



University of
Stavanger

Faculty of Science and Technology

MASTER'S THESIS

Study program/ Specialization:

**Environmental Technology
(Offshore)**

Spring semester, **2012**

Open / Restricted access

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Titel of thesis:

**Reduction of scaling in biological treatment of industrial waste water at
SART**

Credits (ECTS): **30**

Key words:

*Scale potential, scale formation process,
calcium carbonate scale*

Pages: **63**

+ enclosure: **7**

Stavanger, **15.06.2012**

Date/year

ACKNOWLEDGEMENTS

In the beginning of this thesis I would like to express gratitude that people, who was took part and helped this work to be written.

First of all I want to thank Torleiv Bilstad for all the help, advices and guidance during this semester.

Special and deep thanks to SAR Treatment AS and Martin Severin Løklingholm, who suggested such an interesting and practically useful topic for thesis, who helped me with this thesis from the first day, keeping his eye on it, helped to carry out all necessary experiments at SART AS, whose comments gave me inspiration to do my best for this thesis, whose moral support and patience made me believe that what we do is necessary and useful work.

I express my sincere thanks to Gunn Solheim and Liv Margaret Aksland for help and guidance with the lab experiments in the laboratory of the University in Stavanger.

And endless gratitude is for my dear family, who believes in me in spite of time and distance and motivates me to grow up.

ABSTRACT

Scale formation is one of serious problems for oil industry and water treatment. Thanks to well-developed technologies today there is a wide spectrum of solutions, consisting of chemical inhibitors, evaporators and reverse osmosis membranes.

SAR Treatment AS investigates different acceptable for the plant solutions to the calcium carbonate scale formation. This work presents overview of different options for SART AS, and makes stronger accent on a sand cyclone usage.

The experiments and measurements of chemical parameters of cyclone treated water show that the cyclone efficiency in scale removal is significantly high. Also the experiment demonstrates that the cyclone has its own disadvantages, which should be taken in account. Most crucial of them are biomass removal and absence of the dewatering mechanism for the sand cyclone.

According to the SART AS position, the sand cyclone can be used at the plant as scale removal equipment provided some necessary technical changes.

Key words: *Scale potential, scale formation process, calcium carbonate scale.*

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ABBREVIATIONS

TSS – Total Suspended Solids

VSS – Volatile Suspended Solids

TOC – Total Organic Carbon

SART AS – SAR Treatment plant

LSI - Langelier Saturation index

RSI - Ryznar solubility index

TDS – Total Dissolved Solids

DAF – Dissolved Air Flotation

PLS system – Programmerbar Logisk Styring

KLIF - Klima- og Forurensningsdirektoratet

RO – Reverse Osmosis

EDTA - Ethylenediaminetetraacetic acid

ALS AS – ALS Laboratory Group Norway AS

1. Introduction

This thesis is dedicated to find out a practical solution to the problem of scale formation in a biological system at an industrial water treatment plant.

The theoretical part of the thesis looks at the problem from a point of the physic-chemical processes and kinetics of scale formation. It also gives an overview and analysis of technologies available to solve the problem, advantages and disadvantages of every method for the particular industrial water treatment plant.

The practical part of the thesis includes measurements of the main working parameters of the water at the plant during treatment process; measurements of total suspended solids (TSS), volatile suspended solids (VSS), hardness and alkalinity.

A practical experiment using a sand cyclone was performed to see if this would be practical solution. The measurements were done before and after this experiment to support the conclusion.

1.1 Background

The process of scale formation is a focus area for many research institutes all over the world, trying to find better ways to control the process and minimize it's negative impact. Scaling is one of the central problems for water treatment industries and process industries in general.

Scale formation is one of the factors, which needs to be taken into account on the earliest stage of design, equipment development, and choice of a proper material and production of specific equipment. The possibility of scale formation is also one of the criteria to look at before implementing new chemicals in the industry.

Insufficient attention to scale formation problems can lead to such undesirable circumstances as: decreasing performance of the equipment, damages, significant decreasing productivity, economical costs, and time consumption for mechanical removal of already formed scale.

Periodical routines in form of correct design, inspections, control and proper chemical usage can prevent these effects.

Between the solutions for the problem we can name the following use of chemicals such as inhibitors, desalination and mechanical removal. Generally usage of chemicals such as acids or scale inhibitors is most commonly used for scale removal/prevention.

1.2 Objective

This master thesis is focused on the problem of scale formation on a specific industrial waste water treatment plant. This treatment plant is owned by SAR Treatment AS and is located at Tananger, Rogaland, Norway. The purpose of the master thesis is to find a solution for the existing problem of scale formation at SAR Treatment biological treatment system. To achieve the purpose it was identified that the following steps were necessary to be carried out:

- Laboratory measurements define physical-chemical characteristics of treated waste water in bioreactor of SAR Treatment;
- Determine optimal solutions to the problem of scale formation in the particular case;
- Evaluate the information about every alternative;
- Choose most acceptable alternative for observation and measurements;
- Test the chosen solution in the plant and observe the results;
- Provide the necessary guidance/recommendations.



Figure 1 SAR Treatment AS location, Tananger, Stavanger, Norway

1.3 Hypothesis

The following *hypothesis* was set in discussion with SART AS:

Mechanical treatment of water in the bioreactor loop by a sand cyclone improves water quality according to calcium carbonate concentration, along with removal of precipitated scale, without significant time and money consumption.

In other words, a sand cyclone is an available and practical solution to remove scale from the system.

1.4 Composition

The thesis includes 8 chapters. Chapters 2 – 4 present theoretical description of problem and possible solutions. The chapters have the following composition:

Chapter 2: Covers details of scale formation process.

Chapter 3: Gives a description of a concrete problem of scale formation at SAR Treatment plant.

Chapter 4: Presents analysis of available solutions for the scale problem with overview of advantages/disadvantages of every alternative.

Chapters 5: Describes material and methods, and procedures of all measurements which have been done during research.

Chapter 6: Gives a total overview of the results from the sand cyclone experiment.

Chapter 7: Presents discussion on the results of the measurements and their correlation with requirements and possibilities of SAR Treatment AS.

Chapter 8: Presents a summary of the conclusions and recommendations according to the hypothesis based on the results of the experiment.

2. Scale formation process

This chapter presents the theoretical background for scale formation process: definitions, types of scale, its reasons and conditions, kinetics and thermodynamic, methods to calculate scaling potential of the water.

2.1 Definition of scale formation

Before looking at solutions for the issue of scale formation, it is necessary to define *scale formation*. Researching this topic, the following definitions were found:

- *Scale formation is the deposition of sparingly soluble inorganic salts from aqueous solutions* [1];
- *The physicochemical prerequisite for the formation of any mineral solid deposit is the excess of mineral solubility in the respective fluid* [2];
- *Scaling or precipitation fouling involves crystallization of solid salts, oxides and hydroxides from solutions* [3].

It needs to clarify the proper meaning which is put in the word *scaling* in this thesis. As a working definition for this thesis the following have been chosen:

- *Scaling is solid layer deposition on a surface that arises primarily from the presence of dissolved inorganic salts in the flowing solution that exhibit supersaturation under the process conditions* [2].

2.2 Types of scale

The most common scale types encountered in the oil industry in order of prevalence are:

- Calcium carbonate - calcite and aragonite - CaCO_3 ;
- Calcium oxalate – CaC_2O_4 ;
- Sulfate salts of calcium (gypsum – $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$);
- Barium sulfate (barite) – BaSO_4 ;

- Magnesium hydroxide (brucite) – $\text{Mg}(\text{OH})_2$, magnesium oxides - MgO ;
- Sodium chloride (halite) - NaCl ;
- Phosphates (hydroxyapatite) - $\text{Ca}_5(\text{PO}_4)_3(\text{OH})$ [4].

Figure 2.2 shows calcium carbonate scale precipitation.

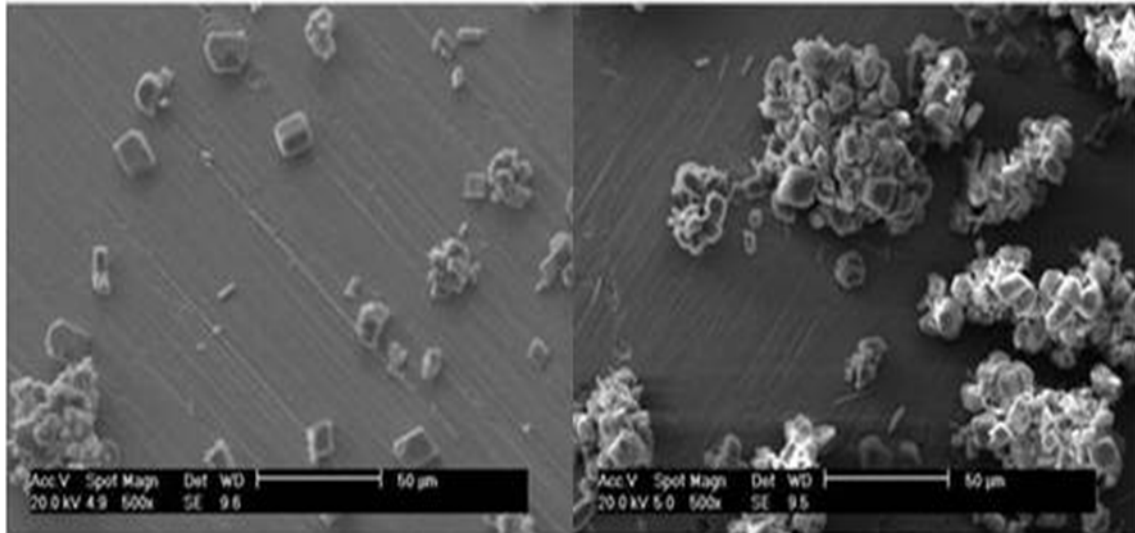


Figure 2.2 Calcium carbonate scale precipitation on surfaces [4]

An external laboratory *Intertek West Lab*¹ did an analysis of removed scale deposit from SART AS maintenance. It was analyzed two samples of scale: one is a scale formation from the wall in the bioreactor, and one – from “sand” (sediment) collected at the bottom. Percentage of calcium carbonate (CaCO_3), phosphorous (P) and chloride (Cl) in the first sample is 94 % - 3.8% - 1.1% respectively, and 96 % - 1.9% - 1.8% in the second sample. The results of the laboratory analysis are presented in Appendix 1.

¹*Intertek West Lab* is independent laboratory, which specializes in analyses of sample collection, operation of client laboratories, control of discharge that is hazardous to the environment, working environment studies and metering services for onshore and offshore businesses. Tananger, Rogaland, Norway <http://www.westlab.no/>.

2.3 Calcium carbonate scale

According to the report from *Intertek West Lab*, the most of the scale from the bioreactor of SART AS consists of calcium carbonate from wastewater treatment, but phosphorous precipitation also takes place. This can be explained by the addition of phosphoric acid as a nutrient.

The essence of scale formation reaction is that concentration of ions exceeds the solubility product of the various species. It initiates precipitation of the ions until the respective solubility products are no longer exceeded. Reasons for solubility products excess are various: the evaporation of water phase, change in pH/ pressure / temperature, and the introduction of additional ions that can form insoluble compounds with the ions already present in the solution. This happens in the biological treatment step. Precipitation of the products of the reaction on the equipment surface leads to adherent scales formation [2].

2.3.1 Conditions for calcium carbonate scaling

Calcium carbonate has an extremely low solubility at any temperature. It is logical that the deposition of calcium carbonate is found along heat transfer surfaces where there is temperature drop such as the reactor wall. Figure 2.3.1 shows the relationship of temperature to the solubility of calcium carbonate.

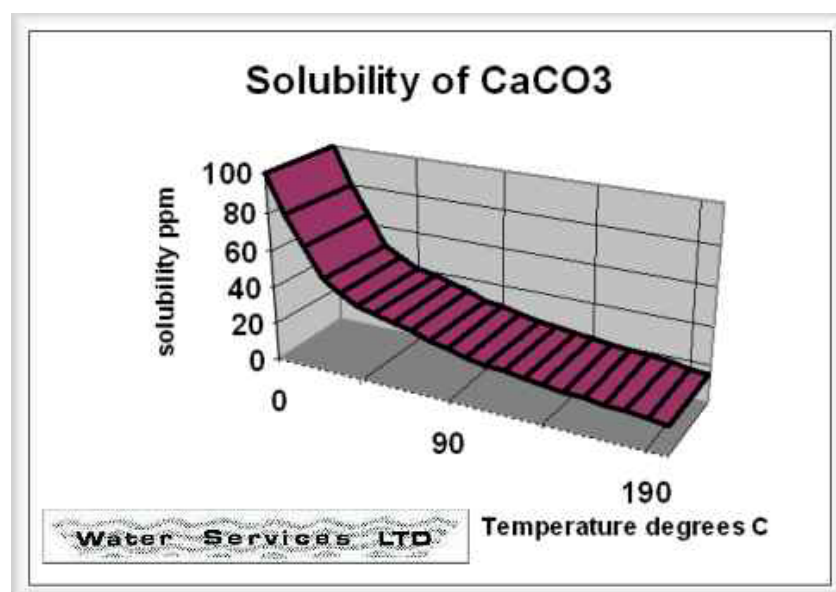


Figure 2.3.1 Relationship of calcium carbonate solubility and temperature [5]

According to the figure 2.3.1, high temperature regime during water treatment leads to a low solubility of calcium carbonate. As a result it gives higher level precipitation of the salt.

The effect of pH on the precipitation of CaCO₃ we can notice that in general, carbonates have high solubility in an acid solution and precipitate in a basic solution.

2.3.2 Stages of calcium carbonate scaling process

Figure 2.3.2 shows a whole process of calcium carbonate scale formation. It starts from the phase of induction of calcium and carbonate ions. Ions pass through stages of development of super saturation and nucleation² and growth of particles. After phases of agglomeration and adhesion the scale is formed.

² **Nucleation** is the extremely localized budding of a distinct thermodynamic phase. Some examples of phases that may form by way of nucleation in liquids are gaseous bubbles, crystals or glassy regions. Nucleation normally occurs at *nucleation sites* on surfaces contacting the liquid or vapor.
(<http://en.wikipedia.org/wiki/Nucleation>)

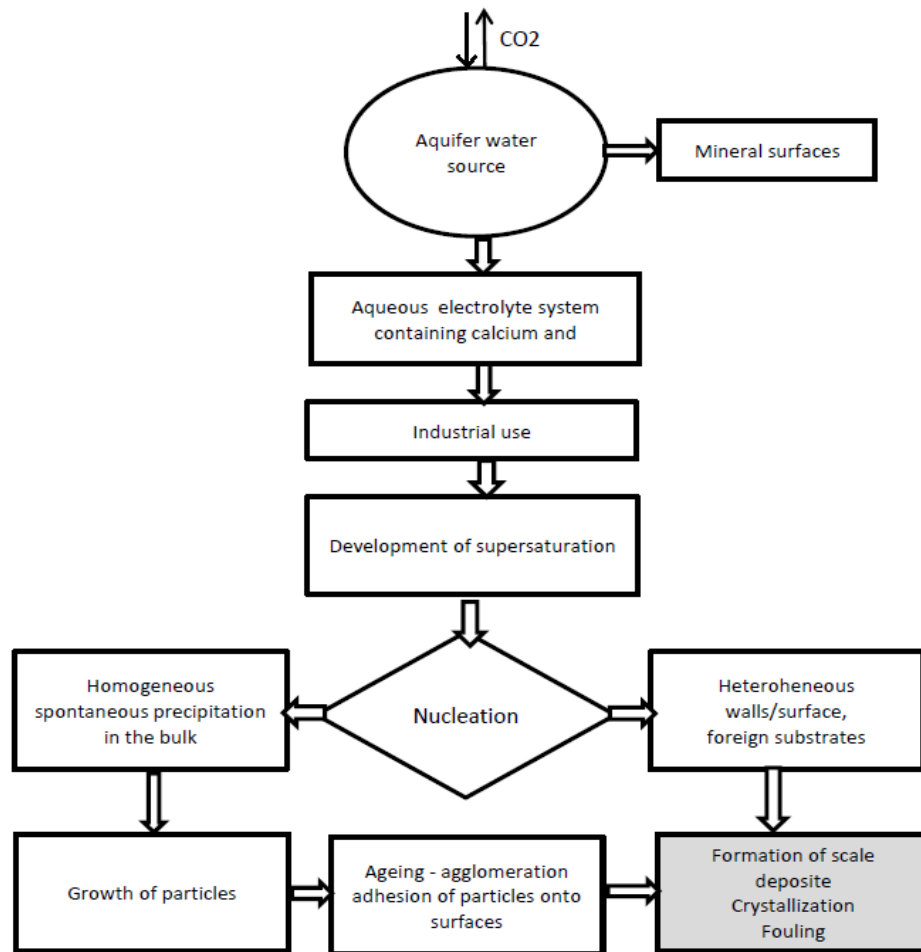


Figure 2.3.2 *Process of calcium carbonate scale formation* [2].

2.4 Reasons of calcium carbonate scale formation

An important observation is that the main reason for precipitation of calcium carbonate on solid substrates is not only the presence of inorganic and organic ions in the solution. Parameters of the solution, such as solution temperature, the flow rate and pH, are crucial for the stabilization of transient polymorphic phases [2], Hence calcium bicarbonate (CaHCO_3) is very water-soluble but CaCO_3 is not.

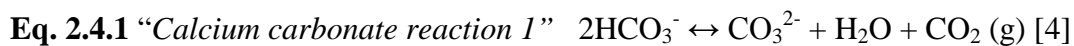
2.4.1 Polymorphic phases of calcium carbonate

Calcium carbonate can be in different polymorphic phases, and the most usual of them are *vaterite*, *aragonite*, and *calcite*. These phases are responsible for increasing of thermodynamic stability, and have different solubility, morphological and crystallographic characteristics. Depending on the fluid conditions (composition, temperature, fluid dynamics and substrate), less stable polymorphs may be stabilized and /or converted into the thermodynamically most stable calcite [2].

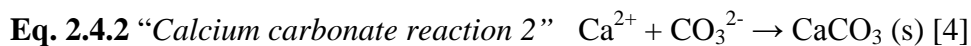
It is known that the formation of amorphous calcium carbonate is a precursor phase, forming upon the development of the appropriate conditions (high pH, high calcium and carbonate concentration). As a rule, industrial waters for most cases are characterized by their increased hardness, which is mainly due to the presence of calcium and carbonate ions. The distribution of carbonic species depends on the solution pH.

2.4.2 Calcium carbonate reactions

Calcium carbonate can deposit as a consequence the following equilibrium moving to the right as it shown in Equation 2.4.1:



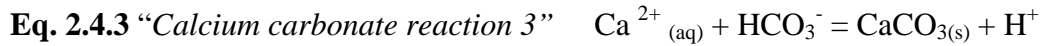
Thus, if the pressure drops, by *Le Chatelier's Principle*³ the above equilibrium will move to the right to try to increase the pressure by forming more CO₂ gas, as a result more carbonate ions are formed and the pH rises. At some point the concentration of carbonate ions may be high enough that calcium carbonate precipitates, shown in the following equation:



³ Le Chatelier's Principle: *If a chemical system at equilibrium experiences a change in concentration, temperature, volume, or partial pressure, then the equilibrium shifts to counteract the imposed change and a new equilibrium is established.*

http://en.wikipedia.org/wiki/Le_Chatelier's_principle

Over a wide pH range round the neutral, the bicarbonate HCO_3^- is the dominant species. The formation of calcium carbonate takes place according to equation:



2.5 Thermodynamics of scale deposit formation

The driving force behind the all chemical processes and reactions - the thermodynamics - describes the process of scale formation with help of chemical/thermodynamic distance – how far the solution is from the equilibrium state. This distance has a quantitative expression as the difference between the chemical potentials of the solute species and the respective values at equilibrium [2].

2.5.1 Saturation states

The processes which take place in the solution is depend on the degree of deviation from the equilibrium state, and can be described with help of *supersaturation* value. The positive value indicates supersaturated solution, negative – under saturated solution, but the value equal zero corresponds to saturation states or equilibrium [2].

Supersaturated region consists of two sub-regions: stable (supersaturation level 0-2) and labile (2-7). In the stable sub-region crystal growth occurs only in the presence of foreign substances. As an example, clay particles can accelerate the rate of calcium carbonate scale formation [2].

In order to evaluate scaling potential of a solution it is necessary to look at certain parameters of the solution such as salinity, activity coefficient and ions interaction [5].

2.5.2 Qualitative evaluation of scaling potential

For qualitative evaluation of the scaling potential of the sample water some thermodynamic indices are used, but they give only rough estimation due to oversimplification of equations. The main indices are *Langelier Saturation index (LSI)* and *Ryznar Solubility index (RSI)*.

2.5.2.1 Langelier Saturation Index

The Langelier Index is an approximate indicator of the degree of saturation of calcium carbonate in water. It is calculated using the pH, alkalinity, calcium concentration, total dissolved solids, and water temperature of a water sample collected at the tap [6].

The LSI shows difference between the measured solution pH and respective pH value at saturation:

Eq.2.5.1 “Calculation of Langelier index” $LSI = pH - pH_s$,

Eq. 2.5.2 “Calculation of pH at saturation” $pH_s = (9,3 + A+B) - (C+D)$

Where:

$$A = (\log [TDS] - 1)/10; \text{ (Total Dissolved Solids - TDS}^4\text{)}$$

$$B = -13,12 \times \log [\text{temperature } C + 273] + 34,55;$$

$$C = \log [Ca^{2+}] - 0,4;$$

$$D = \log [\text{Alkalinity}] [7].$$

⁴ **TDS** was calculated from conductivity. Average conductivity for SART is 46,8 mS/cm = 46800 μ S/cm. TDS = 46800 x 0,68 = 31824 mg/l. (0,68 is coefficient).

2.5.2.2 Ryznar Solubility Index

The Ryznar stability index uses a correlation established between an empirical database of scale thickness observed in municipal water systems and associated water chemistry data [7]. The Stability Index developed by Ryznar makes it possible to distinguish between two such waters. This index is based on a study of actual operating results with waters having various saturation indexes [8].

The RSI is calculated according to Equation 2.5.3.

Eq. 2.5.3 “Calculation of Ryznar solubility index” $RSI = 2pH_s - pH$ [9]

The meanings of the LI and the RSI values are shown in the Tables 2.1 and 2.2.

Table 2.1

Values of the LSI and water characteristics

LSI value	Characteristics
+2.0	scale-forming
+0.5	slightly scaling
0.0	equilibrium
-0.5	non-scale forming
-2.0	non-scale forming

Table 2.2

Values of the RSI and water characteristics

RSI value	Characteristics
4.0-5.0	significant scale forming
5.0-6.0	scaling to small extent
6.0-7.0	little scaling
7.0-7.5	non-scale forming
7.5-9.0	non-scale forming

3. SAR Treatment AS

SAR Treatment AS is a waste water treatment company which runs a plant in Tananger. The purpose of the SART is to separate out such undesirable compounds as heavy metals, oil/hydrocarbons, process chemicals, and to reduce total organic carbon, which presents in high concentrations in industrial wastewaters. SART receives most of its wastewater from offshore activities. To achieve necessary level of treatment, the wastewater goes through two types of active treatment in SAR Treatment plant: chemical process and biological process.

SAR Treatment AS is an integrated storage and treatment facility for waste water at Northern Sea Base in Tananger. SART treats significant amount of waste water, including oil-contaminated water, ballast water, engine-room slop and heavy-metal-contaminated waste water [9]. SART handles mostly slop water, but also some produced water.

3.1 Process at SART AS

The full process of water treatment at SART is shown in Figure 3.1.

The waste water from different locations are collected and sent to SART and is transferred the storage tanks. Next step in process is treatment in *diffusion-air-flotation* system (DAF), which removes some amount of oil and not heavy compounds from the water surface by chemical flocculation/coagulation and gas bubbling. The wastewater exits the DAF unit with a pH of 7, and is stored and continuously fed into the biological system from the “buffer/feed tank”. In the bioreactors the rest of the organic compounds are removed by the microorganisms. Settling chamber is the last stage where biomass settles down to the bottom of the chamber and is returned to the biological system, the effluent water is released to the sea.

In regards to this thesis it is looked at the potential of scaling in waste water and the biological system where scaling is in issue.

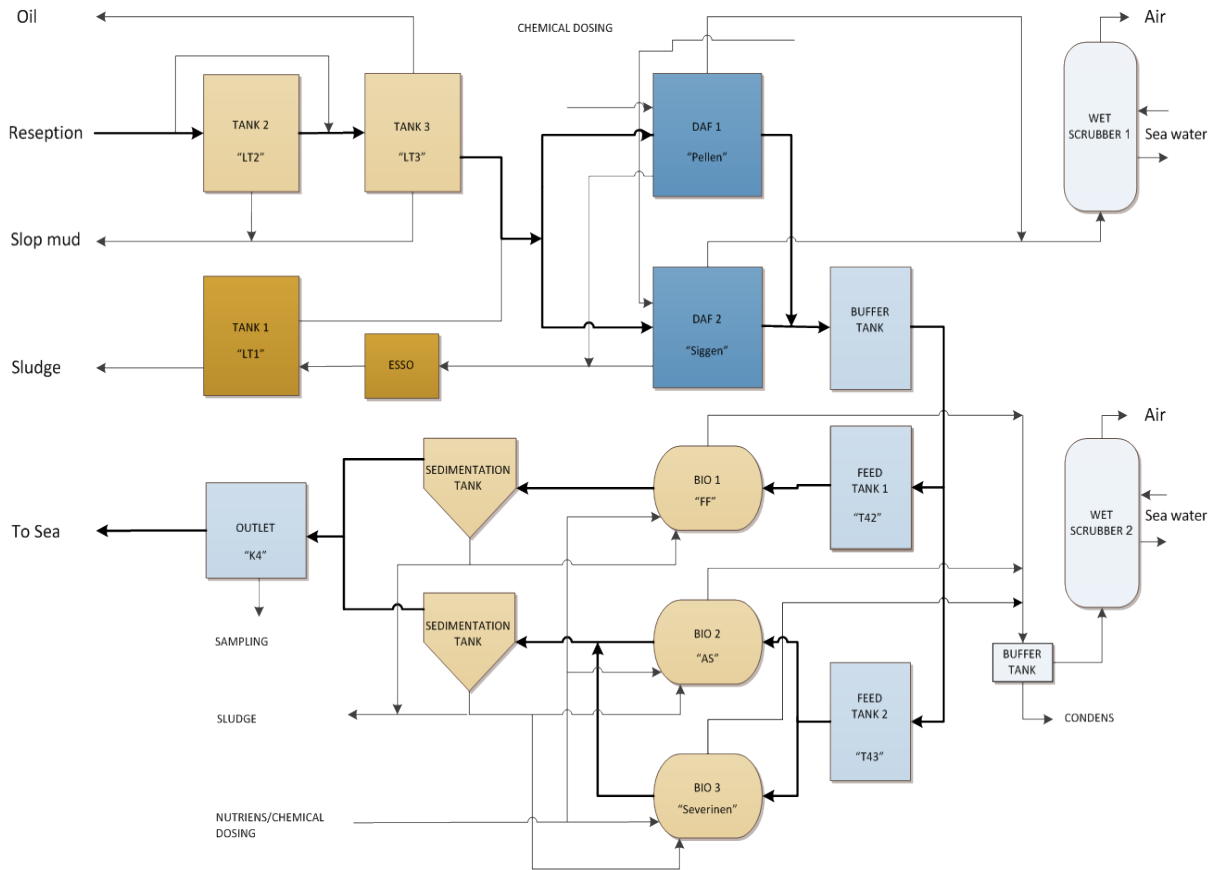


Figure 3.1 Wastewater treatment process at SART [9].

3.2 Biological treatment at SART AS

A bioreactor is an apparatus, such as a large fermentation chamber, for growing organisms such as bacteria or yeast under controlled conditions. Bioreactors are used in the biotechnological production of substances or for the bioconversion of organic waste [10].

The bioreactor which this thesis focused on is operated as an activated sludge system, consisting of a 350 m³ air tank and associated control container. There are three biological systems at SART. Discharge water from the plant goes to the sedimentation tank to return sludge (see Figure 3.1). Bioreactor is a stainless steel insulated tank that added air through diffusers at the bottom. The tank has inlet and outlet on the top to the bottom. The fluid level in the tank is measured with a radar wire. Bioreactor is controlled by the control container, and all inlet and outlet to the bioreactor via the control container. The container contains all process lines and associated components, electricity cabinets with display, work surfaces with

water, wash tank and blower. The plant is automatic and almost all settings of the system are connected to PLS system and *InTouch* system in the computer [11].

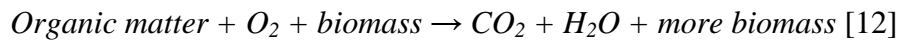
To achieve the desired temperature in air tank the system can use the heat exchanger, and the operation of the plant. For maintenance, the plant has a cleaning system for cleaning of process lines, and a by-pass line for use during maintenance of instruments. The plant also has the ability to close the recycling feed and can thus drive the circulation of the instrument line to perform various tests. The recycling line is used to measure pH, conductivity and oxygen in the air tank and the dosing of pH-regulating chemicals, nutrients and anti-foam. Recycling line also has the ability to circulate the water in parts of the line to perform certain tests [11].

According to the manual for SART AS bioreactor usage, optimal pH is around neutral – 7, but can vary between 6 and 8. Temperature increasing gives biomass growth and as a result – higher rate of TOC removal. Higher than recommended salinity level leads to reduction of biomass growth rate. Maximum level of salinity is, to avoid hindering effect of salinity around 50 g/l TDS (70 mS/cm conductivity). Air mixing can effect on the biomass volume. In order to get high productivity of the biomass it is necessary to have homogenous mixing over whole bioreactor volume [11].

SART biological treatment units can treat approximately 3 m³/h, 7 m³/h and 10 m³/h. The biological treatment requires Phosphorus (P) (as phosphoric acid) and Nitrogen (N) (as urea), and reduces largest part of dissolved organic components. The inlet TOC at SART is 2000 - 15000 mg/L and outlet TOC is around 500 mg/L or less [2]. Water quality after treatment at SART plant satisfies discharge permit by the KLIF' standards and show SART as an effective wastewater treatment plant.

3.3 Biological reactions in the bioreactor

Biological reactions are complex. Any “generic” biological reaction includes some organic matter for consumption by a culture of living organisms that also consume oxygen due to their respiration (aerobic culture) and in the process generate carbon dioxide, water and more biomass. It can be shown as:



The goal of the bioreactor is to remove organic components from the waste water by cultivation of the microorganisms (biomass), which use organic components (TOC) as food for growth. It increases biomass and CO₂, using O₂. As a result, TOC level decreases, biomass volume increases (TSS/VSS).

It can be outlined three types of reactions in the bioreactor:

- substrate consumption;
- biomass growth;
- biomass loss.

a) Substrate consumption

The substrate consumption rate can be presented in terms of the biomass production rate and the appropriate yield coefficient [12].

Energy is used for growth (biomass production, cell synthesis and respiration).



From removal of 1 g TOC 0.38 g goes in new biomass and 0.62 in CO₂.

O₂ consumption is similar to CO₂ production according to molar level: 1 mole CO₂_{produced} takes 1 mole O₂.

1 g TOC_{removed} produces 0.62 g CO₂, which is 0.056 moles C. 0.056 moles O₂ consumed responses to 1.8 g O₂ [11].

The key point of the microorganisms' activity is that increasing of bioactivity leads to increasing the temperature in the bioreactor.

b) Biomass growth

Biomass growth is a process of essential increasing of biomass volume by consuming a substrate. Biomass growth rate (R_x) is proportional to the biomass concentration present in the system (X) multiplied by the specific growth constant (μ), which can vary depending on limiting substrate concentration [12].

$$R_x = \mu X \quad \text{and} \quad \mu = \frac{\mu_m S}{K_s + S}$$

The microorganisms need a proper combination of the inorganic components. If just one of the components is absent, it results in growth stop and TOC removal stop. If one of the components is in low concentration, it results in reduced growth rate and reduced rate of TOC removal.

The waste waters at SART AS have low concentration of some important inorganic components, so that the treatment process does not go in a proper way without adding these components [11].

At SART AS it is needed to add nitrogen (N) and phosphorus (P) to achieve necessary growth rate and TOC removal. Usually microorganisms have 50% C, 14% N and 3% P. For the growth of 1 g biomass it is necessary to consume 0.5 g C, 0.14 g N and 0.03 g P [11].

Food consumption needs are proportional to observed growth of the biomass.

The nitrogen dosage is proportional to the observed growth:

$$N = Y_{\text{obs}} \cdot \Delta\text{TOC} \cdot f_N$$

Y_{obs} : 0.25 g VSS/g COD (0.38 g C_{biomass} /g TOC)
 ΔTOC : Observed TOC removal (mg/l)
 f_N : N concentration in biomass; 0.14 g N/g VSS (0.28 g N/g C)

Phosphorus dosage is proportional to the observed growth:

$$P = Y_{\text{obs}} \cdot \Delta\text{TOC} \cdot f_P$$

f_P : P concentration in biomass; 0.03 g P/g VSS (0.06 g P/g C)

The observed growth (biomass production) is a sum of the growth and breakdown.

$$\Delta VSS_{\text{obs}} = Y \cdot \Delta \text{TOC} - k_d \cdot VSS \cdot t \quad [11].$$

c) Biomass loss

Breakdown rate is proportional to biomass concentration and retention time.

Higher biomass concentration → higher biomass loss.

Longer retention time → higher biomass loss.

Lower biomass production → better conditions for the bioreactor [11]

Consuming O₂, bacteria release CO₂, what results in decrease of the pH and biomass loss.

3.4 Scale problem at SART AS

The main problem at SAR Treatment AS is accumulation of significant amount of calcium carbonate scale inside of bioreactor [9].

The reason of the scale formation in the particular bioreactor is a proper combination of the necessary factors for scale formation. In a simplified way it can be shown as:

The water with high scaling potential (high alkalinity and hardness)

+

The high temperature regime in the bioreactor (thanks to bioactivity)

The characteristics of the temperature regime will be discussed in Chapter 4.4, but here is necessary to mention, that it is difficult to manipulate the temperature in the bioreactor of such size as at SART in order to decrease it. The inability for SART to avoid scaling in the biological system is why the problem of scale formation exists at SART AS and needs a solution.

Until now the solution to the problem was usage of acid and mechanical removal of formed scale from the bioreactor periodically. But such solution is money- and time-consuming.

For example for acid removal it is needed around 2m^3 HCl (≈ 5000 NOK/ m^3). Cleaning can need 10-30 m^3 HCl and cleaning crew of 20 000-100 000 NOK plus down time. [9]. All this expenses should be multiply on amount of cleanings per year to get total cleaning costs a year.

SART would like to find a better solution with the following requirements: a) significant decrease of scale volume; b) at the same or less expenses.



Figure 3.2 *Formed calcium carbonate scale at SART AS*

4. Analysis of different solutions of the scale problem

The amount of scale control methods is numerous. In general, the methods for scale removal can be divided into three groups: physical, chemical and biological.

According to classification by Jitka MacAdam and Simon A. Parsons, shown at Figure 4.1.1, the methods for scale control can be divided by reduction mechanism on micro level.

This classification includes three main categories of methods:

- those that affect solubility,
- those that alter the growth mechanisms of the crystals,
- those that change the potential of a surface to foul [13].

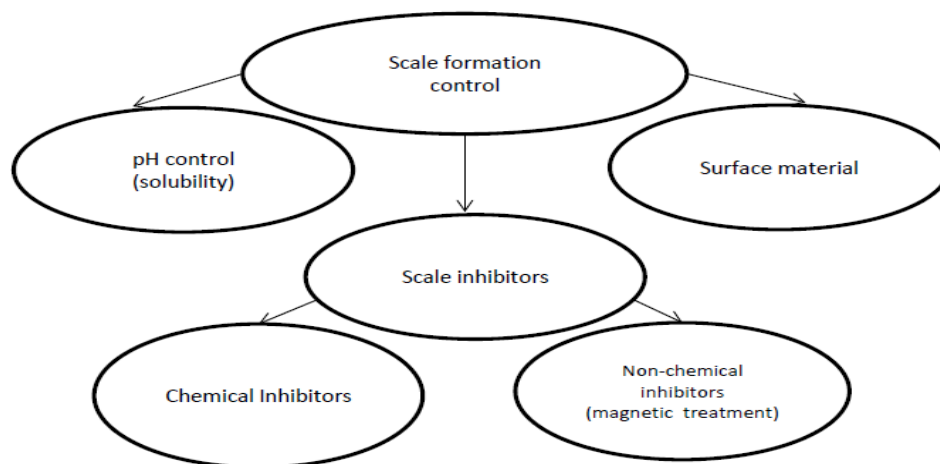


Figure.4.1.1 Classification of scale control methods by Jitka MacAdam and S. A. Parsons

Solubility is the property of a solid, liquid, or gaseous chemical substance to dissolve in a solid, liquid, or gaseous solvent to form a homogeneous solution of the solute in the solvent. The solubility of a substance fundamentally depends on the used solvent as well as on temperature and pressure. The extent of the solubility of a substance in a specific solvent is measured as the saturation concentration where adding more solute does not increase the concentration of the solution [14].

As it was claimed in Chapter 2 the formation of calcium carbonate scales is dependent on the level of supersaturation. Therefore any process that reduces the level of supersaturation will

lead to reduction of the level of scale formation. The main method of this group is water softening. Water softening is the removal of all hardness ions (Ca^{2+} , Mg^{2+}) by exchange with univalent ions [13].

The value of pH has a great influence on the potential to form calcium carbonate scale. A simple way to control scale or precipitate formation is to control the pH. The usage of mineral acids such as sulphuric and hydrochloric acid or organic acids such as citric acids is a popular calcium carbonate scale control method, but not economic for large flows [13].

The main strategy of scale mitigation is scale dissolution by application of calcium carbonate scale inhibitor. Function and mechanism of scale inhibitors will be discussed in Chapter 4.2. Factors affecting the performance and selection of a chemical inhibitor include hardness, alkalinity of the water, temperature, dose, pH and amount of particulates [13].

A more alternative option for controlling scale is anti-scale magnetic treatment [13]. *Magnetic water treatment (also known as anti-scale magnetic treatment or AMT) is a marketed, but scientifically refuted pseudoscientific method of reducing the effects of hard water, as a non chemical alternative to water softening* [15]. Most scientific studies do not support these claims and suggest that magnetic water treatment is ineffective, and claimed to be a humbug.

It is necessary to remember that scale formation is also affected by the physical nature of the material on which its forming and the hydrodynamic conditions. There have been few reports on the effect surface roughness plays in scale formation. It was found that *the energy required to remove a scale deposit from a rough surface (roughness average $\frac{1}{4}$ 20 μm) was as much as 30 times greater than for a polished surface (roughness average $\frac{1}{4}$ 0.1 μm)*. The mechanism increased adhesion can be explained by increased contact area [13]. The roughness of a surface influences the scale nucleation process, time and the strength of adhesion of the scale. Contact between water and polished surface needs longer time to form a complete layer of scale and low deposition rate. Also it provides lower adhesion strength. Once a complete layer of scale had formed then the rate of scale-on-scale growth goes in the same rate as on rough surface. However, it is not used as a common solution due to it is hard to put into real life for larger systems (such as SART).

Zahid Amjad [2] suggests another classification of scale control methods, which is shown at Figure 4.1.2. In spite of differences to compare to the classification by Jitka McAdam and S. A. Parsons, they do not contradict each other, but reflect different points of view.

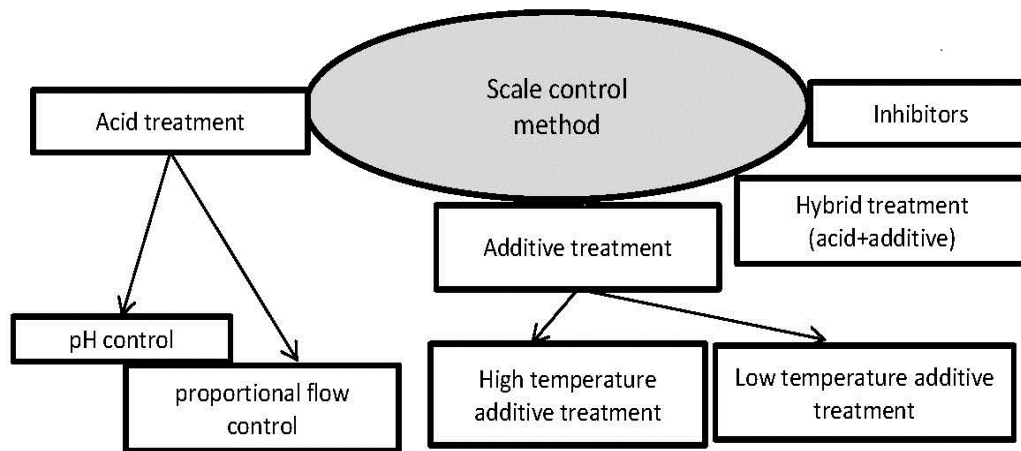


Figure 4.1.2 Classification of scale control methods by Zahid Amjad

Another possible and effective solution for scale problem can be pre-treatment of industrial waste water before treatment in the bioreactor. As an example, it can be evaporation process. In Chapter 4.1–4.6 is given analysis of the possible solutions, their advantages and disadvantages from point of view of SART AS.

4.1 Evaporation

Evaporation as a pre-treatment method for waste water is very popular, especially in the aspect of environment protection due to its effectiveness. Evaporators can significantly reduce the volume of the waste by removing and recovering most of the water in the waste, and is considered to be an effective method for scale formation control [16].

Evaporation is an operation used to remove a liquid from a solution, suspension, or emulsion by boiling off some of the liquid. It is thus a thermal separation, or thermal concentration, process [17].

The evaporation process is defined as *one that starts with a liquid product and ends up with a more concentrated and pumpable liquid as the main product from the process [17].*

Between the key parameters in the design of waste water evaporator can be following:

- flow rate;
- solids concentration in the feed (usually quite low);
- product concentration and the viscosity of the product at that concentration;
- problems with possible volatile components in the feed;
- corrosive nature of the feed (waste water evaporators may have high concentration ratios, the effects of corrosion can be enhanced in the final stages of evaporation);
- potential for fouling (can be very serious in many cases);
- boiling point elevation [16].

According to *SPX Evaporator Handbook*, thermodynamically, the most efficient technique to evaporate water is to use mechanical vapor thermo-recompression (Figure 4.1.3). *However if boiling point elevation is high, the MVR would be limited to the pre concentration and would require a separate steam powered single or multi-effect finisher to arrive at the final concentration. The costs of the compressors are high, and the capital cost of the equipment will be significantly higher than with multi-effect* [16].

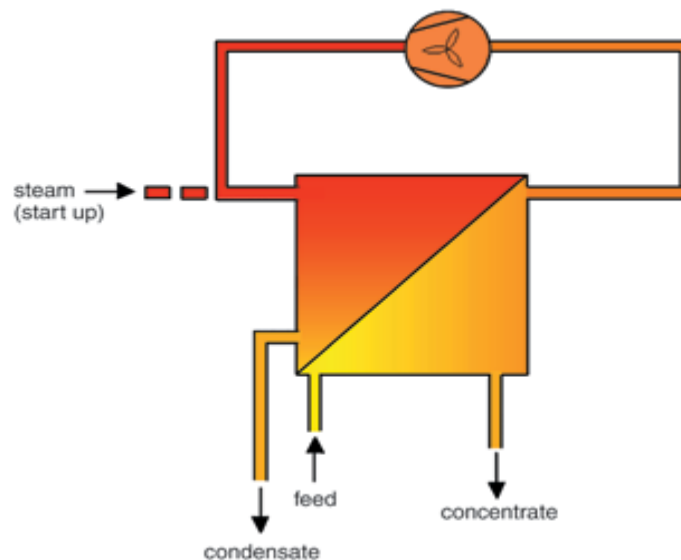


Figure 4.1.3 *Mechanical vapor recompression evaporator* [16].

Selection of a proper type of evaporator is individual and should base on such parameters of waste water as viscosity and fouling tendency. Figure 4.1.4 is an evaporator selection guide based on these parameters of waste water [16].

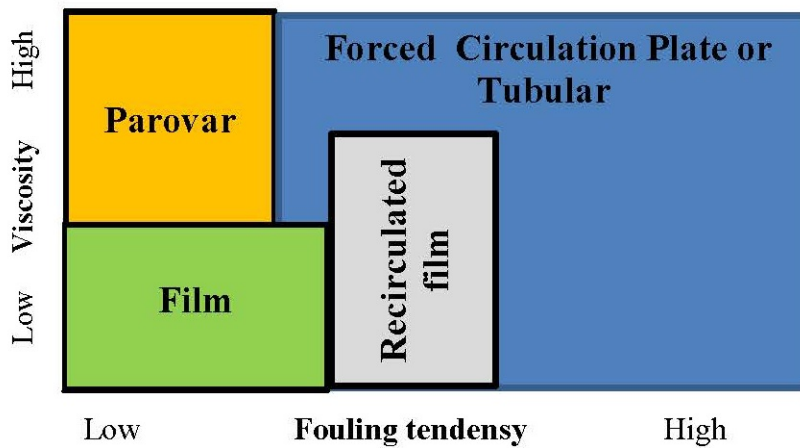


Figure 4.1.4 *Evaporator selection guide* [16].

Waste water as SART AS can be considered to have low viscosity and high fouling tendency. According the evaporator selection guide, forced circulation plate or tubular can be used at the plant as pre-treatment.

Forced circulation evaporators:

- can be operated up to viscosities of over 5,000cp;
- will significantly reduce fouling;
- high electricity consumption;
- are expensive; both capital and operating costs are high [16].

SART AS has previously looked into evaporation as a possible option for to avoid scale problem. But the cost due to it requiring is high as well as quality material requirement due to corrosion (for example titanium). So, the investment cost would be tremendous. Electric heating would be costly too. Using waste oil for heating would potentially make it available in regard to treatment cost, but it is known that getting a permit for burning waste oil is not easy. One is also left with an up concentrated salty waste, which has to be treated in other place, what increases costs for the problem solution. All these reasons make this option unavailable for SART AS.

4.2 Scale inhibitors

Scale inhibitors are chemical substances that, when added to industrial water at very low levels, act to reduce or prevent the formation of scale [18].

The main classification for the scale inhibitors includes three chemical families, according to main functional chemical group:

- Condensed polyphosphates⁵;
- Organophosphates⁶;
- Polyelectrolytes⁷[13].

The process of scale inhibitory can occur by several mechanisms, including *chelation*, *dispersion* and *inhibition* [13].

Chelation is the formation of two or more separate coordinate bonds between a polydentate ligand (chelants) and a single central atom. Chelants, are chemicals that form soluble, complex molecules with certain metal ions, inactivating the ions so that they cannot normally react with other elements or ions to produce precipitates or scale [19].

Dispersion is a system in which particles are dispersed in a continuous phase of a different composition (or state). Dispersion is classified in a number of different ways, including how large the particles are in relation to the particles of the continuous phase, whether or not precipitation occurs [20].

⁵ *Polyphosphate or condensed phosphate*, is created under a controlled progression of temperature and time as salts are carefully added to create various linear molecular chain lengths)
<http://www.sperchemical.com/html/polyphosphate.html>.

⁶ An *organophosphate* is the general name for esters of phosphoric acid. Phosphates are probably the most pervasive organophosphorus compounds. Organophosphates are widely used as solvents, plasticizers, and EP additives. <http://en.wikipedia.org/wiki/Organophosphate>.

⁷ *Polyelectrolytes* are polymers whose repeating units bear an electrolyte group. These groups will dissociate in aqueous solutions (water), making the polymers charged. Polyelectrolyte properties are thus similar to both electrolytes (salts) and polymers (high molecular weight compounds), and are sometimes called polysalts.
<http://en.wikipedia.org/wiki/Polyelectrolyte>.

Inhibition means the process of interruption, changing or blockade of usual activity of particles by an antagonistic influence of an additional compound.

Prolonged and intensive research has developed a polymeric product which action is described as inhibition of scale formation – the product interacts with hard ions and prevents crystallization. Usually scale inhibitors are polymeric products with ionizable functional groups such as $-\text{COOH}$, PO_3H_2 , $-\text{SO}_3\text{H}$ or amino groups [2].

Between polymeric compounds as scale inhibitors the most popular are carboxylic groups (polyacrylic acid, PAA), carboxyl and amino groups (poly-aspartic acid, P-AS). 1-hydroxy ethylidene-1,1-diphosphonic acid (HEDP), aminotremethylene phosphonic (AMTP) and 2-phosphonobutane-1,2,4-tricarboxylic acid (PBTC) were found the most effective scale inhibitors [2].

Prices for scale inhibitors vary from 300 USD to 3000 USD per 5-gallon bucket, which is equal to 15-160 USD or 120–1280 NOK per liter [21]. Average it is 60 000 NOK per m^3 . Necessary volume of the inhibitors depends on volume of waste water per day. The water volume per year can give us total costs for the inhibitors.

This method of scale control is very simple. Efficiency of scale inhibition depends on dosage of the inhibitor, temperature and pH of waste water. In spite of the simplicity, this method most likely not to be effective for SART, since scale formation occurs in the bioreactor. Addition of chemicals can not be as effective as expected, due to following reasoning.

Depending on the dosage and concentration of chemicals it leads to two options: 1) chemicals with weak concentration will be depredated by microorganisms, that means waste of chemicals, money and extra time for water treatment; 2) strong concentration of chemicals will interrupt the biodegradation process, what means that to scale formation problem it will be additional problem to re-new the content of the bioreactor. The interruption of the biodegradation goes rapid due to biodegradation takes longer time that activity of chemicals in a strong enough concentration.

In both cases this method is uncertain and expensive for scale problem. Hence it is not an option for SART AS.

4.3 Low pH treatment

Low pH treatment means to keep acidic conditions in the bioreactor all time for a successful procedure. The pH level for solubility of ions and prevention precipitation should be around 4-5. It can be achieved by constant using a proper organic acid in the water treatment process. Table 4.3 shows that low pH of solution gives highest solubility of ions, that means lowest precipitation. At high pH level just insignificant amount of ions are soluble, and most part of ions precipitate.

Table 4.3 Solubility of CaCO_3 as a function of pH [22]

pH	Molar solubility of CaCO_3
2	170
4	1.70
6	0.020
8	0.0011
10	$1.4 \cdot 10^{-4}$
12	$7.8 \cdot 10^{-5}$

It is known fact that low pH solution has its positive and negative aspects. The positive aspect is prevention of scale formation. The negative one is tendency to corrosivity. We assume that profit of effective scale control by low pH treatment is higher than loses due to corrosion.

Scale formation process at SART AS occurs in the bioreactor. The *microorganisms* that treat waste water in the bioreactor are used to remove organic compounds. Due to microorganism's activity and very delicate chemical reactions they carry out we can say that the bioreactor is a very sensitive area, where chemical balance is easy to be disturbed. The successful removal of oil compounds by the microorganisms can be achieved just in strictly defined conditions.

Tolerable pH level for most biological life is 6-9. Normal pH level that keeps in the bioreactors is 6.5 – 8.5 [23]. We can suggest that running the bioreactor at 6-7 pH can be not harmful for biomass and gives some minor scale formation. Also pH discharge permit for water release for SART is 6-8 pH.

Thus, changing pH in the bioreactor for prevention scale formation leads to failure of the main purpose of the bioreactor and the whole plant – effective removal of oil/organic compounds from industrial waste water.

Another aspect for this control method is cost of acid. Average price for 1 m³ of HCl 33-35% is 5000 NOK. It meant unacceptable high costs for a year. In the light of these facts we can conclude that this method of scale control is considered unreasonable and unacceptable for SART AS.

4.4 Low temperature treatment

According to basic laws of Physics solubility of a substance increases with increasing of the temperature. But behavior of calcium carbonate is opposite of other solubility chart. It is explained by *exothermic* nature of dissolution reaction for carbonate minerals [41].

Calcium carbonate has poor solubility almost at any temperature. Figure 2.1 demonstrates this process very well. Figure 4.4 gives more complete picture of calcium carbonate solubility, showing effect of partial CO₂ pressure as well as temperature of the water.

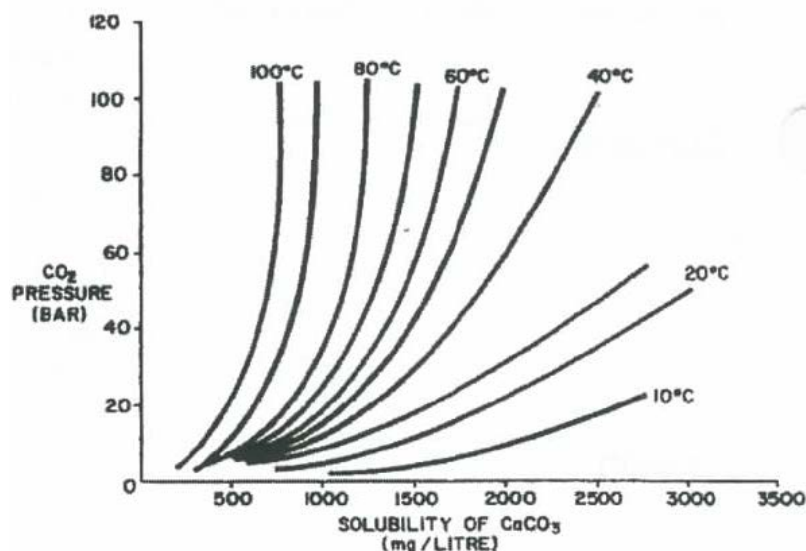


Figure 4.4 Effect of CO₂ partial pressure on the solubility of calcium carbonate⁸

⁸ The figure was taken from Statoil Company.

Produced water. Operational problems. Formation of mineral scaling.

Figure 4.4 shows the following aspects of calcium carbonate solubility:

- Higher temperature leads to lower solubility of calcium carbonate (that proves the information of Figure 2.1);
- Higher partial pressure leads to increasing of calcium carbonate solubility for temperature 10° -50° C;
- High partial pressure does not increase significantly calcium carbonate solubility level at high temperatures (70° - 100° C).

According to Figure 4.4, it can be said, that in temperature manipulation for the bioreactor it needs to pay attention to the combination of “temperature – pressure” in order to achieve maximal calcium carbonate solubility.

In order to avoid problems associated with calcium carbonate scale formation, it is important to keep the cooling water control parameters under such level that minimizes the potential for CaCO₃ formation [5].

The key factor for the reactions is temperature. Carbon dioxide is more soluble at lower temperatures. Concentration of carbonic acid is higher in cold water at a given partial pressure. The concentration is controlling factor for the solubility of carbonate minerals [41].

According to the Figure 2.1, the best temperature regime to avoid calcium precipitation is 0 - 20° C, cause it results in maximal solubility. The temperature around 30 -35° C give solubility 50-60 ppm, which is a half part of maximal solubility. It can be assumed that keeping temperature regime 35-37° C can significantly decrease scale formation in the bioreactor.

Temperature 40° C and higher gives very low solubility and as a result – high precipitation. According to Figure 4.4, best combination between temperature and pressure can be 10° - 40° C under 10 – 40 bar pressure.

High biodegradable activity means high temperature of the system. In case of SART AS, this system is very large – 350 m³, and it is hard to bring down temperature there. Normal temperature in the bioreactor is around 40° C. So, one can say that the temperature is the factor which cannot be manipulated now in order to solve the problem of scale formation. Investment cost in heat exchanger for the required use will be high. That is why this method of scale control is unavailable for SART AS.

4.5 Reverse osmosis treatment

Reverse osmosis (RO) is a membrane-technology filtration method that removes many types of large molecules and ions from solutions by applying pressure to the solution when it is on one side of a selective membrane [24]. The name of the process indicates that solvent moves not like in a normal osmosis process - from an area of low solute concentration through a membrane to an area of high solute concentration, but backwards (Figure 4.5.1). Applying an external pressure to reverse the natural flow of pure solvent is reverse osmosis [24].

RO process is similar to other membrane technology applications. The key difference of reverse osmosis is a diffusive mechanism, where separation efficiency depends on applied pressure [24].

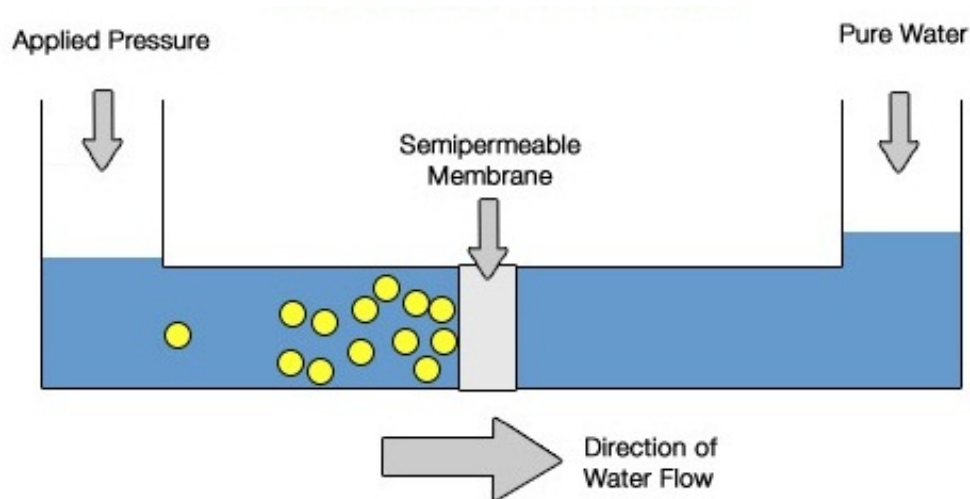


Figure 4.5.1 Reverse osmosis process [24].

The RO membranes have a dense layer matrix and they are designed to allow only water to pass through this dense layer, while preventing the passage of ions. This process requires high pressure to be exerted on the high concentration side of the membrane, usually 2–17 bar (30–250 psi) for fresh and brackish water, and 40–82 bar (600–1200 psi) for seawater. It is necessary to overcome natural osmotic pressure - 27 bar (390 psi) for effective salt ions removal [24].

Since RO membrane removes even monovalent salt ions, this process is widely used for desalination. This fact leads to assume that RO can be effective for the problem at SART.

In connection to the high efficiency, which is achieved thanks to complicated design and constructions, RO membranes are quite expensive type of waste water treatment.

RO units are very effective in water purification, but nevertheless this equipment has its own disadvantages. For example, hollow-fiber structure of RO membrane is getting easy to plug by solids, particles and bio fouling aggregations. For an effective RO treatment it is necessary to apply some pre-treatment measures to avoid blockage of fibers [24]. It can be done with help of usage of simple screen membrane or settlings chamber.

Another problem is possible scale formation inside of RO unit. It can happen in case if waste water has high enough alkalinity and hardness, which give high scaling potential. To avoid this problem it is necessary to include pH adjustment stage as well as additional usage of scale inhibitors to prevent blockage of pores by scale formation [24].

Another side of high efficiency of RO membranes is requirement of high pressure pump, which supplies the pressure needed to push water through the membrane. RO treatment requires large amount of energy. This is addition to high investment and maintenance cost makes RO an effective but expensive treatment process. SART is left with an expensive concentrate plus expensive energy cost, what makes this option not practical for SART.

4.6 Mechanical treatment – Sand cyclone

Mechanical treatment of scale formation includes such types of activity during pre- or post-treatment, which reduce calcium carbonate scale in the waste water without using any chemicals, but by gravitation/sedimentation or with help of membrane separation. As an example, it can be a settling chamber, a membrane plate or a sand cyclone before main treatment process in the bioreactor. Settling chamber needs longer retention time than the sand cyclone, and the membrane plate needs a back-wash system to avoid fouling and flux reduction. Thus, the most attractive and time-saving solution can be the use of sand cyclone.

The hydro cyclones seem to be an effective and important category of equipment for solid-liquid separation. *A sand separator is a device that separates sand or other solids from water* [25]. The structure of a sand cyclone is similar to a hydrocyclone, but design parameters are different.

A hydrocyclone consists of a conic end linked to a cylindrical body, which has a tangential entrance for the feeding suspension. The hydrocyclone has a tube in its upper part for the diluted suspension draining (overflow) and a hole in the under part for the concentrated suspension draining (underflow) [26]. By the pump activity the suspension goes through the feeding tube. After entering the hydrocyclone the suspension is activated by rotation, descendent movement and tends towards the drainage point of the underflow [26].

A sand cyclone as a hydro cyclone has two exits on the axis: the small outlet for reject/underflow on the bottom, and a large outlet at the top of the cyclone for permeate/overflow, as it shown in Figure 4.6.1.

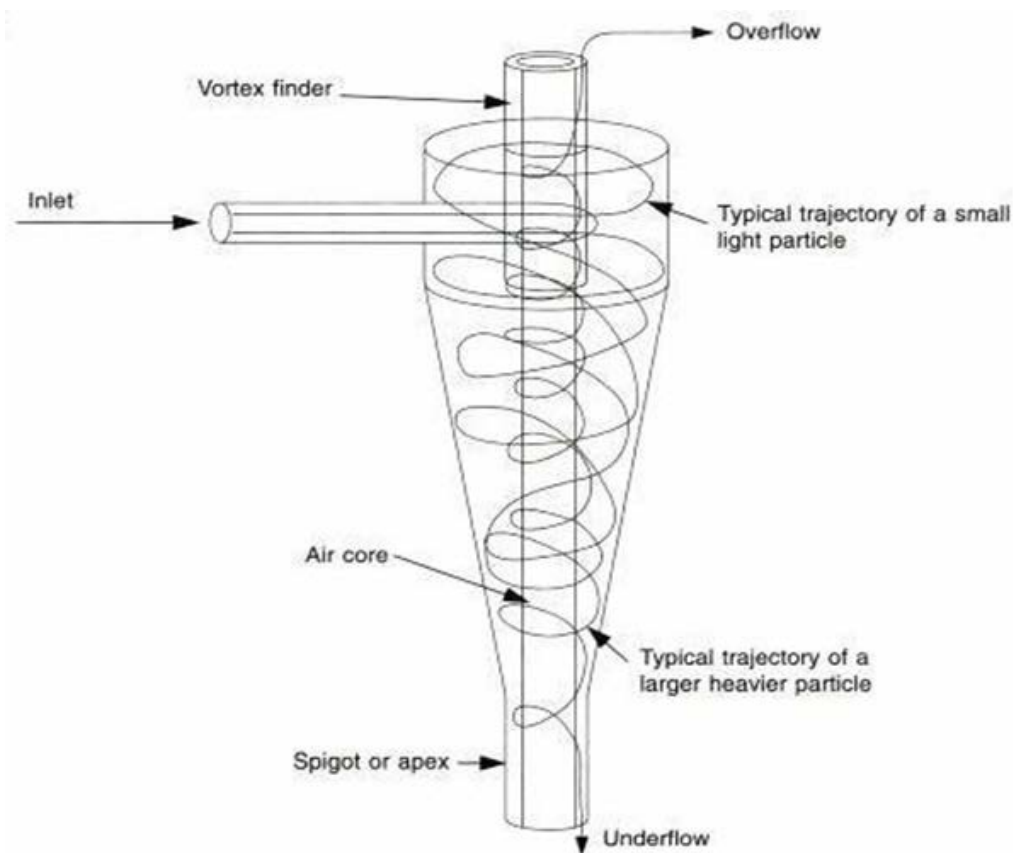


Figure 4.6.1 Structure of hydro cyclone [27].

Usually reject presents solid particles or more dense substance than water, while permeate is presented by the substances with lower density. In hydrocyclone top outlet is for oil, down outlet is for water. In sand cyclone – water is pushed up and sand collected at the bottom [25].

Usage of the sand cyclone gives good results in removal of particles of about 10 mm or more diameter (Figure 4.6.2).

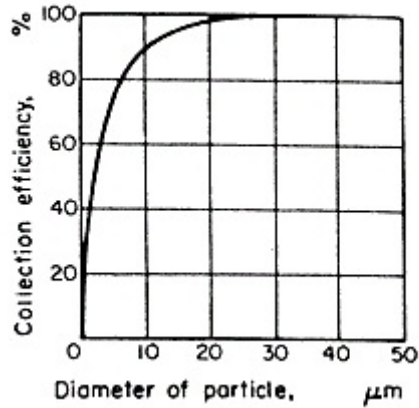


Figure 4.6.2 Cyclone separator efficiency [28].

We can say that the cyclone is a variation of a settling chamber in the form of a vertical cylinder. The particle-laden air spirals round the cylinder to create centrifugal forces which throw the particles to the outside walls. Added to the gravitational forces, the centrifugal action provides reasonably rapid settlement rates. The spiral path, through the cyclone, provides sufficient separation time [28].

Efficiency of removal of particles by the cyclone can be explained in mathematical way with help of Stokes' Law.

Stokes' Law for centrifugal settling of particles is:

$$\text{Eq.4.6.1 "Stokes' Law"} \quad V_c = (d^2 \cdot r \cdot \omega^2 \cdot (\rho_L - \rho_H)) / 18\mu$$

Where:

- V_c = the centrifugal settling velocity
- d = liquid droplet diameter
- ρ_H = density of heavy phase
- ρ_L = density of light phase
- r = radial distance of liquid from rotor axis
- ω = angular velocity (RPM of rotor)
- μ = average viscosity of processed fluids.

Stokes' Law shows that the terminal velocity of the particles is related to the force acting. In a centrifugal separator, such as a cyclone, for a particle, rotating round the periphery of the cyclone:

Eq.4.6.2 “Centrifugal force” $F_c = (mv^2)/r$ where

F_c = centrifugal force acting on the particle,

m = mass of the particle,

v = the tangential velocity of the particle,

r = the radius of the cyclone.

This equation shows that the force on the particle increases as the radius decreases, for a fixed velocity [28]. In this way we can say that the most efficient cyclones for removing small particles are cyclones of smallest diameter. The size of the diameter is limited by the capital costs to provide sufficient output, and the pressure drops [28].

Even though the hydrocyclone may not be separating by centrifugation, a certain amount of solids is removed with the concentrated in a rate that may be defined by the equation:

Eq.4.6.3 “Liquid ratio equation” $R_L = Q_u (1 - C_{v_u}) / Q(1 - C_v)$

where: R_L - liquid ratio, non-dimensional; Q_u - concentrated suspension outflow; Q - feeding suspension outflow; C_{v_u} - volumetric concentration of the concentrated suspension, non-dimensional; C_v -volumetric concentration of the feeding suspension, non-dimensional [26].

The total efficiency is defined as the ratio between the concentrated suspension solid mass outflow and the feeding suspension solid mass outflow:

Eq.4.6.4 “Total efficiency” $E_T = W_{s_u} / W_s$

where: E_T - total efficiency, non-dimensional; W_s -feeding suspension solid mass flow; W_{s_u} - concentrated suspension solid mass flow [26].

The separated solids are transported outside of the sand cyclone into a tank or reservoir where it can be removed later, while the water from top outlet goes for further treatment into the bioreactor. A hydro/sand cyclone cannot be considered as a true filter due to absence of physical barrier to separate out solids. But it is often used upstream of filters or other sensitive elements of equipment to remove the bulk of contaminant. It helps to avoid membrane premature fouling and saves time of treatment, including time for filters cleaning [25].



Figure 4.6.3 *Sand cyclone* [29]

The discussion on a sand cyclone as an option for SART is presented in Chapter 5.

4.7 Comparison of technologies

Comparison of these options on costs, time consumption and degree of complicity is shortly summarized in Table 4.1 below.

Table 4.7 *Comparison of suggested technical options for scale removal*

Option	Efficiency level	Costs	Degree of complexcity	Comment
Evaporation	Very high	Very high	medium	-
Scale inhibitors	High	high	low	Not applicable for biological system
Low pH treatment	High	medium	low	Not applicable for biological system
Low temperature	Medium	low	low	Not applicable for SART
Reverse osmosis	Very high	Very high	medium	-
Sand cyclone	High	medium	medium	Problem with biomass removal

The main experiment in this thesis concerns usage of a sand cyclone, since this method needs less economical and time costs, simple in maintenance, low risk of breakage. For SART AS electrical costs according to sand cyclone usage are acceptable, since usage of the sand cyclone with 2 loops on a single pump gives not high cost. It is an advantage for the plant.



Figure 4.7.1 *Sand cyclone at SART AS*

5. Materials and methods

The laboratory experiment in this thesis can be divided into two main parts. The first one is oriented to measure working parameters of the water in the bioreactor. All the measurements are done at University of Stavanger lab. This information explains the chemical side of scale formation, the kinetic basis, and predicts further development of situation. This information helps to find a possible solution how to avoid scale formation.

Second part is a practical experiment done at SART AS. The experiment represents testing of one of the available solutions – in our case it is a sand cyclone – and shows how effective the solution is for SART AS. Information from the first part of the experiment can be used as basic parameter for comparison of gotten results of water quality after sand cyclone treatment.

All measurements are done in accordance with *Standard Methods for the examination of water and waste water 2002* [30].

5.1 Preliminary measurements

Preliminary measurements of such parameters as hardness, alkalinity, TSS and VSS of the water from SART AS, were done at lab in University of Stavanger in period from 20th of January to 5th of February 2012. In order to get objective results the measurements were done on 12 samples of waste water from different stages of treatment. Average values of the measurements are presented and explained below as well as individual parameters.

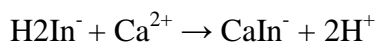
5.1.1 Hardness

Water hardness is usually determined by measuring the total amount of calcium and magnesium present, since the concentrations of these ions far exceed those of other alkaline earth metals. The accepted practice for reporting hardness is mg CaCO₃/L, as if the hardness is from calcium carbonate.

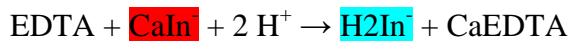
Hardness of the water samples in a lab experiment is usually determined by *EDTA titration method*. The measurement is occurred according to hardness measurement guide [31].

The general procedure for this experiment starts with a sample of hard water that contains calcium and magnesium ions. For titration process it needs an indicator to determine the endpoint – the moment when the Ca^{2+} and Mg^{2+} have bind with the EDTA. To insure that all cations stay in solution and that the indicator works properly, a buffer is used to adjust the pH to 9.9 - 10.1. After the pH is adjusted and the indicator is added, the EDTA titrant is added via a burette.

First the EDTA (H_2Y_2^-) will complex with the calcium ions, forming a red solution:



At the endpoint, the EDTA will complex with the calcium and the indicator becomes unbound, which is indicated by the red to blue color change:



In our experiment the measurements of water hardness are done by the Intertek West Lab. According to the purpose of the thesis, it is necessary to compare the hardness values in the treatment process without the sand cyclone and after the sand cyclone usage in addition to samples of incoming wastewater.

Water sample from the bioreactor where sent to ALS⁹ for analysis, before the bioreactor and the water treated in the cyclone. Inn addition multiple incoming wastewater samples where tested to determine the scaling potential. The difference in hardness value between these three types of water from the treatment process shows calcium concentration differences and as a result it will be used in calculation of scale potential of the waters at SART AS.

⁹ **ALS Laboratory Group Norway** AS is a net of laboratories for different types of environmental analysis of water, salts, sediments, earth and biomass. More detailed information can be found on <http://www.alsglobal.no/>.

5.1.2 Alkalinity

Alkalinity of water is its acid-neutralizing capacity. It is the sum of all the titratable bases [31]. Alkalinity is significant in many uses and treatments of natural waters and wastewaters. Since the alkalinity of any type of water is mainly a function of carbonate, bicarbonate, and hydroxide content, it plays the role of an indicator of the concentration of these components.

Alkalinity measurements are used in the interpretation and control of water and wastewater treatment processes. Raw domestic wastewater has an alkalinity less than, or only slightly greater than, that of the water supply. Properly operating anaerobic digesters typically have supernatant alkalinities in the range of 2000 to 4000 mg calcium carbonate (CaCO_3)/L [31].

The procedure of alkalinity measurement was done according to *Standard Methods for the Examination of Water and Wastewater, Titration method* [32].



Figure 5.1.1. *Alkalinity measurements at UiS lab*

It was taken 12 water samples for the procedure and for more objective results alkalinity measurements were done before and after flocculation. The titrant is 0.1 HCl, the end-point is 4.5 pH and sample volume is 50 ml.

Procedure:

- 1). Preparation of water sample and titration assembly;
- 2). Titrate to the chosen end-point pH level;
- 3). Write down used volume of titrant;
- 4) Make necessary calculations according with formula.

Calculations:

Alkalinity, mg CaCO₃/L = (A x N x 50 000) / ml sample,

where A = ml standard acid used for titration; N = normality of standard acid.

5.1.3 TSS and VSS measurements

TSS and VSS measurements were done according to *the Standard Methods for the Examination of Water and Waste Water* [33].

Procedure:

- 1). Preparation of the filtering apparatus and samples for the procedure. It is necessary to wet filter with a small volume of reagent-grade water to seat it. Stir sample with a magnetic stirrer at a speed to shear larger particles.
- 2). While stirring, pipet a measured volume onto the seated glass-fiber filter. Wash filter with three successive 10 mL volumes of reagent-grade water, allowing complete drainage between washings, and continue suction for about 3 min after filtration is complete.
- 3). Remove filter from filtration apparatus and transfer to an aluminum weighing dish as a support.
- 4). Dry for at least 45 min. - 1 h in an oven at 103°C.
- 5). Cool filters in a desiccator during 15-30 minutes to balance temperature.

6). Weigh the filters and write down the mass of dried filters. Repeat the cycle of drying, cooling, desiccating and weighing [33].

VSS measurements were done in the same way, but dried under temperature 550°C.

Calculation:

Formula for TSS calculation is:

$$\text{TSS} = (\text{A} - \text{B}) \times 1000 / \text{sample volume, ml}$$

where A = weight of filter + dried residue after drying at 103° C, mg; B = weight of filter, mg.

Formula for VSS calculation is:

$$\text{VSS} = \text{A} - \text{C},$$

where C = weight of filter + residue after drying at 550° C [33].

The procedure was done on 12 samples, 50 ml each.

5.1.4 LSI and RSI indexes

From the results of hardness and alkalinity it is possible to calculate LSI and RSI indexes to determine scaling potential of the water. Calculation of LSI and RSI is done in accordance with the respective Equations 2.5.1 – 2.5.3, given above in Chapter 2.5.2.

5.2 Control experiment at SART AS

The control experiment was conducted to find out efficiency of a sand cyclone usage for scale removal from the bioreactor. Efficiency of the procedure is supposed to result in decreasing of already measured parameters: hardness, alkalinity, VSS, as well as LSI, RSI indexes, and it can be seen visually. A small scale test sand cyclone was used in this experiment.

5.2.1 Pre-experimental estimation of cyclone functionality

Usage of a sand cyclone as a mechanical method of scale control has its own advantages and disadvantages in relation to SART AS. The positive points of such solution are:

- no moving parts except for valves and valve actuators;
- no parts to clean or replace;
- effective removal of big particles.

As disadvantages it can be outlined following:

- removal efficiency declines quickly below 90 micron particle size;
- flow rate sensitive [31].

From SART AS point of view, the main disadvantage that can be crucial for scale removal is decreasing of efficiency of removal and possible biomass removal from the bioreactor. But this is the main point of lab research of this thesis – if it works out or not. The small scale experiment will show the efficiency of the usage of the sand cyclone for calcium carbonate ions removal at SART plant.

5.2.2 Description of the experiment

The control experiment location is the bioreactor (see Figure 5.2.) and a sand cyclone, connected by 2 loops – water from the bioreactor to the cyclone and from the cyclone to the bioreactor.

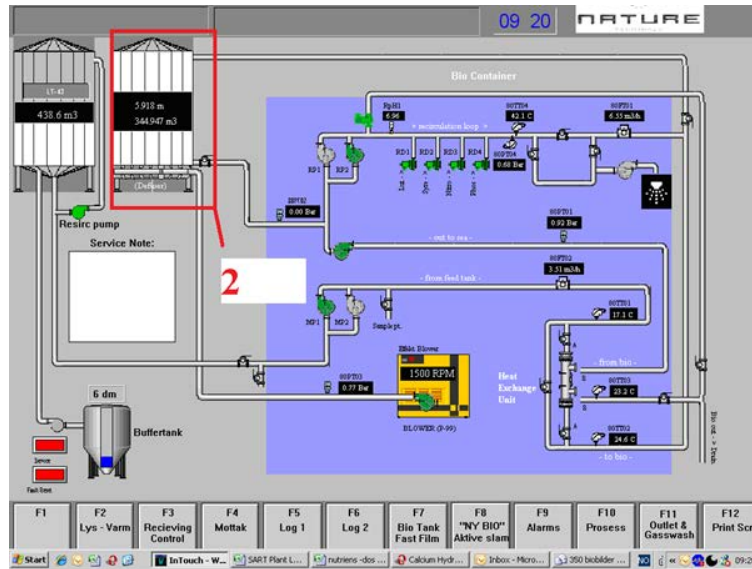


Figure 5.2 The location of the control experiment at SART AS [11]

For this experiment it was used a sand cyclone 50 cm length and 7 cm diameter, as it can be seen at Figure 5.3.



Figure 5.3 Parameters of the sand cyclone at SART AS

For the control experiment the particular sand cyclone model was connected to the bioreactor as a loop (Figure 5.4). This system includes the bioreactor, flow meter, pressure meter and the sand cyclone.

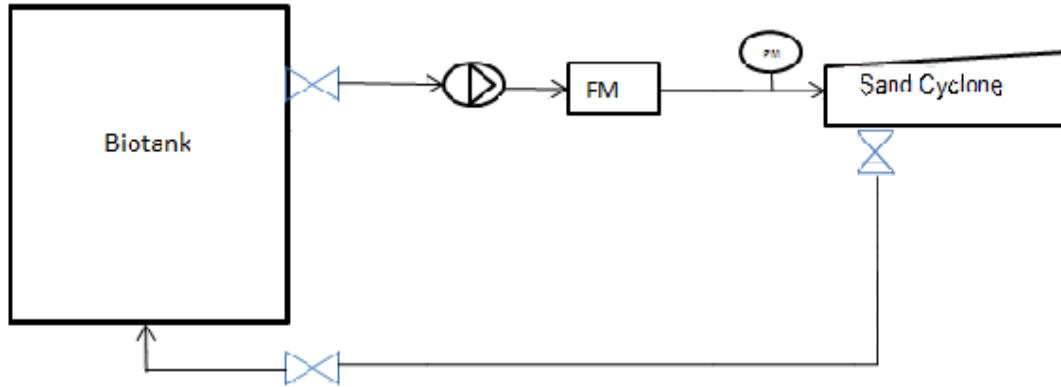


Figure 5.4 *Flow chart of experimental "bioreactor-sand cyclone connection" at SART*

The water was lead through the cyclone with a flow rate – 1.48 m³/h, and under 0.37 bar pressure. The setup is 2 continuous loops where feed is taken and returned to the bioreactor. Calcium carbonate and other heavy particles are retained and removed from the cyclone. The clean water goes to the bioreactor for necessary biological treatment.



Figure 5.5 *Flow meter at the cyclone*



Figure 5.6 *Pressure indicator at the cyclone*

The control experiment includes the same measurements as the preliminary experiment. The difference is that these measurements are done after sand cyclone usage – on *retentate* water (residue water from the sand cyclone) and *permeate* water (clean water going to the bioreactor). This procedure was done by opening the lower valve (where sand collection takes place) to get samples (Figure 5.7). After taking samples all the same measurements of treated water are done according to setup given above. The “bioreactor-sand cyclone” experiment was done 01.05.12.



Figure 5.7 Taking water samples of treated water from the sand cyclone at SART AS

The experiment includes two sets: *Run 1* has 7 samples and *Run 2* has 6 samples. Below in the Table 5.1 there are given types of samples. *Run 2* is short-time experiment compare to *Run1*.

Table 5.1 *Types of water samples taken in “bioreactor-sand cyclone experiment”*

#sample	Run1	Run 2
1	permeate, no waiting time	retentate no waiting time
2	permeate after 5 minutes	retentate after 1 minute
3	retentate after 15 minutes	retentate after 3 minutes
4	retentate after 30 minutes	retentate after 10 minutes
5	retentate after 40 minutes	retentate after 15 minutes
6	retentate after 45 minutes	permeate after DAF before the bioreactor
7	retentate after 50 minutes	-----

6. Results

In this chapter we present results from both experiments. All detailed calculations are given in Appendix 2 - 4.

6.1 Preliminary measurements

Table 6.1.1 summarizes all the results of the preliminary measurement in alkalinity, TSS, VSS, LSI and RSI.

According to Table 6.1.1, biologically treated waste water has significantly lower TSS and VSS level in comparison to biologically treated one. Alkalinity level varies a lot from water to water, not depending on biological treatment, but can be affected by origin, field type and location, possible chemical treatment before SART.

During biological treatment scaling potential of the water significantly increases, thanks to presence of necessary water characteristics and favorable conditions for scale formation and sedimentation.

Table 6.1.1 Values of measured parameters of SART water samples

	Water type	pH	Alkalinity CaCO ₃ mg/L)	TSS (g/l)	VSS (g/l)	LSI	RSI	Scale presence
1	Waste water from bioreactor	7.85	2420	21,34	4.94	1.84	4.16	Scale forming
2	STRIO-166, 91 m ³ , Soil westco tank	6.61	718	1.918	0.236	0.08	6.45	Slight scaling
3	Feed water (already chemically treated)	6.39	1885	1.08	0.284	0.28	5.83	Slight scaling
4	chem.violet, tank A, TOC 736, STRLL- 233	7.94	1087	0.514	0.14	1.58	4.76	Scale forming
5	SAR Kristiansund, 01.12.11.TK 10, 240 m ³	6.38	1145	5.616	0.29	0.04	6.28	Slight scaling
6	23.12.11. fløre, FB 8, 450 m ³ , SG 1,03	8.06	1350	1.126	0.322	1.8	4.46	Scale forming
7	23.11.11, STRIL 246, florø 360m ³ , FB 8, SG 1,04, TOC 9,9 mg/l	7.28	2875	5.038	0.952	1.35	4.58	Scale forming
8	500 m ³ , SG 1,062, TOC 9,081 mg/L	6.8	3800	1.612	0.474	0.98	4.82	Scale forming
9	500 m ³ , SG 1,055, TOC 9,050 mg/L	6.88	3625	6.808	1.27	1.05	4.78	Scale forming
10	TI STRLL-230, TOC 4630 mg/l, SG 1,025, 040m ³	7.81	1500	4.812	0.604	1.59	4.61	Scale forming
11	STRLL-229, SAR KSU T.11, 240 m ³ , SG 1,016, TOC 7, 610 mg/l	4.99	300	0.706	0.314	-1.92	8.83	No scale
12	STRLL- 219, SG 1,020, TOC3, 040 mg/l	5.94	950	1,00	0.232	-0.47	6.88	No scale

6.2 Control measurements

Table 6.2.1 summarizes all the results of the control measurements.

Table 6.2.1 Values of measured parameters of SART water samples after sand cyclone

	#	Water type	pH	Alkalinity	TSS (g/l)	VSS (g/l)	LSI	RSI	Scale presence according to indexes
Run 1	1	Permeate 0 min.	7	220	11.032	4.76	-0,04758	7,095155	No scale
	2	Permeate 5 min.	7	365	74.65	41.6	0,172293	6,655414	Slight scaling
	3	Retentate 15 min.	7	890	54.478	19.462	0,55939	5,88122	Slight scaling
	4	Retentate 30 min.	7	295	102.398	54.456	0,079822	6,840356	No scale
	5	Retentate 40 min.	7	250	53.348	18.056	0,00794	6,98412	No scale
	6	Retentate 45 min.	7	870	34.15	17.36	0,549519	5,900961	Slight scaling
	7	Retentate 50 min.	7	830	47.086	41.606	0,529078	5,941844	Slight scaling
Run 2	1	Retentate 0 min.	7	395	46.138	38.788	0,206597	6,586806	Slight scaling
	2	Retentate 1 min.	7	220	70.55	61.688	-0,04758	7,095155	No scale
	3	Retentate 3 min.	7	260	24.18	13.862	0,024973	6,950053	No scale
	4	Retentate 10 min.	7	370	93.244	68.746	0,178202	6,643597	Slight scaling
	5	Retentate 20 min.	7	430	14.656	3.156	0,942438	5,115123	Slight scaling
	6	Permeate after DAF	7	900	8.296	0.21	0,564243	5,871515	Slight scaling

According to volume of TSS and VSS shown in the Table 6.2, it can be conclude that some significant volume of VSS becomes a part of removed scaling mass, but with time this tendency changes and VSS amount in the removed scale decreases.

The results of the hardness measurements of the waters before and after sand cyclone usage are given in Table 6.2.2.

Table 6.2.2 *Hardness parameters for different water types before and after the cyclone*¹⁰

Water type	Hardness	
	in dH	in mmol/l
After cyclone	324	57.8
Sample incoming water: STR 12-053	319	57.0
Sample incoming water: STR 12-052	78.6	14.2
Sample incoming water: STR 12-053, after chemical treat.	307	54.8
Water from bioreactor	174	31.2
Sample incoming water: Mo-i-Rana vann. MV1	139	24.8
Sample incoming water: STR 12-045	274	48.8
Sample incoming water: STR 12-042	259	46.2
Sample incoming water: Tank 17 Florø 04.04.12	320	57.1
Sample incoming water: STR 12-047	130	23.3
Sample incoming water: STR 12-049	136	24.2
Sample incoming water: STR 12-047/048	132	23.5

The table show, that the water after the cyclone has the highest hardness level (324), when usual water samples have almost two times lower hardness (130 – 250).

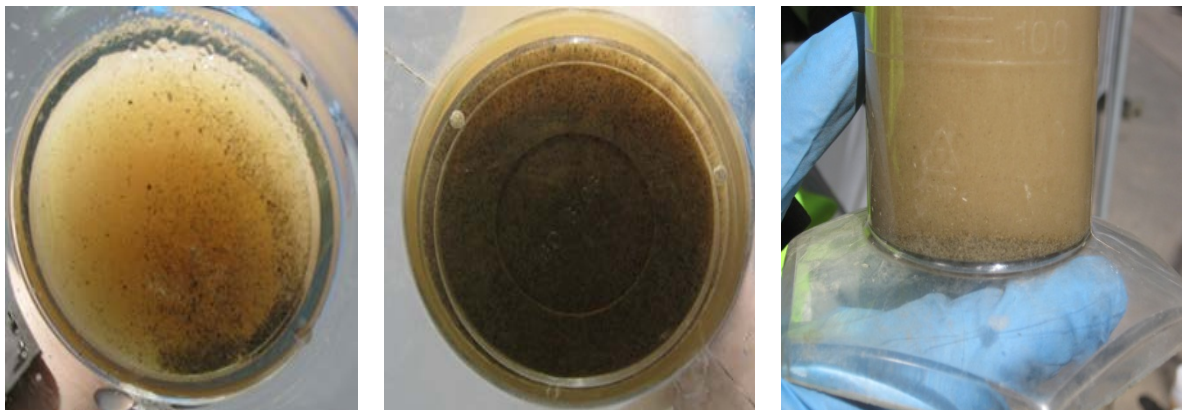
It is explains by that fact, that water samples after cyclone – are retentate samples (residue scale mass and water), where CaCO₃ concentration is very high. It means that permeate water from the cyclone has low hardness level. The feed water to the cyclone (water bioreactor) only has 174. It is impossible to remove dissolved ions by a cyclone; however these are probably in micro particles.

¹⁰ The data from the ALS Lab group report, Appendix 5.

The process of settlings of sand and biomass particles was not homogenous. The differences between Runs and samples are given in the Table 6.2.3 and Figure 6.1 – 6.2.

Table 6.2.3 Visual characteristics of the water samples from Run 1 and Run 2 ¹¹

	Sample #	Biomass volume	Sand volume	Settling velocity
Run 1	1	≈ 75%	Few particles on the bottom	Very slow
	2	≈ 50%	Almost cover the bottom	slow
	3	≈ 45%	≈ 45%	Faster than previous
	4	≈ 30%	≈ 30%	fast
	5	≈ 30%	≈ 25%	fast
	6	≈ 30%	≈ 25%	fast
	7	≈ 30%	≈ 30%	fast
Run 2	1	≈ 50%	≈ 40%	slow
	2	≈ 50%	≈ 40%	faster
	3	≈ 40%	≈ 35%	fast
	4	≈ 25%	≈ 20%	fast
	5	≈ 15%	≈ 20%	fast



0 min.

5 min.

30 min.

Figure 6.1 Sand-biomass ratios changing with time, (Run 1)

¹¹ The observations for this table have been done straight after samples taking and also after settling period.

Figure 6.2 shows very clear zone sedimentation on *Run 2* samples. In sample 1 the settling process was very slow, and every next sample gave better settling (but not sample 6 since there were nothing to settle). This phenomenon can be explained with help of different size of biomass particles and their aggregations with sand particles. According to our experiment, we can say that in first samples biomass particles have small size and weight, but with time in the cyclone all particles aggregate together better, giving heavier flocks, which sink faster.



Figure 6.2 *Zone sedimentation process on Run 2 samples*

6.3 Comparison of measurements

In this chapter the differences in measurements are presented graphically.

In Figures 6.3.1 – 6.3.4 is given comparison of the control experiment *Run 1* (blue lines) and *Run 2* (red lines), showing changes with time of basic chemical parameters of the water after the sand cyclone treatment.

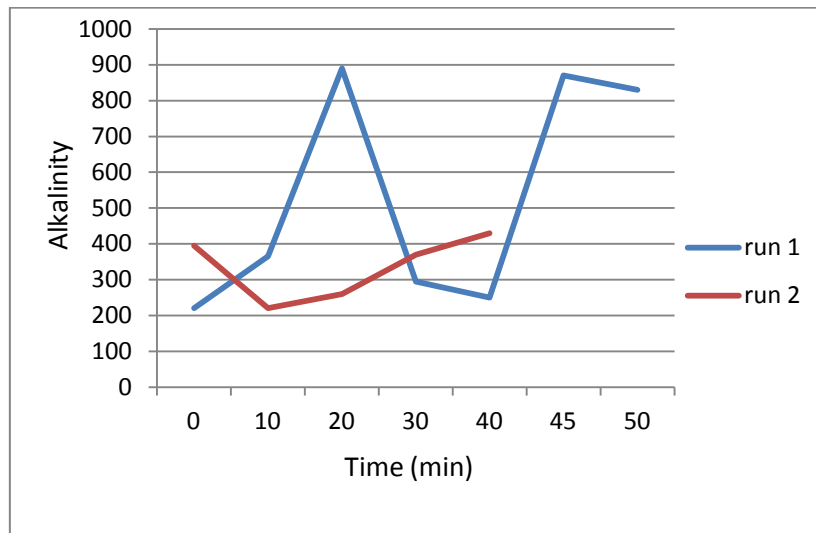


Diagram 6.3.1 Alkalinity values for Run 1 and Run 2 water samples

According to the Figure 6.3.1 the water of the Run 1 shows high amplitude of alkalinity, but Run 2 gives more calm results in 200 – 450 mg/l.

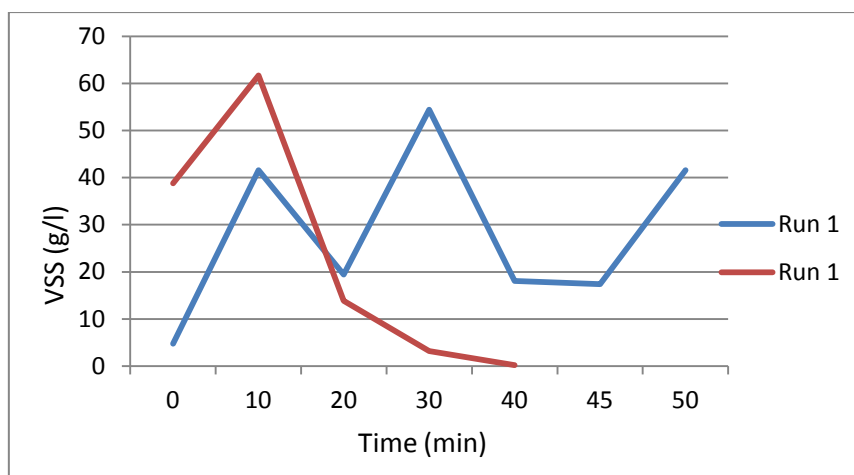


Diagram 6.3.2 VSS values for the Run 1 and Run 2 water samples

The level of VSS for Run 1 is quite dynamic and keeps high values. The VSS level for Run 2 decreases with time according to the Figure 6.3.2.

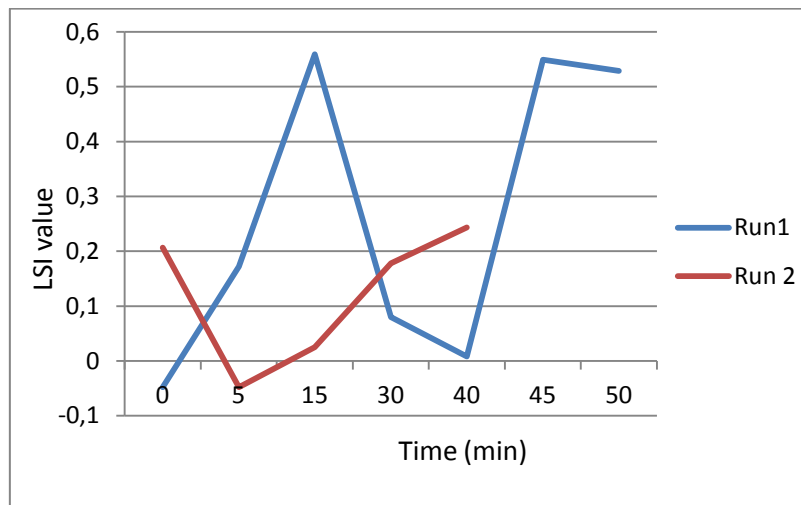


Diagram 6.3.3 LSI values for the Run 1 and Run 2 water samples

The Figure 6.3.3 shows that both Run 1 and Run 2 are in “non-scale forming region”. The values for Run 2 are in $-0.05 - +0.25$, which can be called as close to equilibrium state. Run 1 has little bit higher amplitude of values $- -0.05$ to 0.6 , which is still in “non-scale region”.

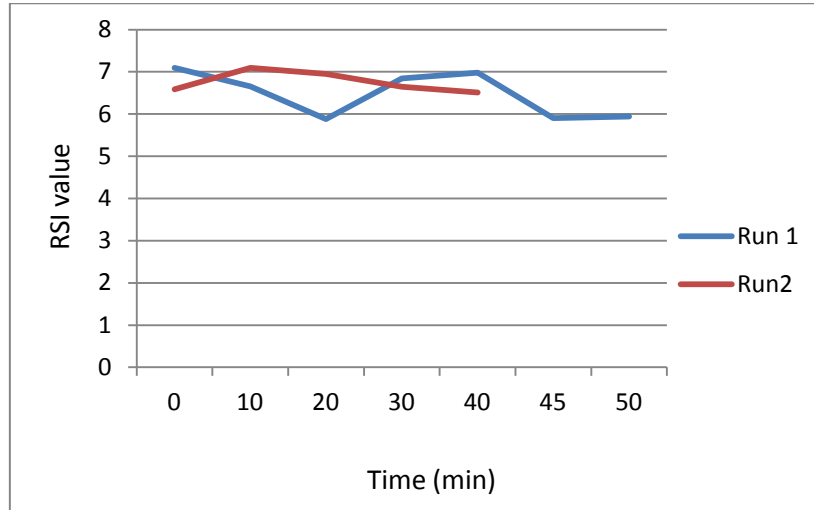


Diagram 6.3.4 RSI values for the Run 1 and Run 2 water samples

On the Figure 6.3.4 we can see that both curves are in the region $5.9 - 7.1$ - “non-scale forming region”. But values for *Run 2* are more stable around 7, when *Run 1* is more dynamic with time.

7. Discussion

This chapter presents a detailed discussion of the results of the preliminary and the control experiments according to calcium carbonate removal by a sand cyclone usage at SART plant.

Also there is given a comparison of the results in regard to the goal of the thesis, and how far the purpose is achieved.

This discussion will lead us to a final conclusion about how effective the sand cyclone can be for this particular purpose – calcium carbonate scale removal, and for this particular waste water treatment plant – SAR Treatment AS.

7.1 Difference between preliminary and control experiment results

According to the Tables 6.1.1 - 6.2.2, the efficiency of the sand cyclone usage at SART is visible. All required chemical parameters of the water, such as hardness, alkalinity, and their reflection in the LSI and RSI, show significant changes.

This confirms decreasing of the calcium carbonate concentration in the cyclone treated water and changing of the chemical water quality before going back to the bioreactor.

Alkalinity values in the preliminary experiment vary from 0.3 g CaCO_3/l to 3.8 g CaCO_3/l ; average value is 1.8 g CaCO_3/l . Alkalinity level for the control experiment with the sand cyclone usage varies from 0.22 to 0.9 g CaCO_3/l ; average value is 0.48 g CaCO_3/l . On the base of this data we can say that the sand cyclone decreased alkalinity power of 3.75 times, what can be accepted as a quite significant result. Such alkalinity decreasing is explained by the basic function of the sand cyclone – removal of sand particles most of which in this type of water are calcium carbonate.

According to calculated LSI and RSI indexes we can say that results of the preliminary experiments show the examined water as the water with quite high potential for scale formation or slight scaling. The results of the control experiment with the cyclone show minimal, close to zero scale forming potential of the examined water. The values of alkalinity, hardness and usual visual observation of the water do not contradict to the indexes.

Significant increasing of VSS became an unexpected part of the results. Following the result tables the water not treated in the sand cyclone has VSS 0.14 – 4.9 g/l with average value 0.85 g/l. The water after the cyclone gives VSS level in 0.21 – 68.746 g/l diapason with average value 29.5 g/l. This phenomenon is explained by ingress of the biomass from the bioreactor together with the water and sand particles. The ingress of the biomass means decreasing of this substance inside of the bioreactor, but for proper waste water treatment it is necessary to keep an optimal level of biomass in the bioreactor.

The biomass ingress is an undesirable part of the results and a big disadvantage of the sand cyclone usage at SART AS, in spite of satisfying results in scale removal. It gives reasons to have a look from another point of view of the sand cyclone usage as potential scale removal method at SART AS. It is possible to look at more advanced cyclones which could eliminate this issue.

7.2 Efficiency of the sand cyclone

The process of taking the control samples of the water after the sand cyclone was done in two runs. The first one was done straight after connection of the cyclone to the bioreactor and the second run was done in one hour – after the run 1 was over.

The average values based on the Tables 6.1.1 and 6.2.1 do not have big difference. But the Diagrams 6.3.1 – 6.3.4 show us dynamic in values of the alkalinity, VSS and LSI between *Run 1* and *Run 2*. It can be explained by not homogenous “water-heavy particles” mixture going out of the bioreactor to the cyclone with the time. It is possible that for the *Run 1* it was started drawing feed from a low point on the bioreactor, where high concentration of the scale was collected. Hence, it gave us good results on heavy scale removal in the *Run 1*. Since with time process mixing gives more homogenous liquid, the *Run 2* presents feed water from the most representative part of the bioreactor with less dynamic values.

Such phenomenon as zone sedimentation, shown on Figure 6.2, confirms that the water mixture becomes more homogenous with the time. Getting these samples we saw, that in the first one the sedimentation process was very slow but with every next sample it gave better and faster settling of the sand particles and the biomass. It means that the biomass volume decreases, and since sand particles are heavy, they settle faster than with high biomass concentration.

This raises a question: “*Is it possible that with longer cyclone usage time the biomass ingress to the cyclone will be minimized to 0 values?*” A more advanced cyclone which excludes lighter particles could be a solution.

In spite the difference between Run 1 and Run 2 values, both of them are in the “region of efficiency” and gives satisfying and inspiring results on the sand cyclone usage for calcium carbonate scale removal.

7.3 Advantages and disadvantages of the sand cyclone at SART

As we can see so far the results of the sand cyclone usage at SART AS are ambiguous. From one side it has very important advantages:

- Effective calcium carbonate scale removal, what is confirmed by the chemical parameters of the water and visual observation;
- Rather simple in connection to the bioreactor and usage;
- Significantly decreases chemical usage;
- Rather low electricity consumption;
- Very robust – can be used during long time period.

But it is necessary to outline such important disadvantages for SART as:

- Removal of the biomass from the bioreactor;
- The need for a dewatering solution;
- Operation and maintenance (need automatic one);
- Creates a waste (inorganic – scale/ organic – organic/biomass).

So, in this way, we can say that advantages are balanced by disadvantages. In what degree it is an acceptable solution depends on the opportunity to fix the problem with the biomass ingress, since in other way it will be scale removal by cost of water treatment efficiency.

It is necessary to mention that the sand cyclone we used is not the ideal model with regard to the purpose, but it showed good results for a test cyclone.

The questions for SART AS:

- Is it possible to have a cyclone which does not trap the biomass, only heavier particles, and also dewater the scale?

8. Conclusions

The goal of the thesis is to find out the level of availability of a sand cyclone for calcium carbonate problem solution at SART AS.

Under the thesis writing it was examined chemical characteristics of the waste water at SART, working parameters of the bioreactor, thermodynamic and kinetics description of the scale formation process, and finally, the experiment was carried out in order to get known if the sand cyclone can be a good enough solution for this problem at SART AS.

Having made all necessary theoretical investigations, study and experiments lead to the following conclusions:

- The waste water in the bioreactor has high scaling potential according to the basic chemical parameters of the water; it explains scale formation there;
- Incoming water has different alkalinity level (due to its origin and type/location of the oil field) and low enough TSS concentration with regards to biowater;
- By examination of different technical options to solve the problem it was found out that a sand cyclone can be hypothetically an acceptable solution for SART AS from economical point of view, simplicity in setup, time- and chemical consumption;
- The experiment with the sand cyclone usage showed good results in calcium carbonate removal, what was concluded according the basic chemical parameters of the water treated in the cyclone;
- Sand cyclone removes calcium carbonate particles, and in this way decreases alkalinity and hardness level of the water.

However some disadvantages have been observed also during the experiment:

- Biomass removal from the bioreactor to the sand cyclone together with waste water and sand particles,
- There is no a proper dewatering mechanism in this model of the sand cyclone.

According to the hypothesis of the work and all discovered points given straight above, it can be conclude that a sand cyclone can be an acceptable solution for SART AS, but with some technical changes related to dewatering and biomass removal questions.

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Appendix 1

Scale type determination (Intertek West Lab report)



Foreløpig Laboratorierapport

Prøvested	SAR Treatment
Prøvemerkning	SAND
Prøve tatt	18.okt.2011
Prøvetype	Fast stoff

Resultater for prøve 2011-07993-001

Parameter	Resultat	Enhet	PKG		Metode/standard	Usikkerhet	
			Nedre	Øvre		Rel	Abs
Tørrestoff og gløderest i slam/faststoff, gravimetrisk							
Tørrestoff innhold	66,6	wt%	0,01	100	NS 4764	5%	-
Gløderest innhold pr/tørr prøve	94	wt% TS	0,01		NS 4764	5%	-
Organisk innhold pr/tørr prøve	6,0	wt% TS	0,01		NS 4764	5%	-
Karbonat i faststoff, kvalitativt							
Karbonat	pos	-			X-012		
H2S	neg	-			X-012		
Elementer i faststoff, XRF							
Aluminium, Al	0,2	wt%	0,1		X-021 (XRF)	10%	-
Barium, Ba	0,1	wt%	0,1		X-021 (XRF)	10%	-
Kalsium, Ca	34,0	wt%	0,1		X-021 (XRF)	10%	-
Krom, Cr	<0,1	wt%	0,1		X-021 (XRF)	10%	-
Kobber, Cu	<0,1	wt%	0,1		X-021 (XRF)	10%	-
Jern, Fe	0,1	wt%	0,1		X-021 (XRF)	10%	-
Kalium, K	0,2	wt%	0,1		X-021 (XRF)	10%	-
Magnesium, Mg	0,4	wt%	0,1		X-021 (XRF)	10%	-
Mangan, Mn	0,1	wt%	0,1		X-021 (XRF)	10%	-
Natrium, Na	0,7	wt%	0,1		X-021 (XRF)	10%	-
Nikkel, Ni	<0,1	wt%	0,1		X-021 (XRF)	10%	-
Fosfor, P	3,8	wt%	0,1		X-021 (XRF)	10%	-
Bly, Pb	<0,1	wt%	0,1		X-021 (XRF)	10%	-
Silisium, Si	0,1	wt%	0,1		X-021 (XRF)	10%	-
Strontium, Sr	0,2	wt%	0,1		X-021 (XRF)	10%	-
Titan, Ti	<0,1	wt%	0,1		X-021 (XRF)	10%	-
Sink, Zn	<0,1	wt%	0,1		X-021 (XRF)	10%	-
Svovel, S	0,6	wt%	0,1		X-021 (XRF)	10%	-
Klor, Cl	1,1	wt%	0,1		X-021 (XRF)	10%	-
Krystalline faser i faststoff, XRD							
Kalsitt, CaCO3	XXX	-			X-031 (XRD)		

Tegnforklaring: PKG = Praktisk kvantifiseringsgrense. # = Analysen er utført av underleverandør.

Usikkerheten er angitt med 95% konfidensintervall. Der det er oppgitt både relativ og absolutt usikkerhet gjelder det argumentet som til enhver tid representerer størst usikkerhet.

Foreløpig Laboratorierapport

Prøvested	SAR Treatment
Prøvemerkning	SAND
Prøve tatt	18.okt.2011
Prøvetype	Fast stoff

Resultater for prøve 2011-07993-001

Tørrestoff er materiale tørket ved 105°C. Gløderest er materiale etter gløding ved 550°C. Organisk innhold er beregnet som vekt differansen mellom tørrestoff og gløderest, i % av tørrestoff.

Syretest (drypping av fortynnet saltsyre (HCl) for kvalitativ påvisning av karbonat og sulfider) er utført på tørket prøve (105°C).

XRD og XRF er utført på tørket prøve (105°C).

Elementene (XRF) er beregnet som oksyder (normalisert til 100%), men rapportert som elementer i vektprosent. Unntatt kalsium (Ca), den er beregnet som kalsiumkarbonat (CaCO₃). Omlag 86 wt% er beregnet som kalsiumkarbonat (CaCO₃).

Mengdeforklaring til XRD-analysen: XXX=hoved,XX=moderat,X=mindre mengder,x=spor,- = ikke påvist

Hovedbestandel av tørr prøve er kalsium karbonat (CaCO₃).

Appendix 2

Preliminary experiment - alkalinity, TSS and VSS measurements

1. Measurement of alkalinity (27.01.12).

Titrant – 0,1 HCl, end-point = 4,5 pH.

#sample	init pH	titr V	alk CaCO ₃ (mg/L)	titr.V after floc	alk CaCO ₃ after Flocculation (mg/L)
1	7,85	24,2	2420	24,2	2420
2	6,61	7,18	718	8,3	830
3	6,39	18,85	1885	22,5	2250
4	7,94	10,87	1087	11,2	1120
5	6,38	11,45	1145	12,7	1270
6	8,06	13,5	1350	12,75	1275
7	7,28	28,75	2875	31,5	3150
8	6,8	38	3800	35,5	3550
9	6,88	36,25	3625	36	3600
10	7,81	15	1500	12,5	1250
11	4,99	3	300	8,2	820
12	5,94	9,5	950	14,3	1430

Average alkalinity= 1804,57 (before), and 1913,75 (after floc).

2. Measurement of TSS and VSS of SART water samples. (02.02.12)

Weight of a filter = 0,1215 g. Weight of cup = 48,7024g. Volume of samples = 50 ml.

#sample	after 103C (g)	pure weight TSS (g)	TSS (g/l)	after 550C (g)	pure weight FSS (g)	pure VSS (g)	VSS (g/l)
1	49,7691	1,0667	2,1334	49,5221	0,8197	0,247	4,94
2	0,2174	0,0959	1,9180	0,2056	0,0841	0,0118	0,236
3	0,1755	0,054	1,08	0,1613	0,0398	0,0142	0,284
4	0,1472	0,0257	0,514	0,1402	0,0187	0,007	0,14
5	0,4023	0,2808	5,616	0,3878	0,2663	0,0145	0,29
6	0,1778	0,0563	1,126	0,1617	0,0402	0,0161	0,322
7	0,3734	0,2519	5,038	0,3258	0,2043	0,0476	0,952
8	0,2021	0,0806	1,612	0,1784	0,0569	0,0237	0,474
9	0,4619	0,3404	6,808	0,3984	0,2769	0,0635	1,27
10	0,3621	0,2406	4,812	0,3319	0,2104	0,0302	0,604
11	0,1568	0,0353	0,706	0,1411	0,0196	0,0157	0,314
12	0,1715	0,05	1,00	0,1599	0,0384	0,0116	0,232

Appendix 3

Preliminary experiment – LSI and RSI calculation

$$pH_s = (9,3 + 0.34 + 1.95) - (2.2 + \log \text{alk}) = 11.59 - (2.2 + \log \text{alk})$$

$$LSI = pH - pH_s$$

$$RSI = 2 \times pH_s - pH$$

#sample	init pH	alk CaCO ₃	log (alk)	pH _s	LSI	RSI	Scale
1	7,85	2420	3,38381537	6,006185	1,843815	4,162369	+
2	6,61	718	2,85612444	6,533876	0,076124	6,457751	Little
3	6,39	1885	3,27531135	6,114689	0,275311	5,839377	Little
4	7,94	1087	3,03622954	6,35377	1,58623	4,767541	+
5	6,38	1145	3,05880549	6,331195	0,048805	6,282389	little
6	8,06	1350	3,13033377	6,259666	1,800334	4,459332	+
7	7,28	2875	3,45863785	5,931362	1,348638	4,582724	+
8	6,8	3800	3,5797836	5,810216	0,989784	4,820433	+
9	6,88	3625	3,55930801	5,830692	1,049308	4,781384	+
10	7,81	1500	3,17609126	6,213909	1,596091	4,617817	+
11	4,99	300	2,47712125	6,912879	-1,92288	8,835757	-
12	5,94	950	2,97772361	6,412276	-0,47228	6,884553	-

Appendix 4

Control experiment – TSS and VSS measurements, LSI and RSI calculation

TSS and VSS measurements (filter mass – 0.1219)

	#	Titrv	Alkalinity	After 105° C	after 103C (g)	Mass of cup	pure weight TSS	TSS (g/l)* ¹²	after 550C (g)	pure weight FSS (g)	pure VSS (g/l)*	VSS (g/l)
Run 1	1	2,2	220	41.2508	0,673	40.5773	0.5516	11.032	0.4355	0.3136	0.238	4.76
	2	3,65	365	44.3690	3.8542	40.5148	3.7323	74.65	1.7741	1.6522	2.0801	41.6
	3	8,9	890	38.8633	2.8458	36.0175	2.7239	54.478	1.8727	1.7508	0.9731	19.462
	4	2,95	295	43.0156	5.2418	37.7738	5.1199	102.398	2.519	2.3971	2.7228	54.456
	5	2,5	250	40.3315	2.7893	37.5422	2.6674	53.348	1.8865	1.7646	0.9028	18.056
	6	8,7	870	33.7103	1.8294	31.8809	1.7075	34.15	0.9617	0.8398	0.8677	17.36
	7	8,3	830	36.6390	2.4762	34.1628	2.3543	47.086	0.3959	0.274	2.0803	41.606
Run 2	8	3,95	395	18.5920	2.4288	16.1632	2.3069	46.138	0.4894	0.3675	1.9394	38.788
	9	2,2	220	18.1503	3.6494	14.5009	3.5275	70.55	0.565	0.4431	3.0844	61.688
	10	2,6	260	16.8573	1.9829	14.8744	1.209	24.18	0.6378	0.5159	0.6931	13.862
	11	3,7	370	19.6585	4.1321	15.5264	4.6622	93.244	1.3468	1.2249	3.4373	68.746
	12	4,3	430	15.6831	0.8547	14.8284	0.7328	14.656	0.6969	0.575	0.1578	3.156
	13	9	900	15.6886	0.5367	15.1519	0.4148	8.296	0.5262	0.4043	0.0105	0.21

LSI and RSI measurement

#sample	pH	alk CaCO3	log (alk)	pHs	LSI	RSI
1	7	220	2,34242268	7,047577	-0,04758	7,095155
2	7	365	2,56229286	6,827707	0,172293	6,655414
3	7	890	2,94939001	6,44061	0,55939	5,88122
4	7	295	2,46982202	6,920178	0,079822	6,840356
5	7	250	2,39794001	6,99206	0,00794	6,98412
6	7	870	2,93951925	6,450481	0,549519	5,900961
7	7	830	2,91907809	6,470922	0,529078	5,941844
8	7	395	2,5965971	6,793403	0,206597	6,586806
9	7	220	2,34242268	7,047577	-0,04758	7,095155
10	7	260	2,41497335	6,975027	0,024973	6,950053
11	7	370	2,56820172	6,821798	0,178202	6,643597
12	7	430	2,63346856	6,756531	0,243469	6,513062
13	7	900	2,95424251	6,435757	0,564243	5,871515

¹² Formula for TSS calculation is:

$TSS = (A - B) \times 1000 / \text{sample volume, ml}$, where A = weight of filter + dried residue after drying at 103° C, mg; B = weight of filter, mg.

Appendix 5

Hardness Measurement (ALS Report)

Rapport

Prosjekt
Bestnr
Registrert **2012-05-10**
Utstedt **2012-05-23**

SAR Treatment AS
Jon Arne Pettersen

NorSea-Basen Kai 5
N-4056 Tananger
Norge

Side 1 (3)

Analyse av vann



N1204514

116YW6WIUA8

Deres prøvenavn	1				
	Vann				
Labnummer	N00197210				
Analyse	Resultater	Enhet	Metode	Utført	Sign
Hardhet	324	°dH	1	1	MORO
Hardhet	57.8	mmol/l	1	1	MORO

Deres prøvenavn	2				
	Vann				
Labnummer	N00197211				
Analyse	Resultater	Enhet	Metode	Utført	Sign
Hardhet	319	°dH	1	1	MORO
Hardhet	57.0	mmol/l	1	1	MORO

Deres prøvenavn	3				
	Vann				
Labnummer	N00197212				
Analyse	Resultater	Enhet	Metode	Utført	Sign
Hardhet	79.6	°dH	1	1	MORO
Hardhet	14.2	mmol/l	1	1	MORO

Deres prøvenavn	4				
	Vann				
Labnummer	N00197213				
Analyse	Resultater	Enhet	Metode	Utført	Sign
Hardhet	307	°dH	1	1	MORO
Hardhet	54.8	mmol/l	1	1	MORO

Deres prøvenavn	5				
	Vann				
Labnummer	N00197214				

Analyse	Resultater	Enhet	Metode	Utført	Sign
Hardhet	174	°dH	1	1	MORO
Hardhet	31.2	mmol/l	1	1	MORO

Deres prøvenavn

6
Vann

Labnummer

N00197215

Analyse	Resultater	Enhet	Metode	Utført	Sign
Hardhet	139	°dH	1	1	MORO
Hardhet	24.8	mmol/l	1	1	MORO

Deres prøvenavn

7
Vann

Labnummer

N00197216

Analyse	Resultater	Enhet	Metode	Utført	Sign
Hardhet	274	°dH	1	1	MORO
Hardhet	48.8	mmol/l	1	1	MORO

Deres prøvenavn

8
Vann

Labnummer

N00197217

Analyse	Resultater	Enhet	Metode	Utført	Sign
Hardhet	259	°dH	1	1	MORO
Hardhet	46.2	mmol/l	1	1	MORO

Deres prøvenavn

9
Vann

Labnummer

N00197218

Analyse	Resultater	Enhet	Metode	Utført	Sign
Hardhet	320	°dH	1	1	MORO
Hardhet	57.1	mmol/l	1	1	MORO

Deres prøvenavn

10
Vann

Labnummer

N00197219

Analyse	Resultater	Enhet	Metode	Utført	Sign
Hardhet	130	°dH	1	1	MORO
Hardhet	23.3	mmol/l	1	1	MORO

Deres prøvenavn

11
Vann

Labnummer

N00197220

Analyse	Resultater	Enhet	Metode	Utført	Sign
Hardhet	136	°dH	1	1	MORO
Hardhet	24.2	mmol/l	1	1	MORO

Deres prøvenavn

12
Vann

Labnummer

N00197221

Analyse	Resultater	Enhet	Metode	Utført	Sign
Hardhet	132	°dH	1	1	MORO
Hardhet	23.5	mmol/l	1	1	MORO

N1204514, 116YW6WUUA8

Dokumentet er godkjent og digitalt signert av Monia Ronningen.