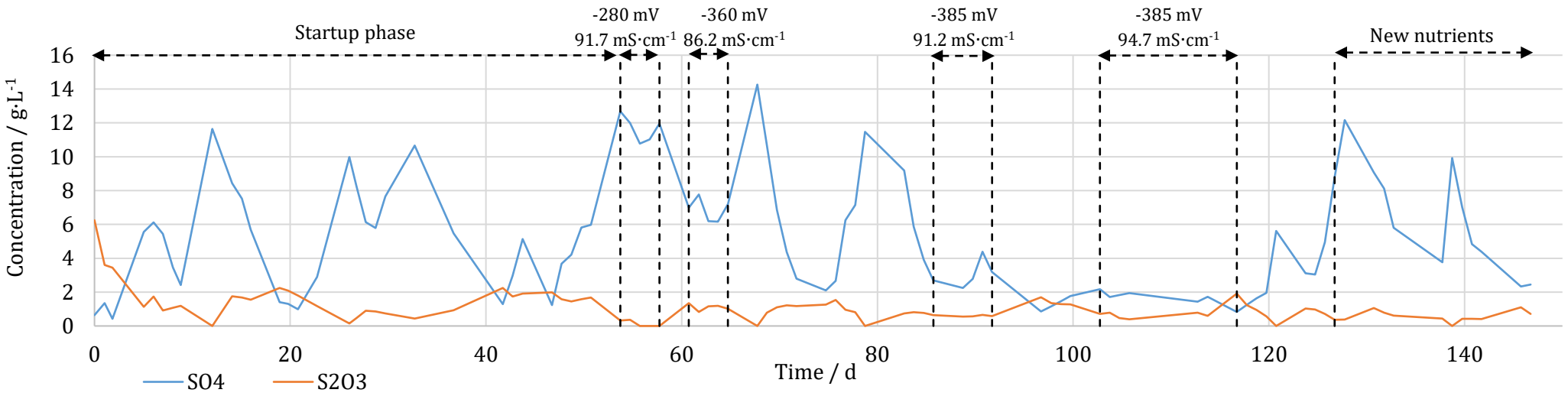

Figure 9 - Concentration of sulfate (SO_4^{2-}) and thiosulfate ($S_2O_3^{2-}$) in the reactor over time. T=36 ℃, pH=8.3, HRT=1.4 d.

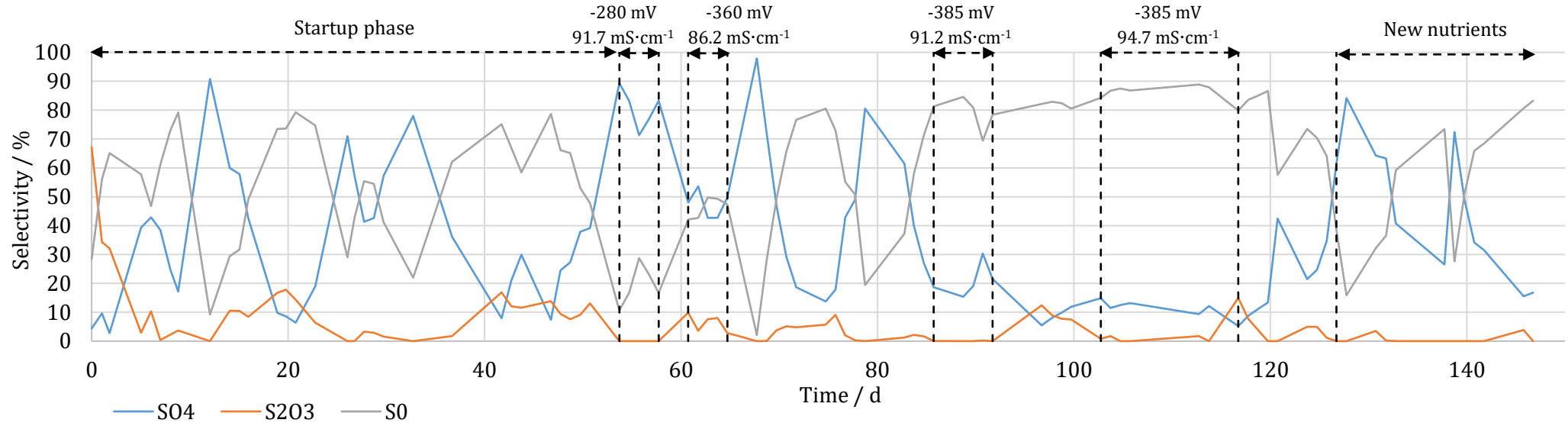

Figure 10 - Selectivity for sulfate (SO_4^{2-}), thiosulfate ($S_2O_3^{2-}$) and elemental sulfur (S^0) over time. T=36 ℃, pH=8.3, HRT=1.4 d.

Table 3 - Operational conditions for each steady-state and corresponding main results.

ORP	pH	[Na+]	Conductivity	Concentrations		Selectivities			TSS	Sludge Settlement
				$[SO_4^{2-}]$	$[S_2O_3^{2-}]$	SO_4^{2-}	$S_2O_3^{2-}$	S^0		
mV	-	$g \cdot L^{-1}$	$mS \cdot cm^{-1}$	$g \cdot L^{-1}$	$g \cdot L^{-1}$	%	%	%	$g \cdot L^{-1}$	$mL \cdot L^{-1} \cdot h^{-1}$
-280	8.13 ± 0.11	25.00	91.68 ± 0.98	11.69 ± 0.78	0.14 ± 0.19	80.80 ± 6.91	0.00 ± 0.00	19.20 ± 6.91	1.68 ± 0.51	16.75 ± 3.89
-360	8.24 ± 0.03	25.00	86.20 ± 3.75	6.86 ± 0.69	1.11 ± 0.20	47.35 ± 4.69	6.39 ± 3.00	46.25 ± 3.59	2.23 ± 0.52	22.10 ± 9.70
-385	8.22 ± 0.05	28.00	91.18 ± 1.30	3.06 ± 0.81	0.60 ± 0.04	21.01 ± 5.67	0.04 ± 0.08	78.94 ± 5.75	4.88 ± 1.69	52.60 ± 18.78
-385	8.25 ± 0.03	30.00	94.67 ± 1.26	1.67 ± 0.43	0.81 ± 0.51	11.26 ± 3.14	2.75 ± 5.42	85.99 ± 3.05	8.94 ± 4.34	80.86 ± 43.46

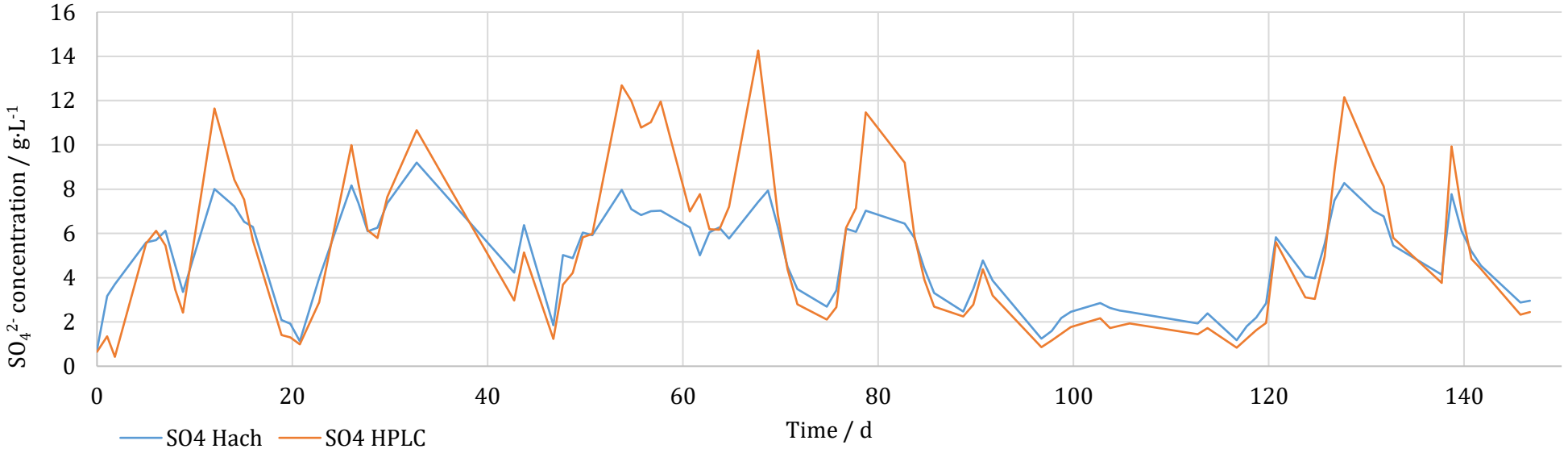

Figure 11 - Concentrations of SO_4^{2-} in the reactor determined by Hach cuvette test and by HPLC over time.

4.2 Celtic Chemicals nutrients

Since the Sulfurex®BR full-scale system is in the USA, the River Bend Labs nutrients (see Figure 12-A) applied in the process are also from there. However, for possible future projects in Europe, DMT Environmental Technology will need another nutrient supplier also in Europe. On that regard, the company also wanted to test new nutrients from Celtic Chemicals (see Figure 12-B), in the UK. At the end of this study (from day 127), these nutrients were therefore applied in the lab-scale bioreactor to demonstrate that SOM could also operate with them. Results from those days show that almost no thiosulfate formation was observed. This means that Celtic Chemicals is a possible nutrient supplier for a future European plant.

Figure 12 - A) River Bend Labs nutrients; B) Celtic Chemicals nutrients.

4.3 Sparger clogging

With elemental sulfur producing conditions (ORP = -385 mV) and high conductivities (91.18 ± 1.30 – 94.67 ± 1.26 $mS \cdot cm^{-1}$), clogging of the air sparger (see Figure 13-A) was observed very often (almost every day) as a result of the high amount of solids in the reactor. To confirm that clogging was caused only by the solids in suspension (elemental sulfur and biomass) and not by precipitation of salts, ORP was increased back to -280 mV on day 147 and the sparger was observed until day 154. During these days, the conductivity was also high (97.06 ± 1.62 $mS \cdot cm^{-1}$). No clogging was observed inside the sparger during this time (see Figure 13-B), indicating that it is primarily caused by elemental sulfur instead of salts.

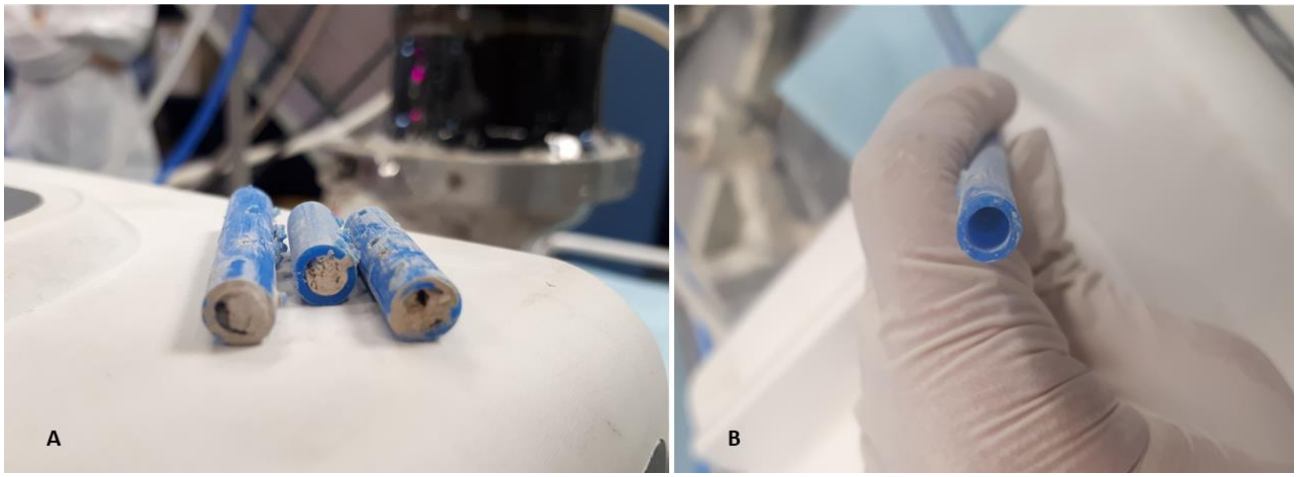

Figure 13 – A) Small portions of the clogged air sparger, with elemental sulfur producing conditions in the reactor (ORP=-385 mV); B) Unclogged sparger, with growth conditions (ORP=-280 mV).

5 Discussion

5.1 Reactor performance at different ORP setpoints and different conductivities

From the results described in the previous Chapter, it is verified that the system performance in terms of selectivity for elemental sulfur is improved when the ORP is decreased, as expected. This confirms that a limiting oxygen concentration in the reactor is favorable to the production of elemental sulfur.

Results also prove that operating with conductivities higher than 75 $mS \cdot cm^{-1}$, not only microorganisms can grow and consume hydrogen sulfide, but also their performance can be enhanced when increasing conductivity in the reactor. The maximum S^0 selectivity (85.99 ± 3.05 %) was achieved at the highest conductivity tested in the reactor (94.67 ± 1.26 $mS \cdot cm^{-1}$).

5.2 Caustic soda saving at higher conductivities

Caustic soda consumption in the full-scale system for a certain conductivity setpoint was estimated using an in-house confidential tool that relates conductivity and caustic soda usage. For instance, at a conductivity of 75 $mS \cdot cm^{-1}$, assuming 90 % of selectivity for S^0 and an alkalinity of 59 $g \cdot L^{-1}$ of $CaCO_3$, 3.25 kilograms of pure caustic soda is consumed per kilogram of treated sulfur to compensate for SO_4^{2-} formation as well as HCO_3^- loss in the bleed stream (see Equations 2.4 and 2.8). Likewise, it was also possible to estimate a consumption of 0.93 $kg_{NaHO} \cdot kg_S^{-1}$ with the highest conductivity tested in this study (94.67 $mS \cdot cm^{-1}$). This implies that, using this value for the conductivity setpoint, it is possible to save 2.32 kilograms of NaHO per kilogram of treated sulfur. For instance, using a daily load of 386 kilograms of elemental sulfur (value applied in Sulfurex®BR), it is possible to save 896.88 kg of pure caustic soda per day. Considering a price of approximately 0.28 US$ per kilogram of 32 % NaHO solution (Caustic Soda Liquid Lye Solution 32% 48% 50% Sodium Hydroxide, *s.d.*) and a currency conversion of 1.13 US$ per 1.00 euro (Dollar to Euro, *s.d.*), that means it is possible to save 1.14 € per kilogram of treated sulfur or 440.17 € per day (using 386 $kg_S \cdot d^{-1}$).

5.3 Scaling problems

Scaling is the deposition of mineral salt on processing equipment as a result of supersaturation of mineral ions in the process fluid. Formation of scale can cause several problems, for instance, blocked pipelines and blocked processing equipment (Nergaard & Grimholt, 2010).

The best performance of SOM was achieved with the highest tested conductivity (94.67 $mS \cdot cm^{-1}$), leading to high elemental sulfur selectivity as seen before in Chapter 4. However, if conductivity was further increased, *i.e.*, sodium concentration in the influent was further increased, some problems could occur as sodium bicarbonate could precipitate. To determine the lowest concentration of sodium (Na^+) in the influent at which precipitation occurs (saturation point), a small lab experiment was performed simulating the influent in a continuously stirred beaker. With that test, it was concluded that the saturation point corresponded to a Na^+ concentration of approximately 36.9 $g \cdot L^{-1}$. This result shows that at that concentration, problems related to precipitation of sodium bicarbonate occur, for instance, scaling issues. Because of that, Na^+ concentration in the influent was not further increased (a maximum of 30.0 $g \cdot L^{-1}$ was applied, as mentioned in Section 3.4). However, the determined saturation point is only valid for the experimental set-up in WAC, since Sulfurex®BR full-scale system has some different conditions than the lab installation (mentioned in Section 3.4), leading to a slightly different composition of the reaction medium.

6 Conclusion

This project for DMT Environmental Technology evaluates the impact of high conductivities in a bioreactor for biogas desulfurization and the reduction of caustic soda use in the process. Results confirmed that a limiting oxygen concentration (low ORP) in the reactor is favorable to the production of elemental sulfur.

Different conductivity setpoints in the reactor were tested and results show that SOM were able to grow, consume hydrogen sulfide and produce sulfate at high conductivities (86.20 – 94.67 $mS \cdot cm^{-1}$). In addition, a maximum elemental sulfur selectivity of 85.99 % was achieved at the highest conductivity tested (94.67 $mS \cdot cm^{-1}$). By applying this conductivity value to the full-scale system, it is possible to save 2.32 kilograms of NaHO per kilogram of treated sulfur. This recent knowledge allowed the optimization of Sulfurex®BR, reducing operational costs in 1.14 € per kilogram of treated sulfur. Considering an elemental sulfur load of 386 $kg \cdot d^{-1}$ (value applied in Sulfurex®BR), it is possible to save 440.17 € per day.

Higher conductivities were not tested as precipitation of salts could occur, leading to scaling problems. However, since Sulfurex®BR reaction medium is slightly different from the one in the lab-scale, higher values of conductivity can still be experimented in the future in the full-scale system.

Different nutrients from a European supplier (Celtic Chemicals, UK) were also tested for a possible future Sulfurex®BR plant in Europe. Results proved that SOM could produce sulfate while almost no thiosulfate formation was observed, which means that Celtic Chemicals is a possible nutrient supplier for a future European plant.

7 Assessment of the work done

7.1 Objectives Achieved

The main goal of this project was to demonstrate that SOM could grow and high elemental sulfur selectivity (> 80 %) could be achieved at a conductivity higher than 75 $mS \cdot cm^{-1}$ (current value applied in the full-scale system). This translates into a reduction of caustic soda consumption and thus operational costs in Sulfurex®BR full-scale system. These objectives were successfully achieved since microorganisms grew and 85.99 % selectivity for elemental sulfur was obtained at a conductivity of 94.67 $mS \cdot cm^{-1}$. Applying this conductivity to the full-scale system, it is possible to save approximately 2.32 kilograms of NaHO per kilogram of treated sulfur, which means approximately 1.14 € per kilogram of treated sulfur.

DMT Environmental Technology also wanted to know how the microorganisms would react to different nutrients from a European supplier (Celtic Chemicals, UK). Thus, at the end of this study, these nutrients were applied in the lab-scale bioreactor to demonstrate that SOM can also operate with them. Results proved that Celtic Chemicals is a possible nutrient supplier for a future European plant.

7.2 Other Work Carried Out

Working for DMT also required having a Basis VCA diploma (Basic Safety Rules). VCA stands for "*Veiligheid (gezondheid en milieu), Checklist Aannemers"*, which means "Safety, Health and Environment Checklist Contractors". VCA training and exam are addressed to all employees who perform practical work duties (including contractors and subcontractors). The training aims to provide information about the basic rules of safe work. The Basis VCA diploma applies to work in occupations with higher risk such as scaffolding, assembly, electrical, insulating, maintenance, petrochemical and others. Therefore, in parallel to the project, I took the VCA training and did the exam on March 20th. The certificate is now valid for ten years.

7.3 Limitations and Future Work

During the internship, there were some limitations to the study, mostly related to the experimental set-up since it was quite different from the full-scale system. As mentioned in Chapter 3, instead of an absorber treating hydrogen sulfide (H_2S) containing biogas, it was decided to operate with a chemical prepared influent. This influent has different salts that change the composition of the medium. This means that this work was developed with a reaction fluid that is

slightly different from the one of Sulfurex®BR reactor. A suggestion for future work would be to experiment only on the full-scale system instead of on a lab-scale set-up.

The air sparger used in the reactor was also a source of problems. On the one hand, small air bubbles improve oxygen transfer from the air to the reaction medium. On the other hand, if the sparger has too small pores, they get clogged by the solids in the system. Besides, big bubbles also facilitate homogenization and keep all the solids in suspension. On this regard, a compromise in the pore size of the air sparger must be found. A stainless steel sparger was first used at the beginning of the study, which was always getting clogged by the solids in the system. This was also an additional cost to the project since spargers had to be ordered frequently. To partially solve this, a new sparger was made by hand, using a pipe and a needle to pierce it. That one was a better solution since it was possible to clean it every time, reducing clogging occurrence.

Another constraint was the old HPLC equipment which slowed down the delivery of results. Also because of that, some problems were only perceived a few days after they started. In that sense, a suggestion would be to invest in more recent HPLC equipment.

7.4 Final Assessment

Results of the work developed during the internship were enriching for DMT Environmental Technology, having a positive impact in the full-scale system. The company is already applying this new knowledge that contributes significantly to the reduction of operational costs. The internship was also beneficial for me, personally and professionally. It allowed me a first contact with a company, in addition to all the technical laboratory experience. Furthermore, all the limitations and problems encountered during this study helped me developed my critical thinking and problem-solving skills.

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Appendix 1 Safety Data

Table 4 - Safety data of Sodium sulfide nonahydrate and hydrochloric acid (Fisher Scientific, 2009).

	Sodium sulfide nonahydrate	Hydrochloric acid
Hazard Statements	May be corrosive to metals. Toxic if swallowed. Causes severe skin burns and eye damage.	May be corrosive to metals. Causes severe skin burns and eye damage. May cause respiratory irritation.
Precautionary Statements (Prevention)	Wash face, hands and any exposed skin thoroughly after handling. Do not eat, drink or smoke when using this product. Do not breathe dust/fume/gas/mist/vapours/spray. Wear protective gloves/protective clothing/eye protection/face protection. Use only outdoors or in a well-ventilated area. Keep only in the original container. Wear respiratory protection.	Do not breathe dust/fume/gas/mist/vapours/ spray. Wash face, hands and any exposed skin thoroughly after handling. Wear protective gloves/protective clothing/eye protection/face protection. Use only outdoors or in a well-ventilated area. Keep only in the original container.
First-aid Measures	**Eye contact** Rinse immediately with plenty of water, also under the eyelids, for at least 15 minutes. Immediate medical attention is required. **Skin contact** Wash off immediately with plenty of water for at least 15 minutes. Immediate medical attention is required.	**Eye Contact** Rinse immediately with plenty of water, also under the eyelids, for at least 15 minutes. Immediate medical attention is required. **Skin Contact** Wash off immediately with plenty of water for at least 15 minutes. Immediate medical attention is required.

	Inhalation	**Inhalation**
	Move to fresh air. If breathing is difficult, give oxygen. Do not use mouth-to-mouth method if victim ingested or inhaled the substance; give artificial respiration with the aid of a pocket mask equipped with a one-way valve or other proper respiratory medical device. Immediate medical attention is required.	Move to fresh air. If breathing is difficult, give oxygen. Do not use mouth-to-mouth method if victim ingested or inhaled the substance; give artificial respiration with the aid of a pocket mask equipped with a one-way valve or other proper respiratory medical device. Immediate medical attention is required.
	Ingestion	**Ingestion**
	Do not induce vomiting. Call a physician or Poison Control Center immediately.	Do not induce vomiting. Call a physician or Poison Control Center immediately.
Most important symptoms and effects	Causes burns by all exposure routes. Product is a corrosive material. Use of gastric lavage or emesis is contraindicated. Possible perforation of stomach or esophagus should be investigated: Ingestion causes severe swelling, severe damage to the delicate tissue and danger of perforation.	Causes burns by all exposure routes. Product is a corrosive material. Use of gastric lavage or emesis is contraindicated. Possible perforation of stomach or esophagus should be investigated: Ingestion causes severe swelling, severe damage to the delicate tissue and danger of perforation.
Storage	Store locked up in a dry well-ventilated place; Store in a corrosive resistant polypropylene container with a resistant inliner and keep it tightly closed.	Store locked up in a dry well-ventilated place; Store in a corrosive resistant polypropylene container with a resistant inliner and keep it tightly closed.

Personal Protective Equipment	**Eye/face Protection:** Wear appropriate protective eyeglasses or chemical safety goggles as described by OSHA's eye and face protection regulations in 29 CFR 1910.133 or European Standard EN166. Tightly fitting safety goggles. Face-shield. **Skin and body protection:** Long sleeved clothing. **Respiratory Protection:** Follow the OSHA respirator regulations found in 29 CFR 1910.134 or European Standard EN 149. Use a NIOSH/MSHA or European Standard EN 149 approved respirator if exposure limits are exceeded or if irritation or other symptoms are experienced. **Hygiene Measures:** Handle in accordance with good industrial hygiene and safety practice.	**Eye/face Protection:** Wear appropriate protective eyeglasses or chemical safety goggles as described by OSHA's eye and face protection regulations in 29 CFR 1910.133 or European Standard EN166. **Skin and body protection:** Wear appropriate protective gloves and clothing to prevent skin exposure. **Respiratory Protection:** Follow the OSHA respirator regulations found in 29 CFR 1910.134 or European Standard EN 149. Use a NIOSH/MSHA or European Standard EN 149 approved respirator if exposure limits are exceeded or if irritation or other symptoms are experienced. **Hygiene Measures:** Handle in accordance with good industrial hygiene and safety practice.
Toxicological Information	**Oral LD50** = 208 $mg \cdot kg^{-1}$ (Rat) **Dermal LD50** < 340 $mg \cdot kg^{-1}$ (Rabbit)	**Oral LD50** = 238 - 277 $mg \cdot kg^{-1}$ (Rat) **Dermal LD50** > 5010 $mg \cdot kg^{-1}$ (Rabbit) **Inhalation LC50** = 1.68 $mg \cdot L^{-1}$ (Rat) 1 h
Disposal	Dispose of contents/container to an approved waste disposal plant.	Dispose of contents/container to an approved waste disposal plant.

Appendix 2 Consumption of influent, nutrients and HCl

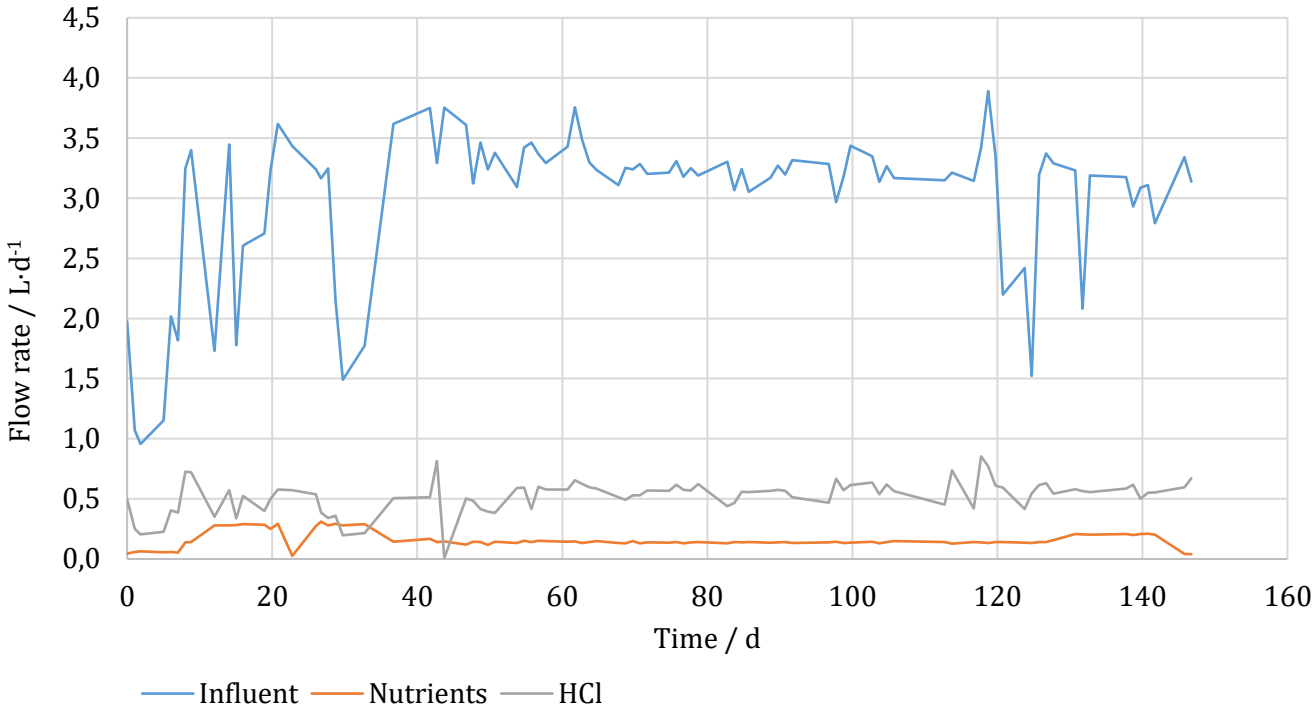

Figure 14 - Influent, nutrients and hydrochloric acid consumption flow rates over time.

Appendix 3 Influent Data

Table 5 - Data obtained from influent measurements for each steady state.

Steady state	pH	Conductivity / $mS \cdot cm^{-1}$	$[SO_4^{2-}]$ / $g \cdot L^{-1}$	$[S_2O_3^{2-}]$ / $g \cdot L^{-1}$
1	9.20 ± 0.01	64.80 ± 3.25	0.08 ± 0.03	0.49 ± 0.21
2	9.17 ± 0.04	64.48 ± 2.44	0.10 ± 0.06	0.61 ± 0.31
3	9.11 ± 0.06	64.60 ± 0.42	0.05 ± 0.00	0.64 ± 0.48
4	9.03 ± 0.05	68.60 ± 0.69	0.06 ± 0.01	0.63 ± 0.17

Appendix 4 Total Nitrogen in Biomass

Table 6 – Total nitrogen (N) concentrations corresponding to biomass.

Steady-state	ORP / mV	Conductivity / $mS \cdot cm^{-1}$	Total N in biomass / $mg_N \cdot L^{-1}$
1	-280	91.68 ± 0.98	12.62 ± 1.16
2	-360	86.20 ± 3.75	8.00 ±2.63
3	-385	91.18 ± 1.30	6.09 ± 2.07
4	-385	94.67 ± 1.26	10.59 ± 6.67