Analysis of fouling rates in black liquor evaporators

A case study of Stora Enso Skutskär pulp mill

Master's thesis in Master Program Sustainable Energy Systems

IRMA BJÖRNWALL

DEPARTMENT OF CHEMISTRY AND CHEMICAL ENGINEERING
CHALMERS UNIVERSITY OF TECHNOLOGY
Gothenburg, Sweden 2022
www.chalmers.se

Master's thesis 2022

Analysis of fouling rates in black liquor evaporators

A case study of Stora Enso Skutskär pulp mill

IRMA BJÖRNWALL

Department of Chemistry and Chemical Engineering
Division of Chemical Engineering
Chalmers University of Technology
Gothenburg, Sweden 2022

Analysis of fouling rates in black liquor evaporators
a case study of Stora Enso Skutskär pulp mill
IRMA BJÖRNWALL

Supervisors: Anders Åkesjö, PhD, Chemical Engineering
Johan Eriksson, engineer, Stora Enso
Examiner: Gunnar Eriksson, Chemical Engineering

Master's Thesis 2022
Department of Chemistry and Chemical Engineering
Division of Chemical Engineering
Chalmers University of Technology
SE-412 96 Gothenburg
Telephone +46 31 772 1000

Cover: Stora Enso Skutskär Evaporation plant

Typeset in LaTeX
Printed by Chalmers Reproservice
Gothenburg, Sweden 2022

Analysis of fouling rates in black liquor evaporator plants
a case study of Stora Enso Skutskär pulp mill
IRMA BJÖRNWALL
Department of Chemistry and Chemical Engineering
Division of Chemical Engineering
Chalmers University of Technology

Abstract

Fouling and scaling is a common problem in most black liquor evaporation plants. These scales stick to the heat transfer surface area in the effects, which in turn disturbs the evaporation. In order to maintain the evaporation plant in a good condition and to avoid production losses, efficient removal of these scales are necessary. Optimizing the black liquor evaporation process will reduce the amount of energy needed, which will enhance the production and make it more lucrative and environmentally sound. Stora Enso Skutskär pulp mill has experienced problems with scaling, particularly in effect 3C, where dT often increases rapidly which forces the mill to stop and perform a wash. This thesis aims to examine the evaporation plant at Skutskär. In an analytical way evaluate process data and investigate the performance of the effects with a focus on 3C, 2C, 1C and the black liquor thickener. Additionally, a study to see if best practice guidelines on operating conditions and washing at the mill are being followed to see if any improvements could be made.

The process data was collected from the last two years with information about the temperatures of the black liquor and the condensed steam, the DS in and out of the effects and the mass flow in to effect 3C. To see changes in the process data over time and in that way be able to evaluate the washes and how the plant operates in general, a MATLAB script was used. With plots provided by the MATLAB script, an evaluation could be conducted. The washing cycles were identified by the change in BPE, dT and the DS. A wash could be assumed to happen when these parameters went down to close to zero or deviated together simultaneously.

The washes were found to be effective for 3C, but not quite as effective for 2C and 1C. On the other hand, the last two were not in need of cleaning whenever a wash cycle was initiated. Most of the scales in effect 3C seemed to be water soluble but there appeared to be some scales that did not dissolve during the wash cycles. These scales are most likely calcium carbonate scaling. The process data was also evaluated in terms of how reliable they seemed, and one notation was made with the DS_{out} from effect 3C. This value could deviate considerably from time to time, implying that one or maybe more sensors are either incorrectly calibrated, or scaling has been built up on those sensor areas. There only appeared 7 wash cycles for the black liquor thickener in total, which through conversations with staff, it emerged that this is not the case. The data from the black liquor thickener appeared to be interpolated and hence has to poor temporal resolution to analyse correctly.
Keywords: falling film evaporators, evaporator cleaning, fouling, scaling, crystallization on black liquor evaporators, calcium carbonate, sodium carbonate.

Analys av inkrustreringsgrad i svartlutsindunstare
fallstudie av Stora Enso Skutskär massabruk
IRMA BJÖRNWALL
Avdelning för Kemi och Kemiteknik
Skogsindustriell kemiteknik
Chalmers Tekniska Högskola

Sammanfattning

Inkrustreringar är ett vanligt och återkommande problem för de allra flest svartlutsindunstare. Dessa kristallina beläggningar fastnar på värmeöverföringsytan och skapar störningar. För att kunna hålla indunstningsanläggningen i ett bra skick och undvika produktionsförluster så är en effektiv borttagning av dessa inkruster nödvändig. En optimering av en svartlutsindunstningsprocess kan minska energiförbrukningen, vilket skulle förbättra produktionen så den blir både mer ekonomisk och miljömässigt hållbar. Stora Enso Skutskärs massabruk har haft problem med inkrustrering, särkilt i effekt 3C där dT ofta hastigt stiger och tvingar bruket till att stanna den delen och tvätta. Syftet med detta arbete har varit att undersöka svartlutsindunstningen i Skutskär med ett fokus på effekt 3C, 2C, 1C och deras slutförtjockare. Dessutom en studie för att se om bästa praxis riktlinjer för driftförhållanden och tvätt på bruket följs för att se om några förbättringar kan göras.

Processdata har samlats in från de senaste två åren med information om temperaturer på svartluten och den kondenserade ångan, TS in och ut ur effekterna och massflödet in till effekt 3C. För att se förändringar i processdata över tid och på så sätt kunna utvärdera tvättarna och hur anläggningen fungerar i allmänhet användes ett MATLAB-skript. Med plotter som tillhandahålls av MATLAB-skriptet så kunde en utvärdering göras. Tvättcyklerna identifierades av förändringen i KPF, dT och TS. En tvätt kan antas ske när dessa parametrar gick ner till nära noll eller avvek samtidigt.

Tvättarna visade sig vara effektiva för 3C, men inte riktigt lika effektiva för 2C och 1C. Å andra sidan var de två sista inte i behov av att rengöras när en tvättcykeln påbörjades. De flesta av inkrusterna i effekt 3C verkade vara vattenlösliga men det verkade finnas några inkrustreringar som inte löstes upp med vatten överhuvudtaget. Dessa inkrustreringar kan troligen vara kalciumkarbonatinkrustrering. Processdatan utvärderades också av hur tillförlitliga de verkade, och en notering gjordes med TS_{ut} från effekt 3C. TS_{ut} kunde avvika anmärkningsvärt från sitt börvärde ibland, vilket kan vara en antydan att en eller flera sensorer antingen är felaktigt kalibrerade eller att inkrustrering har byggts upp på dessa sensorer. För slutförtjockaren så kunde bara 7 tvättar identifieras och genom samtal med personal kan det fastställas att så inte var fallet, utan det tvättas oftare än så. Data från slutförtjockaren verkade vara interpolerad vilket gör det komplicerat att kunna fastställa en analys.

Acknowledgements

I would like to express my special thanks of gratitude to my supervisor Anders Åkesjö at Chalmers. Your support has been invaluable and I am grateful that you always found time to answer my many questions and discuss the problems I encountered along the way.

A special thanks is directed to my supervisor at Stora Enso, Johan Eriksson, for sharing your expertise about the pulp industry in general and about black liquor evaporation in particular. Thank you for all the information you provided me with about the evaporation station at Skutskär, and of course the nice photography used on the cover page.

I would like direct a special thank you to my examiner, Gunnar Eriksson, here at Chalmers who has been very supportive during this master thesis.

I want to also thank the employees at Stora Enso Skutskär for their time and patience answering my questions.

Finally, a large thanks addressed to the department of Chemistry and Chemical engineering and everyone working there. I have appreciated these five months a great deal.

Irma Björnwall, Gothenburg, May 2022

List of Acronyms

Below is the list of acronyms that have been used throughout this thesis listed in alphabetical order:

BPE	Boiling Point Elevation
CTO	Crude Tall Oil
CSD	Crystal Size Distribution
DS	Dry Solid Content
dT	the change in temperature between the condensing vapor and the temperature of the out going black liquor
HBL	Heavy Black Liquor
WBL	Weak Black Liquor

Nomenclature

Below is the nomenclature of the chemical formulas that have been used throughout this thesis.

Chemical formulas

NaOH	Sodium hydroxide
Na_2S	Sodium Sulfide
Na_2CO_3	Sodium Carbonate
Na_2SO_4	Sodium Sulfate
$CaCO_3$	Calcium Carbonate

Contents

List of Figures

List of Tables

1

Introduction

1.1 Background

The concern for the climate change has put the whole world in action towards trying to minimize the human impact on the environment. There are many different areas where there is potential for improvement. The industries have a huge impact on the environment and even small decreases in energy use makes a big difference. There is a natural incentive to try and reduce the amount of energy needed and optimize the production since it makes the process more lucrative and environmentally sound. Furthermore, it is generally good for the company's image to make efforts towards a more sustainable future since it makes it more viable for potential investors.

The forest industry is one of Sweden's most important means of production. It accounts for around 9-12 % of Sweden's total employment, exports, sales and values. The major part of the products produced from the forest is being exported and the year 2019 Sweden was the 5th biggest exporter in the world of pulp, paper and sawed wood products. The pulp production itself produced 12 millions tonnes 2020 [18].

There are many different methods that can be used for producing pulp, two examples is e.g mechanical and chemical pulp production. For chemical productions is the sulphite or the kraft method the most common ones. The kraft process is for the most pulp mill an energy self sufficient process with a lot of different steps within the cycle. One important step for it to be an energy self sufficient process is the burning of the lignin, hemicellulose, extractives and other residues from the cooking step. The burning of these takes place in the black liquor in the recovery boiler that gives process steam for the rest of the mill. To make the combustion of black liquor beneficial the water needs to be evaporated first. The evaporation plant is itself the most energy demanding process step, hence the incentive is high to reduce the energy demand in this step as much as possible. One reason for increased energy losses in the evaporation plants is fouling and scaling. This is very common in almost every evaporation plant. Scaling can occur on the heat exchange surface area and if it does there is a high risk that it causes disruption and energy losses. Cleaning and washing the evaporation equipment is therefore necessary to keep the problem with fouling and scaling under control. The washing intervals often do get shorter and shorter if a mill experience a lot of problem with scaling. If the washing intervals are getting shorter this will lead to inferior heat economy. This due to lower average amount of water evaporating from the liquor per provided volume of new steam. The washing of evaporators is a mill productivity loss. If the scaling is large enough it can cause the evaporation plant to shut down and ultimately the entire mill has to shut down.

1.1.1 Skutskär pulp mill

The evaporation plant at Stora Ensos pulp mill in Skutskär consists of two lines, the side 6A-B and the side 6C, with a shared black liquor thickener. Together their total capacity of evaporated water is 670 tonnes/h, this corresponds to a yearly pulp production of 550 000 tonnes.

The 6C side was built in 1996 and delivered by Andritz. This side consists of 5 falling film evaporators, one pre-condenser, one post-condenser and one integrated stripper between effect 4 and 5. In total there are 6 effects which are of lamella-type. The black liquor flows from effect 4 to 5, to 1-2-3 and lastly to the black liquor thickener. The total capacity of evaporated water is 348 tonnes/h. The dry solid content increases from 18,5 % to 72 %. The usage of fresh saturated steam is 75 tonnes/h. This description of the plant can be viewed more extensive in Appendix 1 together with a flow chart. This can also be viewed in a simplified flow chart in figure 1.1.

Out of the two sides the 6C is the side that has had the most problems with fouling, scaling and experienced washing problems. Still at the same time being the most important side since it produces more of the final product than the other side. The effect 3C has historically had the most problems which forces the washing intervals to be shortened. If effect 3C needs to be washed, this causes also that effect 2C and 1C needs to be stopped and washed at the same time. This due to there is no possibility to redirect the black liquor and bypass 3C. This limits the production rate of black liquor which in turn causes production losses in the pulp mill.

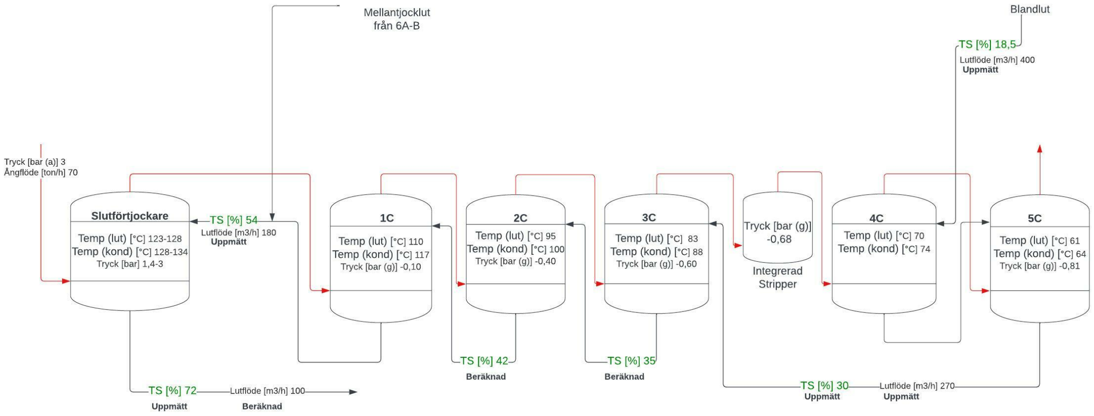


Figure 1.1: Schematic overview of the 6C side of the evaporation plant

1.2 Objective

The aim of this master thesis is to examine the evaporation plant at Stora Enso Skutskär pulp mill. Furthermore, investigate the performance of the effects where a focus lays on effect 3C, 2C, 1C and the black liquor thickener. These are inspected in order to see where fouling and scaling stems from. Additionally, investigation to see if best practice guide lines on operating conditions and washing at the mill is being followed to see if any improvements could be made. In order to decide if any improvement could be made this thesis needs to consider analysed process data combined with literature.

1.3 Scope

The boundaries in this thesis will include the evaporator plants 6C side which includes 5 falling film evaporators and one black liquor thickener. This means that the 6A-B side of the evaporation plant is not included within the scope.

The thesis will focus on the inorganic types of scales such as sodium and calcium scaling, and will not focus on other types of possible scaling.

The analysis will only be made with data from the last two years, from April 2020 until Mars 2022. The reason being that there is no available data from before this time period.

2

Theory

2.1 Kraft pulping process

Dry softwood consists mainly of three major components that together constitute the wood structure. These are cellulose (41-46%), hemicellulose (25-32%) and lignin (26-31%) [8].

There are different methods of producing pulp from wood, but the most common one and the main chemical pulping process is the alkaline Kraft pulping process. A schematic overview of the alkaline kraft process can be viewed in figure 2.1.

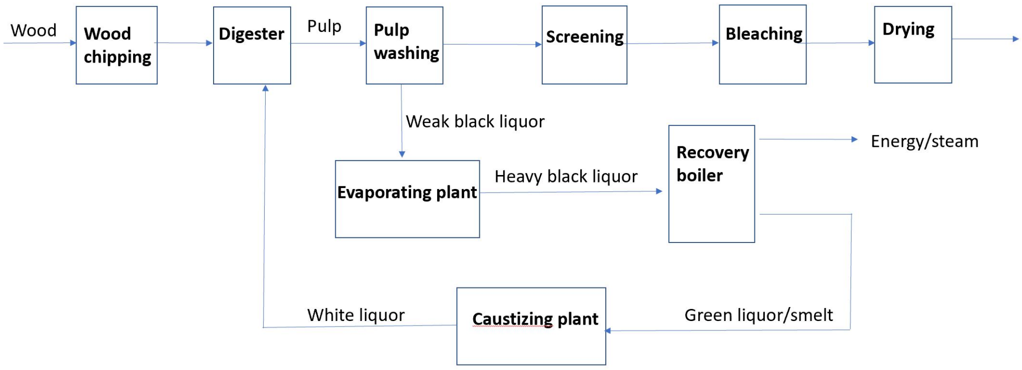


Figure 2.1: Schematic overview of kraft pulping process

In this process the wood logs are often shredded into chips after being debarked. The debarking step is important since most of the metal ions are located in the bark which could have a negative impact for the rest of the process. The wood chips are then cooked in a digester where they are treated at 150-180°C with white liquor at a high pH. The white liquor consists of sulfide, sulfhydryl and polysulfide, mainly in the configuration as sodium hydroxide (NaOH) and sodium sulfide (Na2S). Some of the sodium sulfide is oxidized to Na_2SO_4 and some of the sodium hydroxide is oxidized to Na_2CO_3 during the cooking step [4]. The next step for the pulp fibers is filtering and washing. The dissolved lignin together with the remaining cooking chemicals is removed from the pulp fibers. The pulp fibers are then bleached and dried, after this the cellulose can be used for pulp and paper products [7].

The solubilized lignin and most of the hemicellulose is found in the spent cooking liquor, the so called weak black liquor (WBL). The lignin in the WBL is often used as a fuel for the kraft mill and is important since it contributes for a major part of the mills energy self-sufficiency [2]. Because of economic and environmental reasons is the WBL sent to the recovery side of the pulp mill to be recycled. In the recovery cycle is the WBL first being evaporated in a multistage evaporation plant to increase the dry solid content (DS), this is important to get a more energy efficient economy as possible [8]. The WBL has a DS of around 15 % and is dried to a DS around 65-85 % to get a efficient energy recovery and is now called heavy black liquor (HBL) [1]. The HBL is sent to a recovery boiler so that the expensive cooking chemicals can be recovered and at the same time produce steam. The cooking chemicals are localized in the smelt which is later dissolved to produce first green liquor and then once again, white liquor in the caustizing plant [7].

2.2 Black liquor

The viscous, alkaline residue from the digester is called black liquor. The black liquor contains both organic and inorganic compounds where two thirds is organic. Among the organic part is lignin, hemicellulose and extractives the most prominent types. One third is inorganic compounds which originates from the wood chips and the cooking chemicals [5].

The black liquors viscosity is a function of concentration and temperature and depends on the wood species, cooking methods etc. The viscosity increases when the DS increases, and a pumping limit is often 300 to 500 cP. This is often not a problem in an evaporation plant [8].

A low surface tension in the black liquor will increase the tendency to foam, and when the DS increases, so does the surface tension as well. The surface tension decreases in relation to when the temperature of the black liquor increases. Soap and crude tall oil (CTO) is often separated from the liquor if the content is to high. This is due to that soap and CTO decreases the surface tension [8].

The inorganic material are mostly bound to the organic dissolved compounds but there are some minor parts such as NaOH, Na_2S, Na_2CO_3 and Na_2SO_4 that dissolves as salt in the weak black liquor. Sodium and potassium, compared to inorganic material, has a higher solubility. In the evaporation plant when the DS is around 50 % the Na_2CO_3 and Na_2SO_4 with their double salt Na_2SO_4*Na_2CO_3 starts to precipitate. The sodium salts is, however, completely dissolved in the aqueous portion of the liquor if the DS is below 50% [9]. The fraction between Na_2CO_3 and Na_2SO_4 can vary and the formation of different types of crystal depends on temperature and mole fraction. Either burkeite ($2Na_2SO_4$*Na_2CO_3) or dicarbonate (Na_2SO_4*$2Na_2CO_3$) can be formed, and under some rare occasions, sulphate or carbonate. These composition regions and the different solutes is viewed in figure 2.2[7].

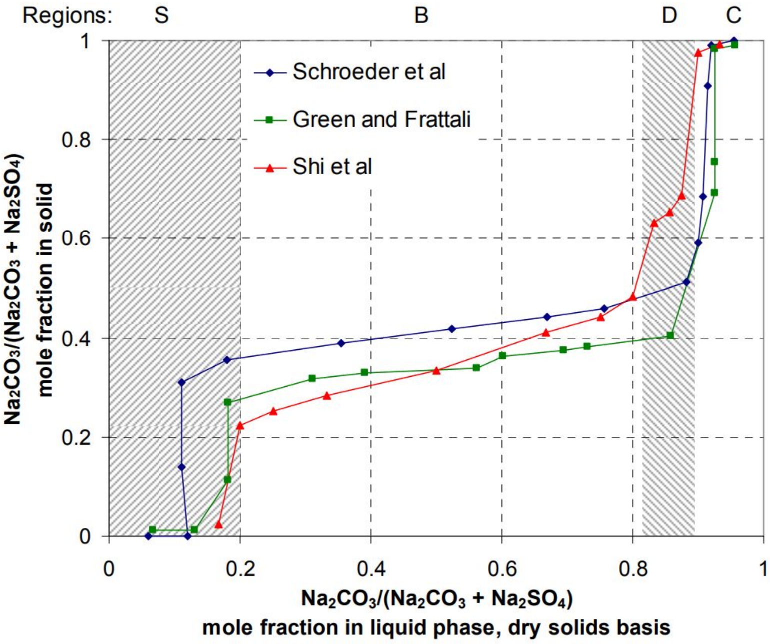


Figure 2.2: Compositions regions for the formed crystals as a function of different solute compositions. Where the different regions stands for sulphate (S), burkeite (B), dicarbonate (D) and carbonate (C). Equilibrium data from Schroeder et al. (1936), Green et al. (1936) and Shi et al. (2003). Figure reprinted in courtesy of Gourdon, Mathias (2009)[7].

The critical concentration of the liquor is the concentration when burkeite starts to precipitate. The heating surface area is affected by these crystallized salts but they are washable. The black liquor has normally a pH level of 12 with 5-10 g/L of Na_2S and NaOH. The evaporator heating surface can start to foul if the alkaline material decreases to a pH below 11 and the residual concentration below 7 to 9 g/L since the lignin compounds starts to precipitate and foul [8].

The composition of the black liquor varies depending on the wood specie, cooking method etc. But in a study made in 1997 on 19 different pulp mills, an average composition of the different species was established. This composition can be viewed in table 2.1. In this table, the investigated analyte is presented in either weight percentage or in a mole/mole fraction, with a mean value, and a standard deviation (Std. Dev) [16].

Table 2.1: Black liquor properties from analyses performed by and reprinted in courtesy of Schmidl and Frederick (1998) [16].

Analyte	**Mean**	**Std. Dev**	**Range**
Na2CO3 [wt%]	10.0	2.6	4.77-14.5
Na2SO4 [wt%]	6.03	4.18	1.94-16.1
Na2CO3/Na2SO4 [mole/mole]	2.49	1.67	0.51-6.33
Residual active alkali as Na2O [wt%]	5.69	1.36	2.81-7.66
Na [wt%]	18.4	1.65	14.0-20.3
K [wt%]	2.02	1.19	0.82-5.05
Residual soap [wt%]	0.85	0.48	0.32-2.02
Fiber [wt%]	0.23	0.24	0.04-1.08
Critical solids [wt%]	52.2	2.8	49.0-60.3
Carbon [wt%]	34.6	2.32	31.4-40.4
Inorganic carbon [wt%]	1.14	0.30	0.54-1.64
Organic carbon [wt%]	33.5	2.50	30.2-39.7
Hydrogen [wt%]	3.43	0.23	3.05-3.96
Oxygen [wt%]	35.1	2.57	26.4-38.4
Sulfur [wt%]	4.74	0.89	3.34-6.64
Sulfate [wt%]	4.08	2.83	1.31-10.9
Thiosulfate [wt%]	3.98	1.25	2.40-6.49

2.3 Black liquor evaporator

Evaporating the WBL into HBL is crucial since it would require more energy to combust the WBL than what would be generated. The principle of evaporators is the separation of a solution containing nonvolatile solutes and water. The vaporization of the water is caused by heat supply where the heating media is often steam or vapor whilst black liquor is the media that is being heated. There is often several heat transfer units connected in an evaporation plant, and one evaporation stage is referred to as an effect. An effect is one heat exchanger that operates at the same steam pressure level. Normally, an evaporation plant exists of 5 to 7 effects in series [8]. There is different types of evaporation equipment used in the industry but the rising film evaporators and falling film evaporators are the most common ones, wheres the last mentioned one is the most commonly used out of the two, today.
The heat transfer through a heating element of an evaporator can be expressed with the following equation 2.1 [8]:

$$Q = U * A * \Delta T \tag{2.1}$$

Where Q is the rate of heat transfer (W)
U is the heat transfer coefficient (W/m^{2}C)
A is the total heat transfer area (m^2)
ΔT is the temperature difference between the steam and the black liquor.
The magnitude of Q gives an indication if the heat is efficiently transferring between the steam to the black liquor. A higher value on Q means a more efficient heat

transfer process.
The heat transfer coefficient can also be expressed as the inverse of the sum of the heat transfer resistances, defined in equation 2.2 [8]:

$$\frac{1}{U} = R_C + R_A + R_S + R_L \tag{2.2}$$

where R_C is the resistance of the condensate film
R_A is the resistance of the heating surface material
R_S is the resistance due to scaling
R_L is the resistance of the liquor side.
The problem pulp mills often meet is scaling, which lowers the heat transfer coefficient [8].

2.3.1 Boiling point elevation

The salts that can be precipitated in the black liquor cause a boiling point elevation (BPE). This means a rising in the boiling point between the addition of non-volatile species to the pure solute at the same pressure [17]. Pure water will hence, compared to a mixture containing organic and inorganic dissolvents, boil at a lower temperature at the same pressure. In this thesis, black liquor represents water with dissolved organics . So an increase of DS will increase the BPE. The BPE also depends on the composition of the dissolved substances. The transferred heat between the steam and the black liquor in the evaporator is dependent on the temperature difference between the evaporating black liquor and the condensing steam. The BPE is therefore central when designing black liquor evaporators since it can reduce the driving potential for transferred heat. The BPE is not supposed to increase rapidly for black liquor if the DS is below 50%. Above that limit of DS the BPE increases fast. [9]. The BPE can be written as

$$BPE = BPE_{50}\frac{S}{1-S} \tag{2.3}$$

where BPE_{50} is the BPE at 50% DS and S is the DS in w fractions. This calculation is only valid for a DS under 50% [9].

2.3.2 Density

The density of black liquor at a low DS is, not so surprising, close to the density of water. With a higher DS make the density more dependent on the organic and inorganic materials in the solution. The density for inorganic components can be twice the density compared to waters [1]. It is necessary to know the density of black liquor. This will help during mass flow calculations which is often used to create mass and energy balances. The density can be used to decide the DS as well. A low temperature and a higher DS of the black liquor will naturally increase the density. It is possible to calculate the density with temperature and DS as parameters and this correlation is shown in equation 2.4, [9].

$$\rho = \rho_{H2O}[1 + S(0.571 + 0.0008T)] \tag{2.4}$$

Here T is in degree C°.
Black liquors density can be affected by entrained air. The following equation 2.5 is developed similar as the correlation mentioned before [9].

$$\rho = (997 + 649S)(1 - 0.000369(T - 25) - 0.00000194(T - 25)^2) \tag{2.5}$$

Where T is in degree C°.

2.3.3 Falling film evaporators

There are often two different types of falling film evaporators;

- Plate lamella-type with liquor flowing on the outside of the vertical plates, viewed in figure 2.3.
- Tubular-type which can either have the liquor flow on the inside or outside of the vertical tubes, viewed in figure 2.4.

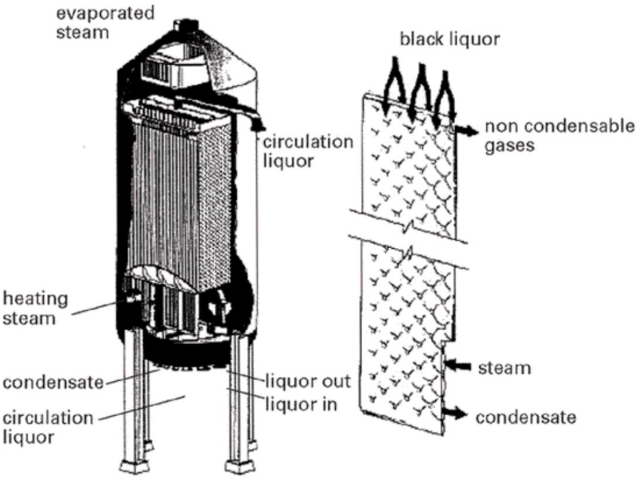


Figure 2.3: Schematic diagram of falling film evaporator, lamella type. Reprinted in courtesy of Ek, Monica Gellerstedt, Göran Henriksson, Gunnar. (2009) [6].

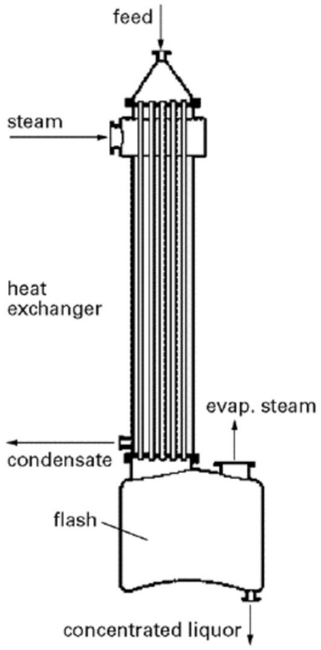


Figure 2.4: Schematic diagram of falling film evaporator, tube type. Reprinted in courtesy of Ek, Monica Gellerstedt, Göran Henriksson, Gunnar. (2009) [6]

A circulating pump helps the liquid to rise to the top of the heating element. Due to that the circulation rate can be seen as constant as well as the concentration within the effect makes the falling film evaporators insensitive to variations in the evaporation load [8].

The lamella-type falling film evaporator has the black liquor being fed to the bottom of the effect and with help from the circulation pump the black liquor lifts to the top part. The black liquor flows down along the plates and spreads evenly on the heat surface area. The steam, used as the heating media, goes inside the lamella heat transfer surfaces. The vapor generated from when the black liquor starts to boil is separated instantly. The secondary vapor goes from the effect to work as a heating media in the effect before. A drop separator is put to the top of the effect where the vapor has to passes through before exiting, to ensure the purity of the secondary vapor [8].

The tube-type falling film evaporator has liquor that flows on the outside of the tubes. In this type the tubes are connected to headers that allows the liquid to be evenly distributed over the heat surface area. The liquid is being heated by the steam inside the tubes which condenses. A disadvantages with this type of design is that it limits the vapor side cross-section area and can hence not be used in the last effects since the vapor do not get enough of room to pass through [8].

The tube-type falling film evaporator that has liquor on the inside of the tubes has the liquid pumped up to the liquid distributor which is a tray with perforated bottom. This could also in some cases be a spray nozzle type instead [8]. A liquid film is formed and flows downwards due to gravitation inside the tubes. The formed vapor and the liquor that remains separates at the bottom of the effect. To clean the vapor before it exits the vapor passes through a drop separator. The heating media condenses outside of the tubes [6].

2.4 Crystallization

Out of the three general states of matter (gaseous, liquid and solids) solids can be either amorphous or crystalline. The amorphous and the crystalline structure differs from each other in the matter of different arrangement, where crystalline structure has regular arrangement of the constituents molecules, atoms or ions in a rigid, fixed pattern. This is noted as a lattice [14].

2.4.1 Supersaturation

The amount of collisions an atom, ion or molecule does is depending in the number of units per unit volume of the fluid phase, which equals the molar concentration times Avogadro's number, shown in 2.6:

$$C \times N_a \tag{2.6}$$

To ease the calculations in practice, the mass concentration, denoted c [kg/m^3 = g/dm^3 = g/l], is being used [13].

If the concentration is C* in a saturated fluid phase it is thermodynamic equilibrium in the solid phase. The saturation concentration depends heavily on temperature but also on pressure if the solution is liquid. A fluid phase is said to be supersaturated if it has more units than C* $\times N_a$. For crystallization to occur, the fluid phase has to be supersaturated. The degree of the supersaturation often determine the rate of crystallization [13].

2.4.2 Nucleation

Crystal growth as well as the kinetic processes of nucleation depend on supersaturation. Supersaturation can typically be obtained by a change in temperature, by adding a drowning-out agent or by removing the solvent[13]. It is not always sufficient enough for a system to start crystallize by the condition of supersaturation. There must exists some type of solid bodies, nuclei, seeds etc to act as a centre before crystals can be developed. Nucleation can then be spontaneous or induced by e.g agitation or pressures[14].
Crystals has a varying bond forces keeping it together. The crystals are highly organized in a three-dimensional periodic arrangement of units in a spatial lattice. They are created when nuclei are formed[13].
There are two different types of nucleation called primary and secondary.Further on, primary consists of different types called homogeneous or heterogeneous nucleation.

Homogeneous nucleation is formed if the solution contains neither solid foreign particles nor crystals of its own type. It is the opposite for the heterogeneous nucleation, it is formed if the solution has foreign particle presented. These two nucleation types are both known as primary nucleation. When the metastable supersaturation is obtained in the system, primary nucleation can occur. It is noticed that nuclei can appear at very low supersaturation when solution-own crystals are present. This is called secondary nucleation[13].

2.4.2.1 Primary nucleation

For primary, homogeneous nucleation has it been found that spontaneous nucleation has been induced in some way. In fact, true homogeneous nucleation is not an common event at all. For primary, heterogeneous nucleation can the presence of impurities affect the nucleation rate considerably. Here is the size of the foreign body important since it has been found that the most active hetero-nuclei in liquid solutions is within the range of 0.1 to 1 μm [14].

2.4.2.2 Secondary nucleation

The supersaturated solution nucleate much faster if there already is crystal present in the solution. This means that it can nucleate at a lower supersaturation [14]. Secondary nucleation is depending on suspension density, agitation and supersaturation. There is several mechanisms such as initial breeding, contact nucleation and sher breeding for secondary nucleation to occur. The most important mechanism is contact nucleation. This is a result from collisions of crystals with the impeller and other crystals [17].

2.4.3 Metastable zone

The region where crystallization process normally can be found is called the meta stable zone. Undesired nucleation can occur, which can produce an excessive of crystals. This can happen if temperatures or concentration happens beyond the metastable zone. This zone lays between the solubility limit and the metastable limit, here can crystals be detected in a fixed period of time. This region is viewed in figure 2.5 [17].

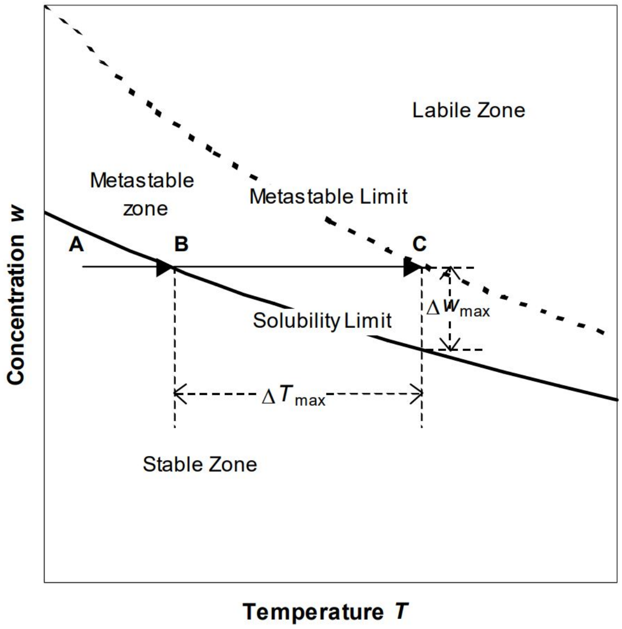


Figure 2.5: The metastable zone for a system of inverse solubility can be determined by increase the solution temperature from A though B to C at a constant rate. Reprinted in courtesy of Shi B, 2002 [17].

The metastable limit is a function of different factors, and depends on system properties, operation conditions, impurities, thermal history, waiting time etc. The metastable zone's width is defined as either the horizontal distance (DT$_{m}ax$) or the vertical distance (Dw$_{m}ax$) between the curves of the metastable limit and the solubility limit, this is also viewed in Figure 2.5 [17]. The thermal effect can greatly affect the metastable zone width. If the temperature a solution has been stored in has been higher than the saturation temperature makes the metastable zone be wider compared to if the solution had been stored in temperature below the saturation temperature [14].

Impurities in the solution can affect the nucleation and crystal growth. The crystal size, ratios, distributions and even the crystallization kinetics and mechanisms can change due to impurities. The concentrations of impurities is generally low in process solutions but can be diverse. Metallic ions, surface-active agents and polymers containing carboxylate groups are more likely to affect crystallization. Often is these impurities not identified due to the extensive experimental efforts, even though they can influence the process greatly [17].

2.4.4 Agglomeration

Agglomeration can be described as particles unifying with a various type of naturals forces. These forces includes crystal bridges, electrostatic attractive forces, Vand der Waals and so on. There are types of agglomerations which are called primary and secondary agglomeration. The primary agglomerations is caused by mal-growth of crystals while secondary agglomeration is a due to crystal-crystal collisions in supersaturated solutions. The fluid dynamics, crystal growth rates and suspension density is all different factors that affect agglomeration [17].

The rates of agglomeration, attrition, fines dissolving, nucleation and crystal growth does all determine crystal size distribution (CSD). For secondary nucleation, it is important to know how attrition fragments grow in a supersaturated solution since they affect the influence of the population and the CSD [13].

Crystallization occur in black liquor evaporators, causing scaling. As the evaporation train increases the DS content of the black liquor, salt crystals starts to precipitate [7]. In the black liquor can the sodium carbonate and sodium sulfate crystallize mainly into four different species at higher temperatures. These are sodium sulfate, sodium carbonate monohydrate, burkeite and a specie which consists of a double salt of sodium carbonate and sodium sulfate. It is similar to burkeiete except that it is distinguished by substantially higher carbonate content with a different pattern. It is mainly the carbonate-sulfate ratios in the liquid phase that determine the different species of crystallization. The most common ones of the inorganic substances in the solid phases to precipitate is burkeite and the double salt of sodium carbonate and sodium sulfate [17].

2.5 Fouling and scaling

If scaling is being formed on the heating surface area it will decrease the heat transfer coefficient remarkably. It is therefore important that the heat transfer between the black liquor and the steam or vapor is satisfactory. Fouling or scaling should be removed, otherwise it could cause a shutdown of the evaporator plant and even the entire pulp mill [8].
Fouling can be caused by lignin, soap and/or fibres. If fouling occurs at the evaporators heating surface it could be an indicator that there may be a problem somewhere else in the pulp mill. Fiber fouling can appear and plug the distribution boxes of the evaporator if the content of fiber exceeds 50-100 mg/L. This happens most commonly in the effects 2, 3 or 4, i.e the effects with medium concentration. When the concentration of fibers gets to high it can hinder the soap separation. The fiber content could be controlled via a filter in the black liquor flow from the pulp washing plant. By keeping the soap content below 0.8 to 1.0% CTO of the liquor dry solids after the soap skimming, soap fouling can be avoided. If the pH level is not significantly decreased, lignin will stay in the solution [8].

Besides lignin, soap and fibres can the inorganic salts in the black liquor crystallize and form scales on the heating surface. The three main types of scales that forms in the evaporators are

- Aluminium or silicate scaling
- Calcium carbonate scaling
- Sodium carbonate or sulfate scaling

It is usually very difficult to measure the thickness of the scales directly on the equipment since it can only be done during non operating conditions. This often occurs during planned stops at the mill. Before the evaporation plant is stopped it is also common to wash the effects and therefore the scales may be altered before a visual inspection. It is important to note that the thickness is often not uniform along the surface. Variations occur where for example in a lamella evaporator the scales are thicker on the welding points [19].

Mills often do, instead of measuring the thickness of scales during stops, measure the change in temperature between the condensing vapor and the temperature of the out going black liquor, noted dT. dT can change short term and long term. A short term change in dT is often associated with brukeite or sodium carbonate scaling where insoluble scales, such as calcium carbonate, $CaCO_3$, scaling, is often associated with long term changes of dT. Though, measuring $CaCO_3$ scaling via long term changes of dT in not always achievable due to the fact that it is not only insoluble scales that can affect the dT to change long term. It was found in a study that soluble scales occur far below their solubility limits. This happen because the lignin, soap, fiber or other lumps of material can attach to the surface causing disruption in the fluid flow. The sodium salts can then start to precipitate when the fluid passes around the lump, creating more turbulence. When the crystallization starts to grow it can in some cases clog the space between two lamellae or the tube. Weak liquor, or even water, has a hard time removing this types of scales since their flow is altered as well [19].

2.5.1 Aluminium silicate scaling

The aluminium silicate scales is described as hard and glass-like, making them hard to remove. Even just a thin layer of these scales affect the heating surface. They are to be found in effect 1 or the final concentrators most frequently. Due to the low content of these elements in the black liquor, they grow very slow and the concentration of the aluminium regulate the scaling rate. They can be avoided by elusive the accumulation of the non-process elements [8].

2.5.2 Calcium scaling

The calcium originates from the causticizing part of the mill where it is used to prepare the white liquor. The calcium can, in the evaporation plant, bind to the organic compounds such as lignin complexes, oxalate or soap which makes calcium scaling sensitive to temperature. The calcium ion becomes free when the temperature reaches 90-130 °C, making it possible to form $CaCO_3$ and precipitate on the heat transfer area. To remove calcium scaling, acid washing or hydroblasting is often needed. To achieve a low content of calcium in the black liquor is efficient filtering of the white liquor necessary [11]. When a mill has problem with calcium scaling it is almost always calcium carbonate that is meant. Scaling problems with calcium silicate and calcium oxalate are relatively minor problems [10].

Methods of measuring intensity of $CaCO_3$ scaling in an effect is for example analysing how much dissolved calcium a sample of black liquor contains. This is possible since dissolved calcium is specific for precipitation of calcium carbonate. If a sample has a high content of dissolved calcium it can be assumed that calcium carbonate scaling also is intense. However, it is important to note that dissolved calcium does not equal calcium carbonate scaling due to the fact that a large part of calcium is dissolved as particles and does not precipitate and stick to the heat surface area [19]. There is four parameters that control the calcium carbonate scaling, these are calcium concentration, carbonate concentration, pH and temperature [10].

2.5.3 Sodium scaling

Due to the fact that sodium is a fundamental part of the kraft process makes it impossible to reduce the content in the black liquor. The precipitation of sodium carbonate and sodium sulfate appear when the concentration of black liquor exceed the critical concentration which was mentioned earlier. This is most commonly found in black liquor thickener where the solubility limit is far above their solubility. The concentration of these salts are high in black liquor which is why scaling can occur fast. The rapid formation of sodium scales can make the evaporator loose its capacity within hours. The sodium carbonate and sodium sulfate can be removed by being washed with weak liquor or vapor condensate. The design of the black liquor thickener is important to mitigate scaling. Designing is to ensure sufficient wetting is one thing. It is also important to have stable operation conditions. Avoiding fluctuations reduces the risk of to put the plant in an unstable state which can result in severe scaling. By recirculating the liquor, and hence get more bulk crystals can too mitigate scaling [11].

It is more benign in a mill to favor the crystallization of burkeite over the crystallization of dicarbonate. This can be done by increasing the concentration of sulphate compared to the concentration of carbonate. It is complicated though to minimize the carbon content. This can be done with improving the causticzing plant. The problem is that the causticzing is an equilibrium reaction determined by the total strength of the liquor, hence not all of the carbonate can be removed [11].

2.6 Cleaning process

If scaling is a fact in an effect, then cleaning and washing is vital for it to not loose all its capacity. Insoluble scales, e.g calcium carbonate, can not be washed away with just water to be removed while soluble scales, e.g burkeite, can be. To remove insoluble scales acid wash or high pressure water cleaning is often needed. High pressure water cleaning is also often called hydro blasting [12]. Soluble scales on the other hand, is relatively easily removed with water. A so called “boil-out” method is common were fresh water, condensate or weak black liquor is used to clean the surface area [3]. The black liquor stream is bypassed when the effect is being cleaned. The outflow is either going to a mix liquor tank or collected in a separate wash liquor tank and the wash liquor can enter the unit. Primary steam can still be supplied since it is favourable to maintain the vapour flow to minimize disturbances in the plant. The primary steam can then be changed and the effects that does not undergo a wash cycle can be feed a higher distribution [11]. A wash cycle is most preferably performed with condensate, and can go on for everything between 1 hour up to 12 hours or more, depending on the conditions of the pulp mill since a wash cycle reduces the temporary capacity. A boil-out method is highly effective and the wash liquid is being recirculated via the recirculation pump, this continues for as long as possible [15].

3

Methods

The general approach for this project has been analytical and could be divided in three main parts. At the start of this thesis a literature study was conducted. This was done in order to gain enough knowledge about operation, crystallization and fouling in evaporators. Frequent dialogues and interviews were held with the operators and staff at Stora Enso Skutskär. The main intention with those interviews was to see how the problem with fouling was experienced at the mill.

The second part was when the process data was being collected and a deeper investigation was conducted to see what kind of data was available at the mill. The process data was examined to see what information was measured with a sensor and what was calculated based on that information.

After this the third and final part of the thesis could take place. The process data was analysed in MATLAB. The main purpose of this analysis was to distinguish what problems exist today and in what part of the plant are these problems the most prominent? Furthermore, the analysis quantifies how reliable the measurements are and see if there is any success with the washes.

3.1 Literature study

In the first phase the literature study was conducted to gain enough knowledge to get a solid foundation for the upcoming project. The references and sources were collected from course material, articles and knowledge from researchers at Chalmers with experience in this subject. Dialogues were held with staff at Skutskär to get a deeper understanding of their view of the problem on site and to understand how the evaporation train was operated. The different key words that were used to search for the sources included topics such as falling film evaporators, evaporator cleaning, fouling, scaling, crystallization, sodium carbonate, sodium sulphate and calcium carbonate.

3.2 Collection of data

During the dialogues with the operators it was concluded that there was currently no scaling occurring and causing problems in the effects since September 2021. Effect 3C had been cleaned very thoroughly during the stop at the mill in September 2021 and large pieces of scaling had been washed off. It was then that the decision was made to only analyse process data before and after the stop and not to try out direct tests on the site. The process data was collected from both the program WinMops and ABB control system. At first process data was only collected from effect 3C and 2C for 10 months back in time, between may 2021 and mars 2022. The data was taken in 8 minute intervals and the parameters that were gathered were

- BPE in °C
- Temperature of the outgoing black liquor in °C
- Temperature of the outgoing condensed steam in °C
- DS into the effect in %
- DS outgoing of the effect in %
- Black liquor flow going into the effect in m^3/h

It was established that more data was needed for the analysis to be more extensive and meaningful. Process data was once again collected, this time from effect 3C and 2C between April 2020 and April 2021 with values every 30 minutes. The data from effect 1C was gathered between April 2020 and April 2022 with values every 30 minutes. Finally data from the black liquor thickener was taken between April 2020 to April 2022 with values every hour. The parameters that were compiled were the same as the ones mentioned above. The values taken every hour were found to not be enough and they were again collected from the black liquor thickener every 10 minutes between the same days as previously mentioned.

3.3 Calculations and MATLAB script

From the collected data, dT was calculated according to

$$dT = T_{condensed\ steam,\ out} - T_{blackliquor\ flow,\ out} \tag{3.1}$$

To calculate the U-value, the rate of heat transfer, Q, must be known. Q was estimated via a mass balance since there was a lack condensate and DS measurements. The black liquor flow out of the effect and the evaporated water also needed to be calculated. The density was calculated with equation 2.5. The black liquor mass flow could be calculated with the black liquor flow. This was one of the values that was gathered and measured times the now known density of the black liquor, according to

$$\dot{m}_{BL} = \frac{q_{BL} * \rho_{in}}{3600} \tag{3.2}$$

The water evaporated from the effect is the amount of water that comes in with the black liquor differentiated with the amount of water leaving with the black liquor, which now can be calculated. Q was determined with the enthalpy of vaporization times the water evaporated. Finally, U could be determined according to equation 2.1. This calculation can be seen more extensively in Appendix 2.

To see changes in the process data over time and in that way be able to evaluate the washes and how the plant operates in general, a MATLAB script was used.

MATLAB was considered to be a tool for displaying large amounts of data, making it easier to visualize. The script that was run in MATLAB was provided by the project supervisor, Anders Åkesjö.

3.4 Analysis

The collected data was processed with the MATLAB script and the plots were then evaluated. The first evaluation was from a broader point of view where the main purpose was to identify trends over a longer period of time. Then the analysis became more focused from a time perspective in order to see changes day by day. Efforts were made to see how much time passed between washes, how long it took for dT to rise again after a wash to a value that indicated that scaling had started to build up again, and if this duration was affected by the duration of the wash. The values were also compared to how normal values are described in the literature. Here it was discovered, among other things, that the DS value was off. The data was also analysed for all effects and for the black liquor thickener in the same manner that was used previously.

4

Results and discussion

This section of the report presents the findings from the analysis. The plots shown in this section, views the change in time for the following parameters

- BPE in °C
- dT in °C
- Temperature of the outgoing black liquor in °C
- The DS into the effect in %
- The DS outgoing of the effect in %

The temperature was there as a reference, or base line, to ensure that there were stable operating conditions. The washing cycles were identified by the change in BPE, dT and the DS. A wash could be assumed to happen when these parameters went down to close to zero or deviated together simultaneously.

4.1 3C

The inlet DS for effect 3C is, as viewed earlier in figure 1.1, desired to be at 30 % and the outlet at 35 %. The inlet is measured, and the outlet is calculated from the BPE. The change from the time period between April 2020 until Mars 2022 could be viewed in figure 4.1 as well as in figure 4.2. The difference between the figures is that BPE an DS_{out} is removed from figure 4.2 for an easier overview.

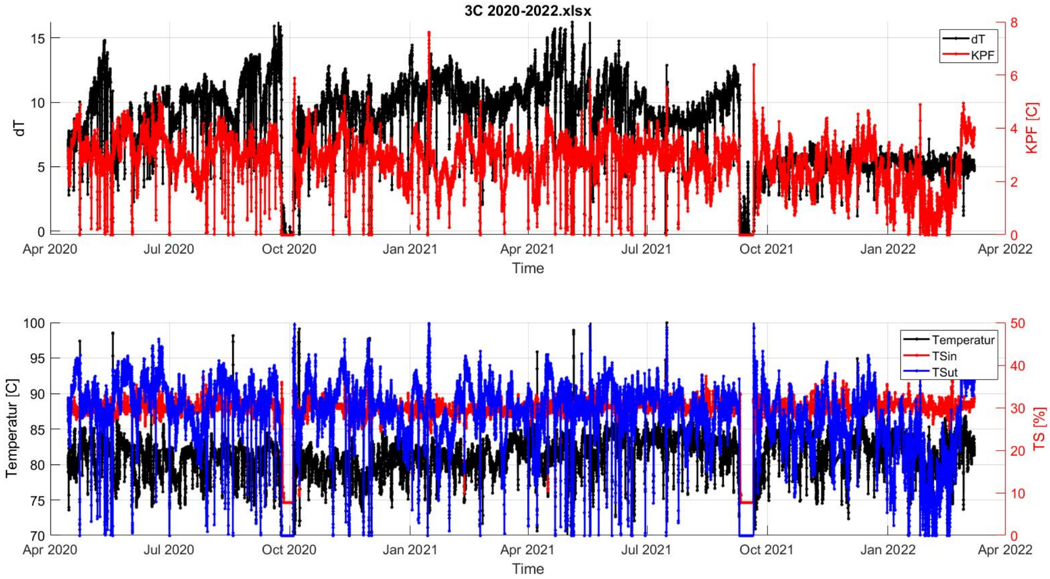


Figure 4.1: Overview of the change in time for the BPE, dT, temperature of the black liquor, DS_{in} and DS_{out} for effect 3C, between April 2020 to Mars 2022

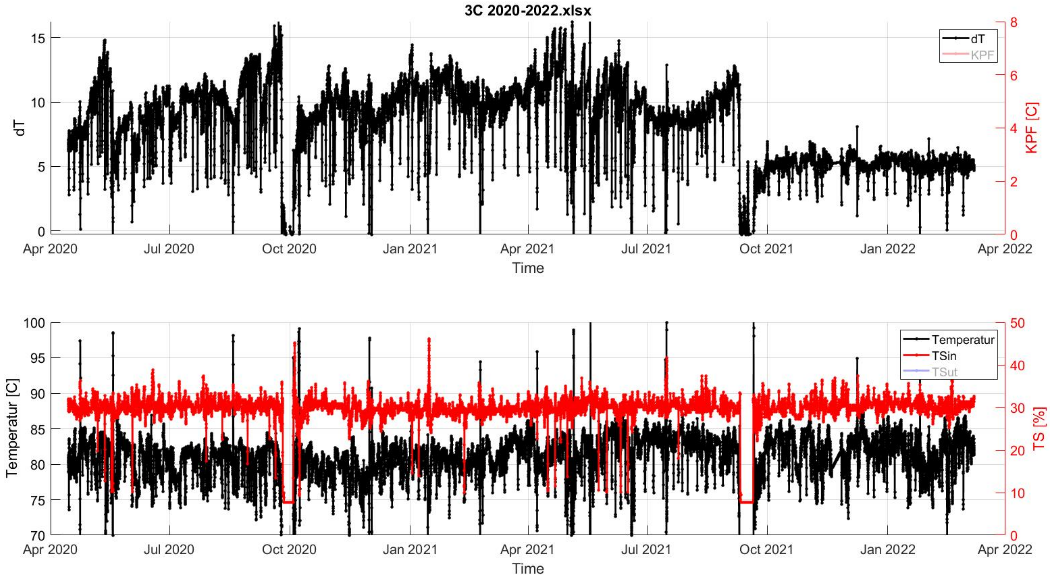


Figure 4.2: Overview of the change in time for the dT, temperature of the black liquor, DS_{in} for effect 3C, between April 2020 to Mars 2022

There was a stop at the mill in October 2020 as well as in September 2021, hence the deviating pattern at those times. First thing that can be noticed is the variation in dT, and especially the sharp decrease as well as how much more steady dT is after September 2021. dT varied greatly between 8 and 15 °C, and after the stop in 2021 it decreased with up to 10 degrees. This decline indicates clearly that the wash during the stop in September 2021 was highly effective. dT can also be observed as volatile during the time period before the stop. This shows that washes are effective in combating this. Comparing the two figures 4.1 and 4.2, it is clear that the DS_{out} (the blue line) is more erratic compared to DS_{in} (the red line). Stable operating conditions can be assumed most of the times due to how stable the temperature change is.

During the time period from April until December in 2020, the mill had 28 noticeable wash cycles, giving a mean value of 1.5 washes/two weeks. Taking into consideration a stop of 2 weeks during the Autumn and no washes are performed at least 1 week prior and after the stop, gives a mean value of almost 1 wash/week. From January until December 2021, the mill had 27 noticeable wash cycles, which gives a mean walue of 0.5 wash/week, with the same considerations as mentioned above. Lastly, 4 wash cycles could be distinguished between January til Mars 2022. A summary of all the washes from the year 2020, 2021 and 2022 can be viewed in the tables in Appendix 3. The tables exhibits the time and date for the wash cycles, the duration of a wash cycle, how much dT differed from before and after the wash cycle. It also exhibits between which degrees dT varies before it rapidly rises and how long it takes for dT to rise again.

The duration of a wash could be anything from 2 hours up to 13 hours, but normally a wash cycle is around 3 hours. The length of a cycle is difficult to regulate since it almost exclusively is controlled by the production rate in the mill. A washing cycle is often started when it is perceived as suitable to do so. And it is not always when it is the most needed. Sometimes a wash cycle is initiated in a preventative manner because it can not be done in the near future.

For effect 3C it turned out, which is also shown in the tables in Appendix 3, that almost all of the wash cycles started were necessary. Effect 3C usually decided if a wash needed to be initiated due to the often quickly rise in dT. dT is almost always over 11 degrees before a wash cycle is started, and it usually decreases with 2-3 degrees. Sometimes, e.g wash number 7 and number 20 in 2020, dT decreased with more than 5 degrees. This is a reduction of more than 49,2 % and 37,2 % respectively, which affects the heat transfer remarkably. While the reduction were noticeably lower sometimes, e.g wash number 16 in 2020. A correlation between the length of the wash and the effectiveness of the wash was hard to notice. Some of the most ineffective washes were 2,5-4,5 hours long while the most effective one was 4 hours. Furthermore, looking at wash 13 in year 2021 which was the longest one that year (12,5 hours), the long duration made no difference. In fact, dT almost increased afterwards. However, for most of the times the wash cycles seemed to have a big impact and it did indeed seem to help with the scaling problem. Figure 4.3 depicts how washes were detected, and in this specific time period 7 washes occurred.

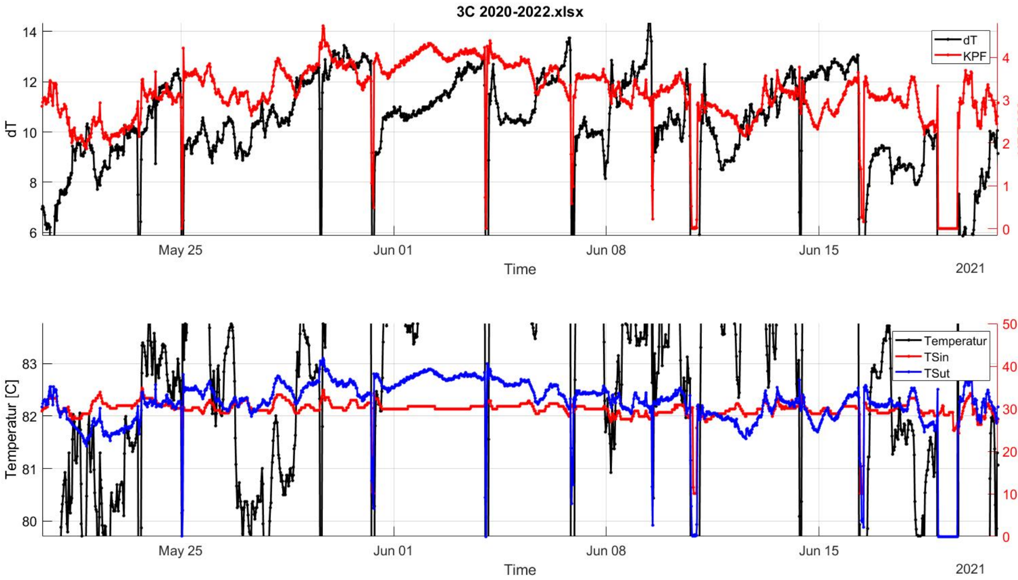


Figure 4.3: Example exhibiting 7 washes detected during the time period May/June 2021 for effect 3C

It is apparent that dT is reduced after a wash and also that dT quickly increases again. This is also prominent in the tables in Appendix 3. Scaling starts to build up after just a few days, meaning that the need for washing is apparent once again shortly after a wash cycle has ended. This is certainly not great for the mill since it causes stops in production and a decrease in production rate. dT is most often going from around 12-13 °C down to 8-9 °C when the effect is being cleaned. Considering this, the scaling seem to be able to solve with water. Though, after the stop in September 2021, dT decreased down to around 4-5 °C, implying that there was always some scaling that did not come off during the washes. These types of scales are most probably not water soluble, otherwise they would have come off at some point. Since sodium scaling happen almost exclusively in DS over 50 %, i.e from effect 1C and forward in the train, and are for the most part water soluble, makes that it is probably not sodium scaling. The type of scales that wont come off with water can probably originate from calcium scaling. If the scaling comes back and is as severe as it has been, it might be an idea to look over other parts of the mill, especially the caustizing part.

Another discovery that was made was the strange behaviour for the DS_{out} from effect 3C, which is also the inflow to effect 2C. The DS_{in} to effect 3C is a measured value, which originates from a calculation based on a refractometer. The DS_{out} is calculated from the BPE, thus a calculation based on the temperature. In general, a DS based on a refractometer is a more reliable option. The DS_{out} was quite often lower then the DS_{in}. This is viewed in two examples in figure 4.4 as well as in figure 4.5.

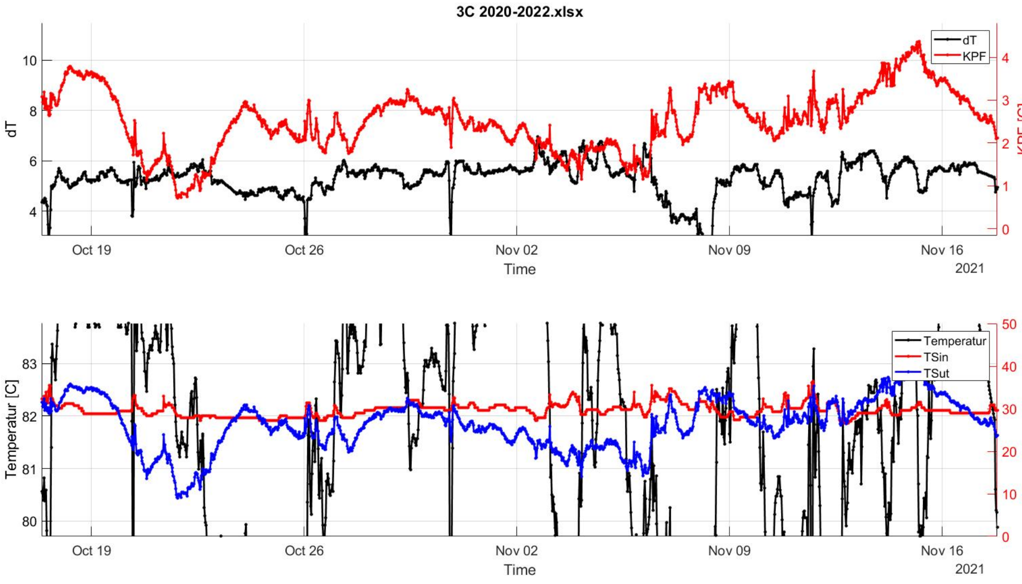


Figure 4.4: Example of when the DS$_{out}$ was lower than DS$_{in}$, deviating from a normal curve during the time period October/November 2021

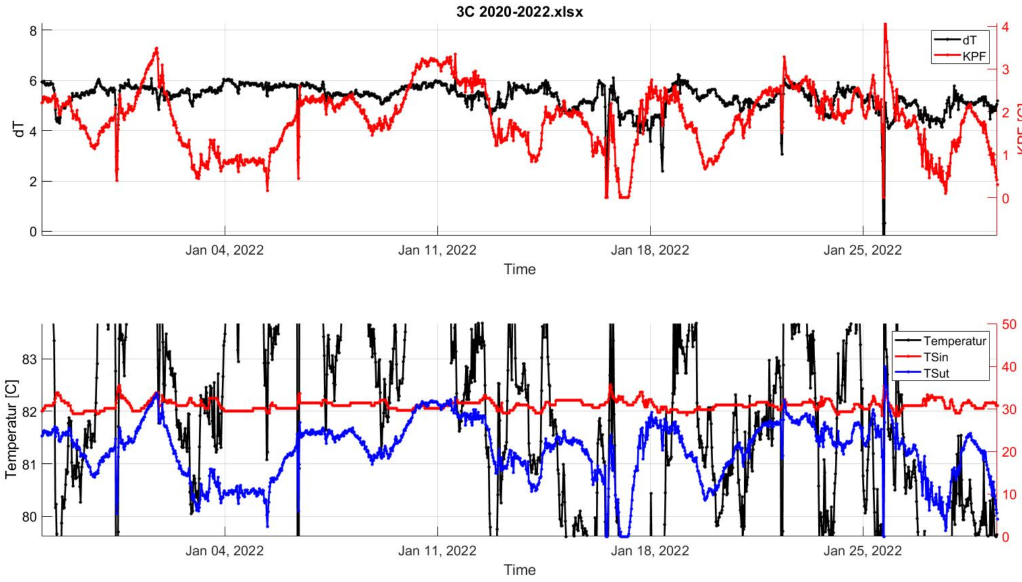


Figure 4.5: Example 2 of when the DS$_{out}$ was lower than DS$_{in}$, deviating from a normal curve during the time period January 2021

That the DS$_{out}$ is lower than DS$_{in}$ is surely not the case, but it could be an indication that one or some of the sensors are not calibrated correctly or that they deviate for some other reason, thereby giving an incorrect value. It can also make it difficult to follow up certain time periods since the BPE also takes irrational paths. It may also be an indication that scaling may have occurred on some sensors, making them show nonsensical values. If this has happened on some sensors, this opens up the possibility to believe that it also can be the case for some unusual high dT values that occur sporadically. Meaning that the scaling may be bad, but not as severe as it might show up in dT. A proposal to this problem could be that whenever the DS outflow decreases without any other explanation, take a laboratory sample to see how far away the DS content is in the sample compared to the calculated value.

4.2 2C

The DS$_{in}$ for effect 2C is desired to be at 35 % and 42 % out, as viewed earlier in figure 1.1. Here both the inflow and outflow are calculated from the BPE, and DS$_{in}$ for effect 2C is the same as the DS$_{out}$ for effect 3C. Meaning that, as mentioned above, DS$_{in}$ is behaving strange from time to time. An overview for effect 2C can be seen in figure 4.6, and for an easier examination of dT, in figure 4.7 without BPE and DS$_{in}$.

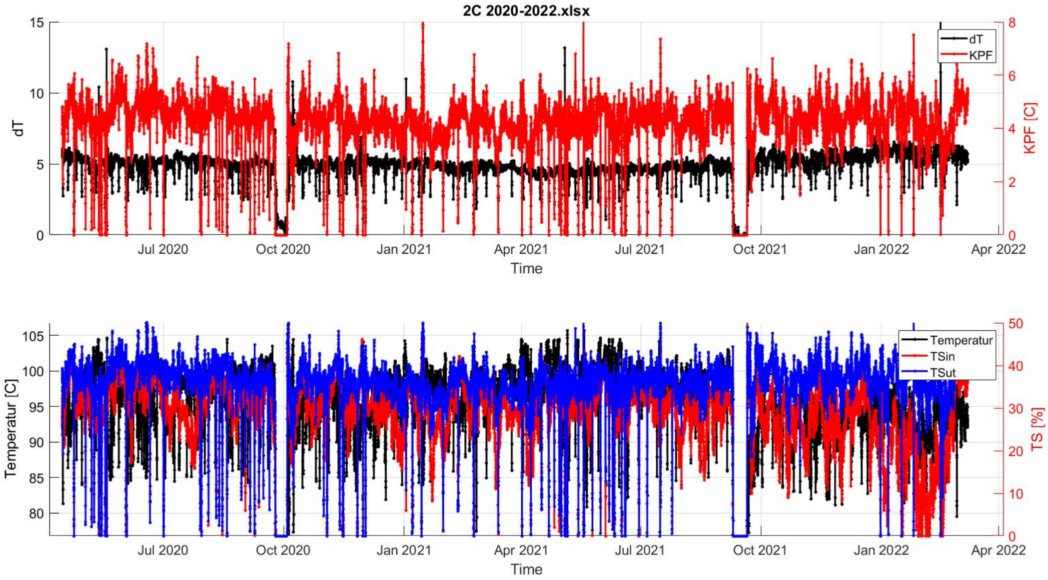


Figure 4.6: Overview of the change in time for the BPE, dT, temperature of the black liquor, DS$_{in}$ and DS$_{out}$ for effect 2C, between April 2020 to Mars 2022

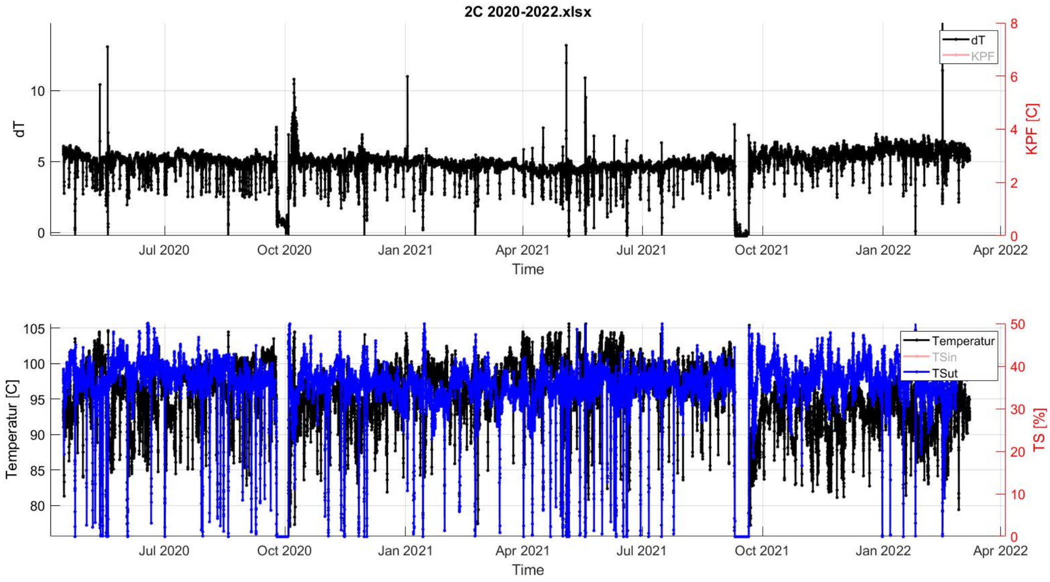


Figure 4.7: Overview of the change in time for the dT, temperature of the black liquor and DS$_{out}$ for effect 2C, between April 2020 to Mars 2022

Comparing effect 2C with 3C it is clear that dT is much more stable, and lower with up to 10 degrees sometimes. Theoretically it should be the other way around. During the analysis, 28 wash cycles were detected in 2020, 27 cycles were detected in 2021 and 4 in 2022, same time period as earlier. This is the same amount of washes as for 3C, which is expected since when a wash cycle is started for one of the three effects (1C, 2C, 3C), the other effects are included in that wash cycle as well. There is no way to bypass the black liquor around one single effect. The summary of all the washes for effect 2C is shown in the tables in appendix 4. The difference in these tables, compared to the ones for effect 3C, is that these do not have the last two columns, since it was not considered to be necessary. dT did not once seem to increase rapidly during this analysis. Instead it was steady around 4-6 °C. The washes did not affect dT noticeably. This is also viewed in figure 4.8 down below.

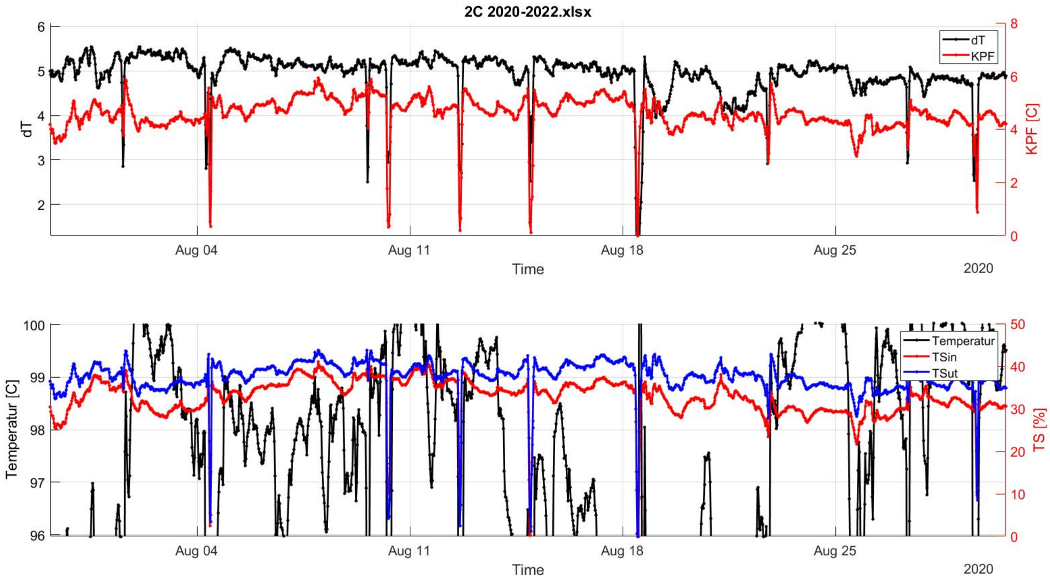


Figure 4.8: Example exhibiting 6 washes detected during the time period August 2020 for effect 2C

It is prominent when comparing figure 4.3 to figure 4.8 that dT for effect 2C did not increase prior to, nor decrease after a wash cycle. One can then argue that the washes were redundant for 2C since dT was not affected. However, just because it does not make a difference, it can still be preventative to wash, but maybe not that frequent since due to the low DS in effect 2C, fouling is not a big concern. If there was a possibility to bypass the black liquor when 3C undergoes a wash cycle, this would make the efficiency of the entire evaporation plant higher. It conveys the impression to be a capacity loss since 2C seems to not always have a need for cleaning.

It is also the same here as for 3C, that the DS inflow is acting out sometimes, which makes follow up a bit more difficult. It is interesting however that the outflow for effect 2C, which also is a calculated value on the same was as the inflow, seems to be much more reliable. This indicates once again that there might be something deviating with one of the sensors for that calculation.

4.3 1C

The DS$_{in}$ for effect 1C is desired to be at 42 % and 54 % out, as viewed earlier in figure 1.1. Here is the inflow calculated from the BPE, and DS$_{in}$ for effect 1C is the same as the DS$_{out}$ for effect 2C. DS$_{out}$ from effect 1C is a calculation based on a refractometer. An overview of the change over time for effect 1C is shown down below in figure 4.9 and without the BPE curve and the DS$_{in}$ curve in figure 4.10.

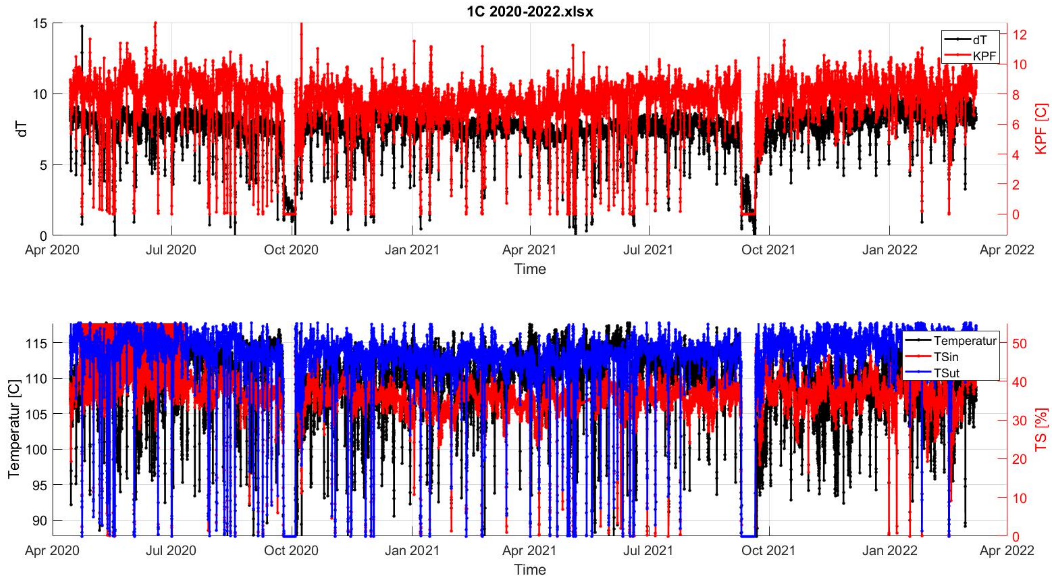


Figure 4.9: Overview of the change in time for the BPE, dT, temperature of the black liquor, DS_{in} and DS_{out} for effect 1C, between April 2020 to Mars 2022

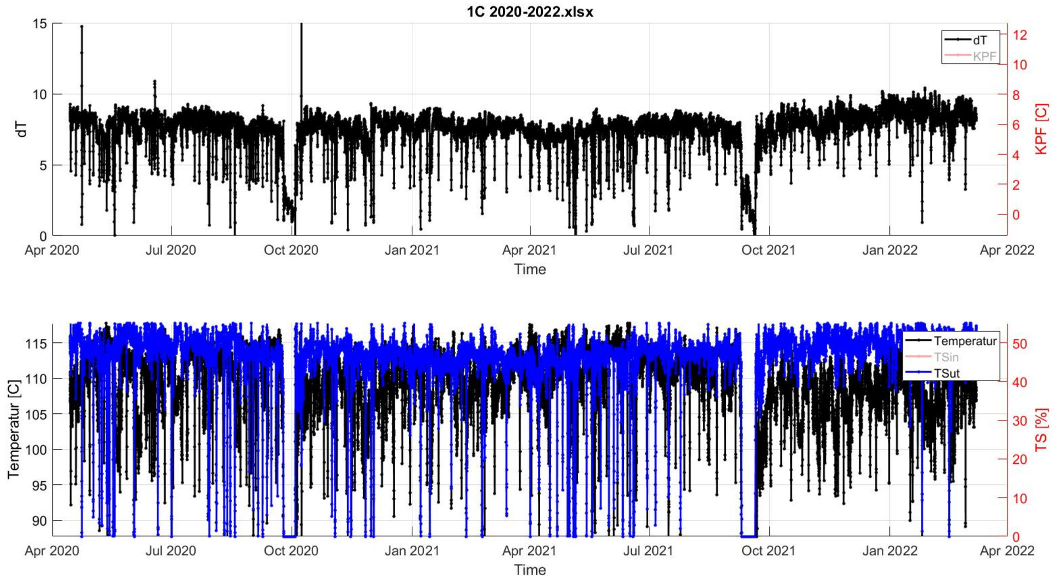


Figure 4.10: Overview of the change in time for the dT, temperature of the black liquor and DS_{out} for effect 1C, between April 2020 to Mars 2022

Just as for effect 2C, dT is very stable even though the DS is now around the critical concentration and that there is a risk for sodium to start to precipitate. There was 22 detected washes 2020, 20 washes in 2021 and 4 in 2022 for 1C, as displayed in the tables in appendix 4. The reason that there seems to be less wash cycles for 1C compared to 2C and 3C even though the amount of washes should be exactly the same there were no significant difference between before and after, and the DS did not always follow which may cause this confusion. It was for the most part noticeable when a wash occurred when the BPE deviated from its pattern. dT did not differ from before and after wash cycle for most of the time, indicating that most often they were unnecessary for 1C. However, similar to 2C, just because a wash seemed to not make a difference does not mean it can not work as preventative measure. A minority of the washes, e.g wash 23 in 2020, showed that the wash was effective and reduced dT. Yet, the majority of the time it looks like dT increases after a wash cycle rather than decreases. This can be viewed in figure 4.11.

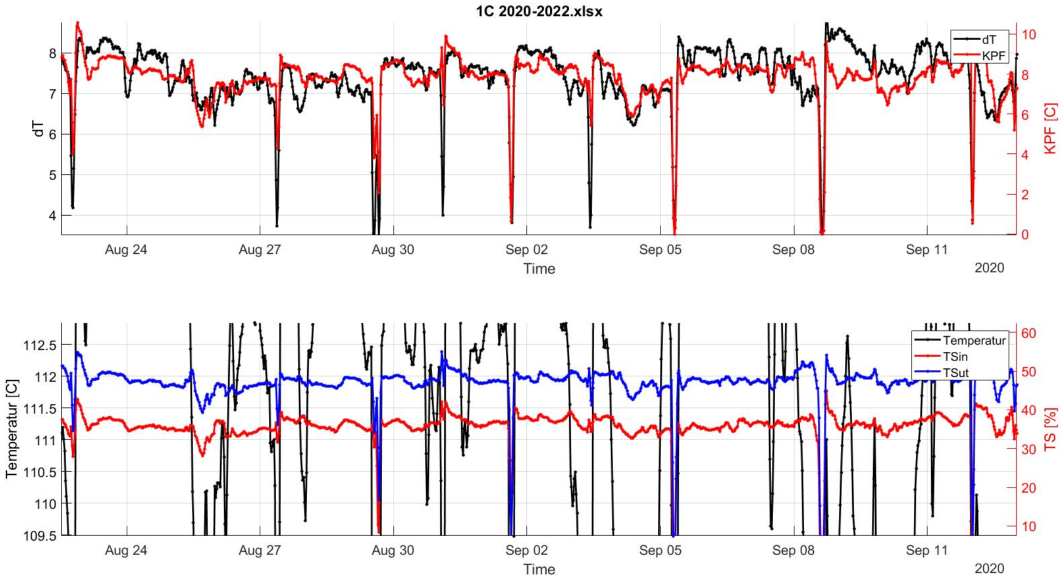


Figure 4.11: Example of how dT is affected prior and after wash cycles for effect 1C during August 2020

4.4 Black liquor thickener

The analysis of the black liquor thickener, which consists of 3 compartments, started with side A. The overview for side A can be seen in figure 4.12.

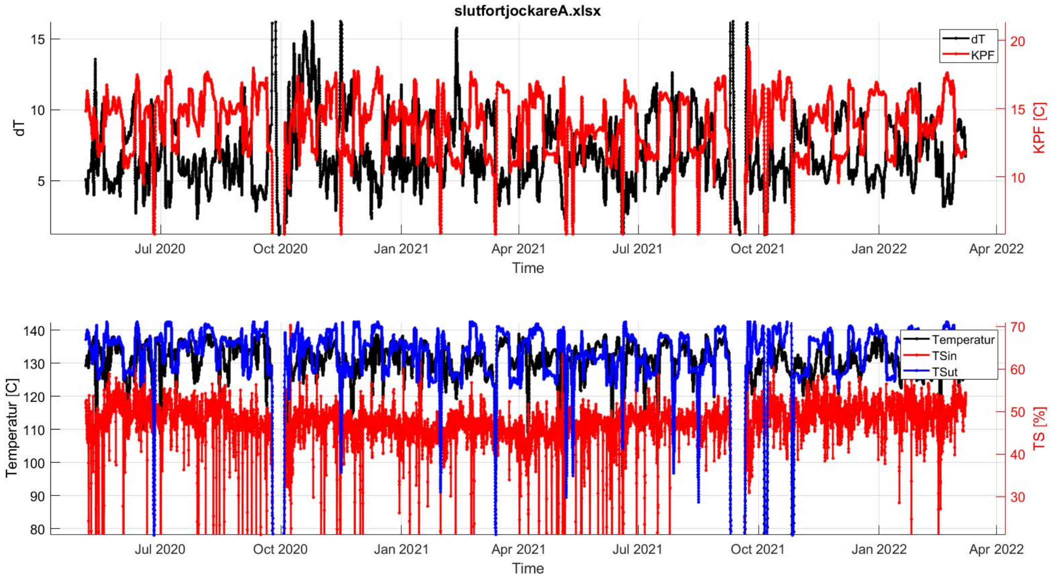


Figure 4.12: Overview for the black liquor thickener, side A

At first sight it stands out that the curves are different from previous curves for the other effects. Comparing to the effects analysed before where data was collected either each 8 minutes or each 30 minutes, to the black liquor thickener it is clear that it looks more interpolated. From figure 4.12 can it be seen that there is 11 noticeable wash cycles under the two years studied. After dialogues with the operators at Skutskär, it was discovered that the black liquor thickener undergoes a wash cycle around every 10 to 14 days [15]. After analysis of the curves for the black liquor thickener, shown in figure 4.13, no real correlations can be seen. It looks as if the values are every whole day at 00:00 o clock. This can be seen even more clearly in 4.14. It is probably due to this that a lot of the wash cycles passes through unnoticed. Since the black liquor thickener operates at a DS over 50 % makes it inevitable to avoid scaling. However, there does not seem to be a major problem with scaling here and the routine the mill has of the wash cycle for the black liquor thickener seems to be well adapted.

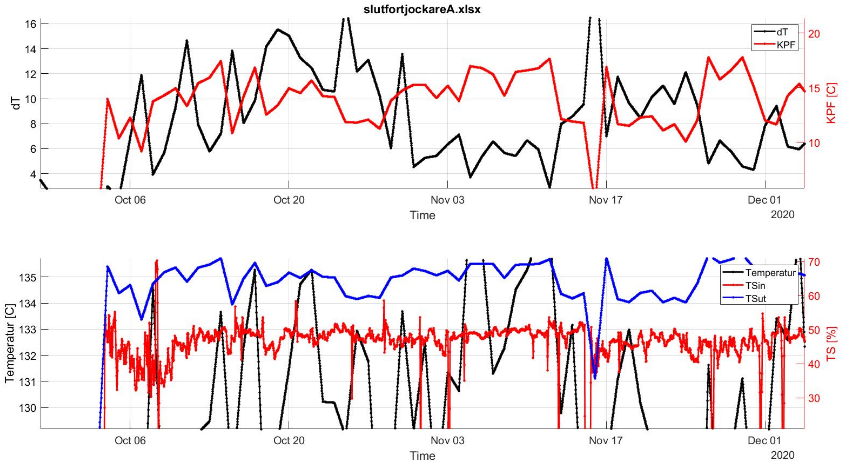


Figure 4.13: Black liquor thickener from October to December 2020

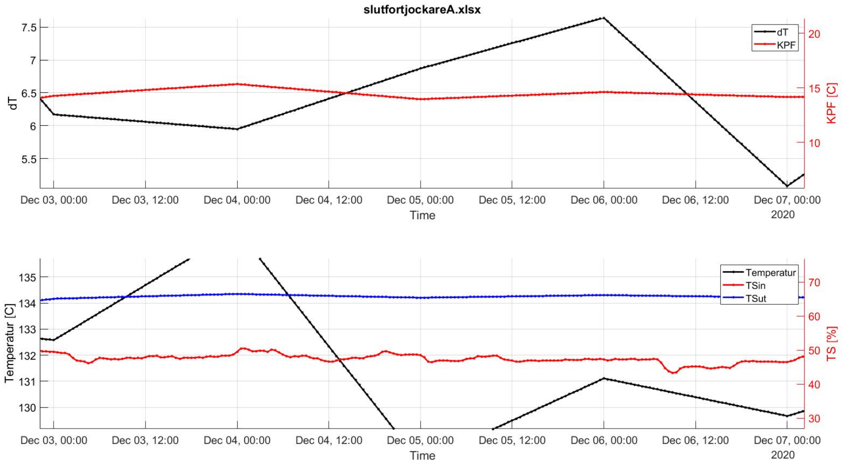


Figure 4.14: Black liquor thickener from the 3rd of December to the 7th of December 2020

5

Conclusion

In this thesis, an analysis of the washing sequences have been conducted. What could be observed from the analysis is that the effects has been washed often, but at the same time the data has indicated that the it was necessary and the washes were effective and made the effects cleaner. A wash sequence lasted anywhere from between 2 hours up to 13 hours, and would occasionally last longer than that. There was, however, difficulties in observing a correlation between the length of the wash versus how effective it turned out to be. The most effective ones were around 4 hours, but on the other hand, that was the length of some of the most ineffective ones as well.

The washes were indeed effective for effect 3C, where they managed to decrease dT significantly almost every time. 1C and 2C also had to be washed just as frequently even though they were not in need of it. Important to note is that even though dT did not decrease for 2C and 1C, hence making it look like an ineffective wash cycle, it does not mean it was not preventative. It is essential to maintain the effects and prevent scaling to start to precipitate. Though there could be an idea in order to reduce production losses, if there was a way to bypass 3C.

During the time period when 3C experienced the most severe scaling problem, dT could decrease by almost 50 % after a wash cycle. There appeared to be a limit for how low dT could go after a wash cycle, it never went below 8 °C. After the stop in September 2021 when 3C was cleaned thoroughly, dT was down at 5 °C. This implies that there is some scaling that was not water soluble, hence why it was hard to get rid of with just a normal wash cycle. This type of fouling is most likely calcium scaling, and to get rid of these non water soluble scales hydro blasting is needed.

It seems that some sensors are showing nonsensical values, making the DS outflow of 3C and inflow to 2C, which is based on the BPE, deviate from the normal curve. This could open up the probability to believe that it also can be the case for some unusual high dT values that occur sporadically. Meaning that the scaling may be bad, but not as severe as it might show up in dT. A proposal to this problem could be that whenever the DS outflow decreases without any other explanation, take a laboratory sample to see how far away the DS content is in the sample compared to the calculated value.

Bibliography

[1] Adams TN, Frederick WJ, Grace TM, Hupa M, Iisa K, Jones AK, Tran H, Boilers KR. Tappi press. Atlanta, GA. 1997. URL: http://www.tappi.org/content/pdf/bookstore/0102b064.pdf. ISBN: 0-9625985-9-3.

[2] Aresta M, Dibenedetto A, Dumeignil F, editors. Biorefineries: an introduction. De Gruyter; 2015. Retrieved from https://app.knovel.com/hotlink/toc/id:kpBAI00005/biorefineries-an-introduction/biorefineries-an-introduction Chapter 11.2.3

[3] Clay DT. Evaporator fouling. Jacobs Engineering Group Inc. 2008.

[4] Ek M, Gellerstedt G, Henriksson G, editors. Wood chemistry and biotechnology. Walter de Gruyter; 2009.

[5] Ek M, Gellerstedt G, Henriksson G. Ljungberg Textbook: Pulp and Paper Chemistry and Technology. De Gruyter Open; 2007. ISBN: 978-3-11-021340-9

[6] Ek M, Gellerstedt, G, Henriksson, G. Pulp and Paper Chemistry and Technology - Pulping Chemistry and Technology, Volume 2. De Gruyter; 2009 Retrieved from https://app.knovel.com/hotlink/toc/id:kpPPCTPC03/pulp-paper-chemistry/pulp-paper-chemistry

[7] Gourdon M. Sodium salt scaling in black liquor evaporators. Chalmers University of Technology; 2009.

[8] Gullichsen, J and Fogelholm, C. Chemical pulping. Book 6. Helsinki [etc.]: Fapet Oy [etc.]. 1999. ISBN: 952-5216-06-3.

[9] Johansson M. Heat transfer and hydrodynamics in falling film evaporation of black liquor. Chalmers University of Technology; 2008.

[10] Karlholm I, Ziesig R, Samuelsson Å, Wadsborn R. Solubility of calcium during kraft cooking - Mill sampling campaigns and mass balance calculations; 2011 April

[11] Karlsson, E. The formation and dissolution of sodium salt scales in black liquor evaporators. Chalmers University of Technology (Sweden); 2017. URL: http://publications.lib.chalmers.se/records/fulltext/248068/248068.pdf

[12] Konopa JP. Multiple effect evaporator throughput extension with unique chemistry. InTAPPI PULPING CONFERENCE 1997 (pp. 1041-1044). TAPPI PRESS.

[13] Mersmann A, editor. Crystallization technology handbook. CRC press; 2001 May 8. ISBN: 0824705289

[14] Mullin, J.W., Crystallization, 4th ed., Butterworth-Heinemann, Oxford; 2001 May 9.

[15] Operatör vid Stora Enso. 2022. Intervju 1 mars.

[16] Schmidl W, Frederick WJ. Current trends in evaporator fouling; March 1998. Related ISBNs: 9780128034118. 9780128034286.

[17] Shi B. Crystallization of solutes that lead to scale formation in black liquor evaporation. Georgia Institute of Technology; 2002.

[18] Skogsindustrierna. Statistik om skog och industri [Internet]. Stockholm; 2020. [cited 2022 Jan 25] Available from: https://www.skogsindustrierna.se/om-skogsindustrin/branschstatistik/

[19] Ulmgren P, Samuelsson Å, Sirén K. Status report for project: Behaviour of NPES under technical conditions - Subproject $CaCO_3$ scaling; 2013 December.

A

Appendix 1

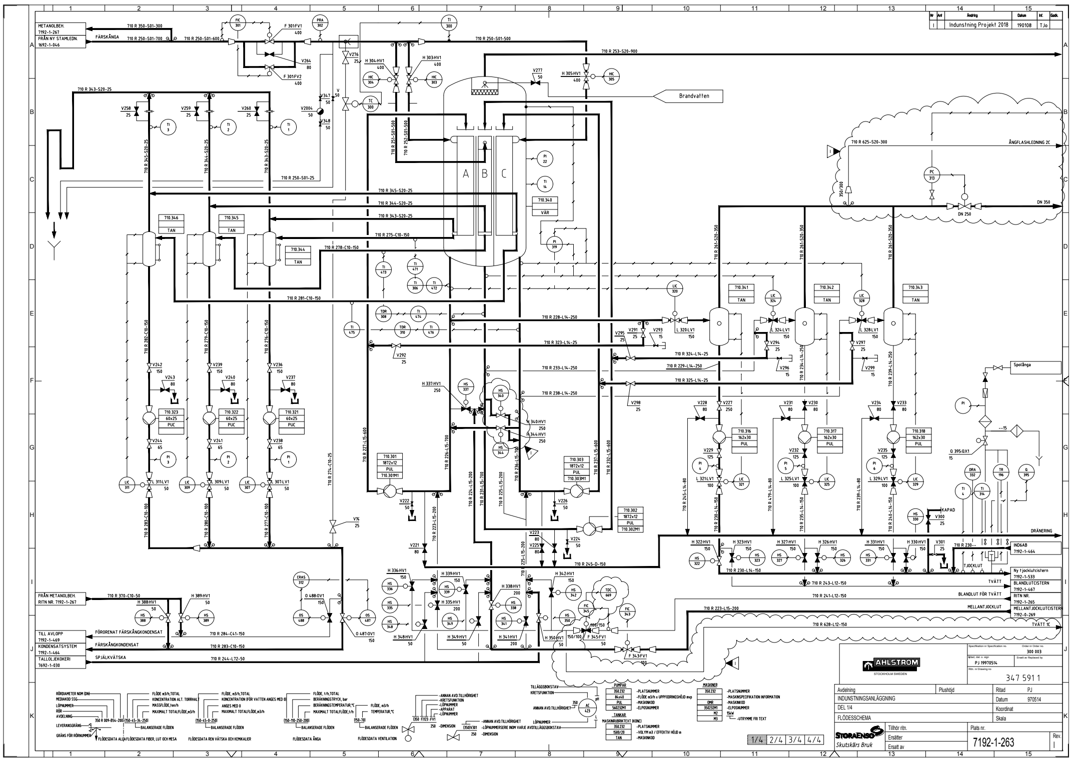


Figure A.1: Flow chart of Skutskär evaporation plant pt.1

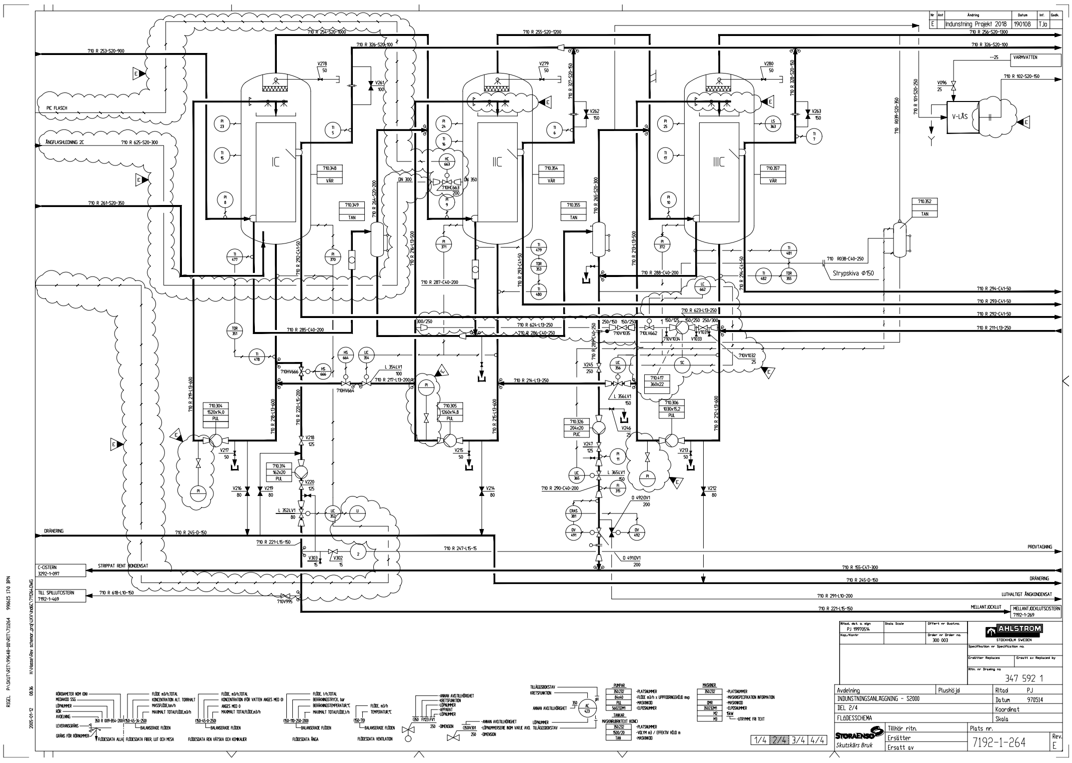


Figure A.2: Flow chart of Skutskär evaporation plant pt.2

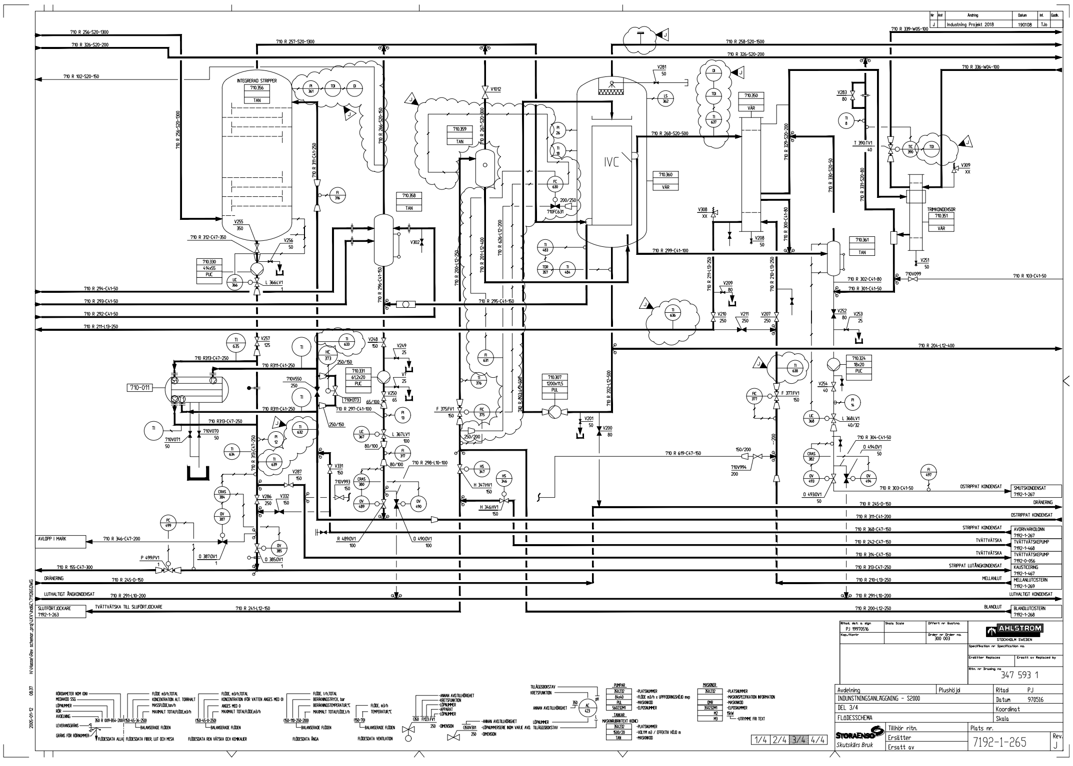
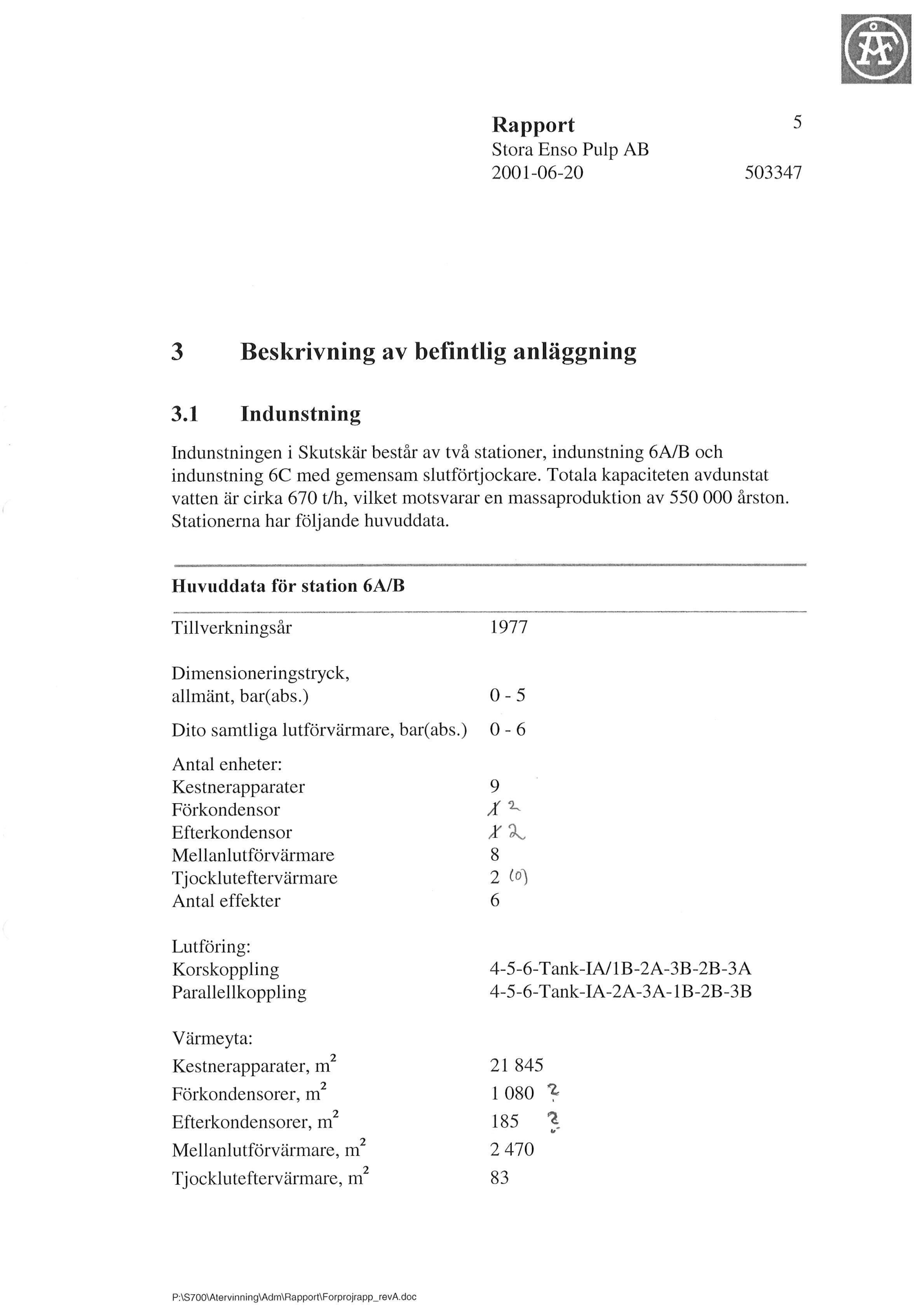


Figure A.3: Flow chart of Skutskär evaporation plant pt.3



Rapport 5
Stora Enso Pulp AB
2001-06-20 503347

3 Beskrivning av befintlig anläggning

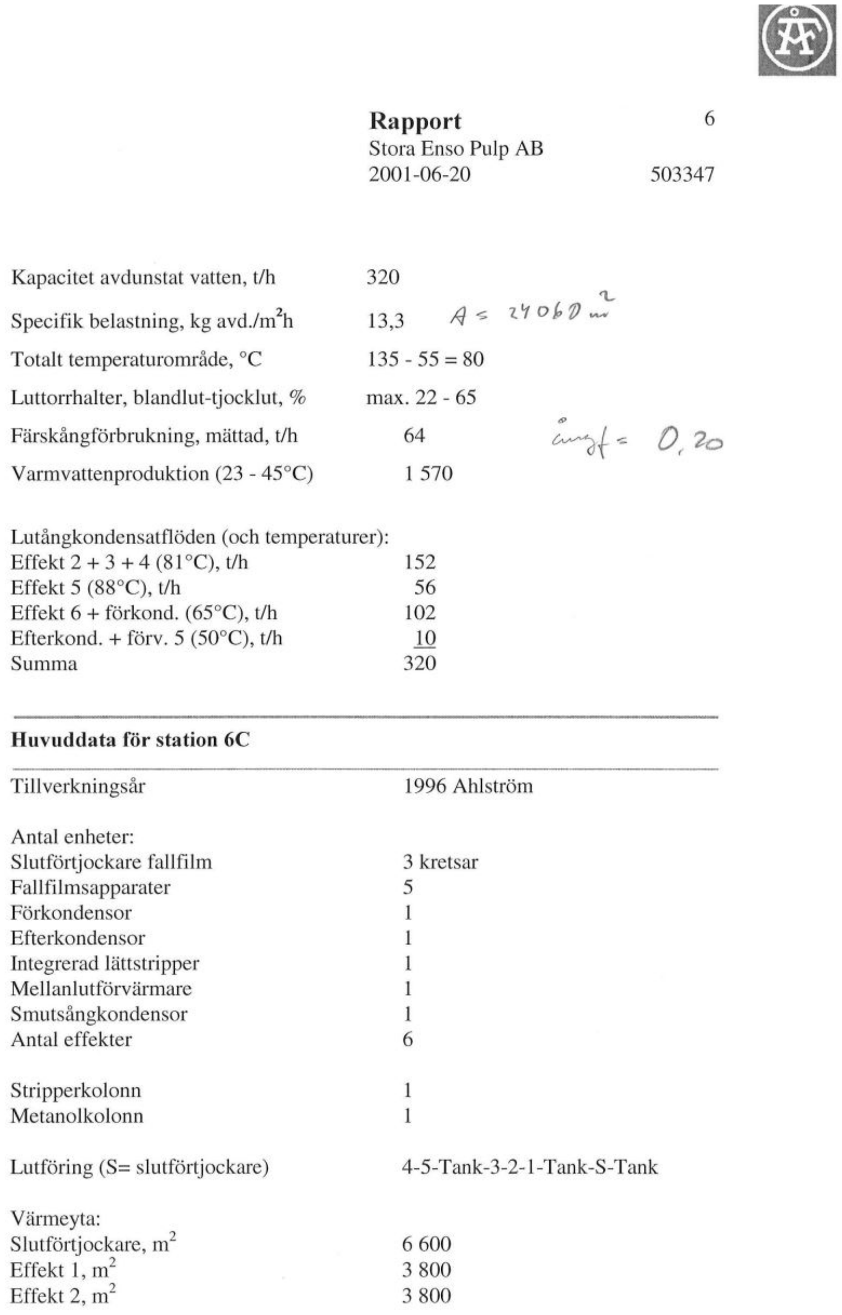
3.1 Indunstning

Indunstningen i Skutskär består av två stationer, indunstning 6A/B och indunstning 6C med gemensam slutförtjockare. Totala kapaciteten avdunstat vatten är cirka 670 t/h, vilket motsvarar en massaproduktion av 550 000 årston. Stationerna har följande huvuddata.

Huvuddata för station 6A/B	
Tillverkningsår	1977
Dimensioneringstryck, allmänt, bar(abs.)	0 - 5
Dito samtliga lutförvärmare, bar(abs.)	0 - 6
Antal enheter:	
Kestnerapparater	9
Förkondensor	~~1~~ 2
Efterkondensor	~~1~~ 2
Mellanlutförvärmare	8
Tjockluteftervärmare	2 (0)
Antal effekter	6
Lutföring:	
Korskoppling	4-5-6-Tank-IA/1B-2A-3B-2B-3A
Parallellkoppling	4-5-6-Tank-IA-2A-3A-1B-2B-3B
Värmeyta:	
Kestnerapparater, m^2	21 845
Förkondensorer, m^2	1 080 ?
Efterkondensorer, m^2	185 ?
Mellanlutförvärmare, m^2	2 470
Tjocklutefterværmare, m^2	83

P:\S700\Atervinning\Adm\Rapport\Forprojrapp_revA.doc

Figure A.4: Summary report for Skutskär evaporation plant pt.1



Rapport 6
Stora Enso Pulp AB
2001-06-20 503347

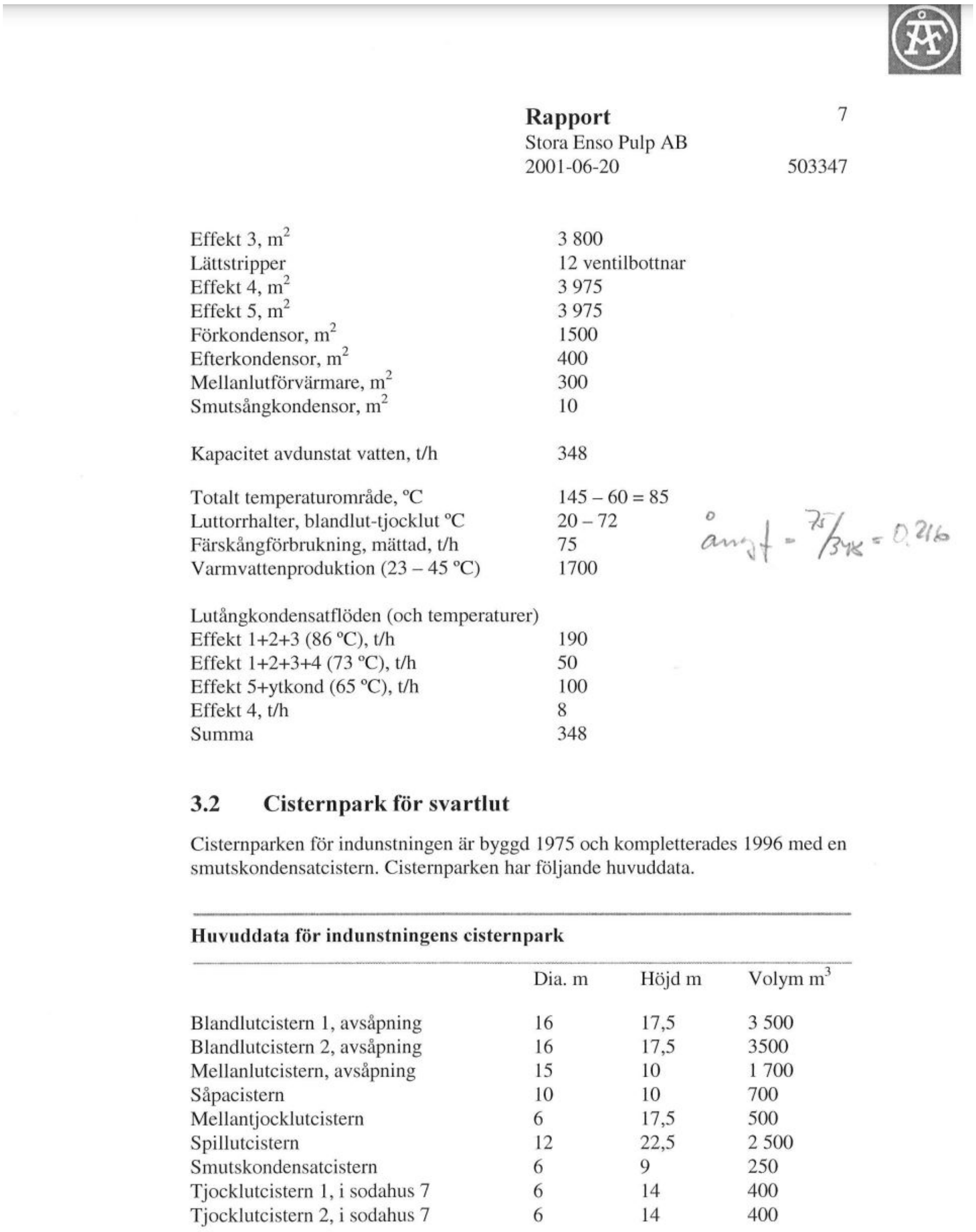
Kapacitet avdunstat vatten, t/h	320	
Specifik belastning, kg avd./m²h	13,3	A = 24060 m²
Totalt temperaturområde, °C	135 - 55 = 80	
Luttorrhalter, blandlut-tjocklut, %	max. 22 - 65	
Färskångförbrukning, mättad, t/h	64	ångf = 0,20
Varmvattenproduktion (23 - 45°C)	1 570	

Lutångkondensatflöden (och temperaturer):	
Effekt 2 + 3 + 4 (81°C), t/h	152
Effekt 5 (88°C), t/h	56
Effekt 6 + förkond. (65°C), t/h	102
Efterkond. + förv. 5 (50°C), t/h	10
Summa	320

Huvuddata för station 6C

Tillverkningsår	1996 Ahlström
Antal enheter:	
Slutförtjockare fallfilm	3 kretsar
Fallfilmsapparater	5
Förkondensor	1
Efterkondensor	1
Integrerad lättstripper	1
Mellanlutförvärmare	1
Smutsångkondensor	1
Antal effekter	6
Stripperkolonn	1
Metanolkolonn	1
Lutföring (S= slutförtjockare)	4-5-Tank-3-2-1-Tank-S-Tank
Värmeyta:	
Slutförtjockare, m²	6 600
Effekt 1, m²	3 800
Effekt 2, m²	3 800

Figure A.5: Summary report for Skutskär evaporation plant pt.2



Rapport 7
Stora Enso Pulp AB
2001-06-20 503347

Effekt 3, m^2	3 800
Lättstripper	12 ventilbottnar
Effekt 4, m^2	3 975
Effekt 5, m^2	3 975
Förkondensor, m^2	1500
Efterkondensor, m^2	400
Mellanlutförvärmare, m^2	300
Smutsångkondensor, m^2	10
Kapacitet avdunstat vatten, t/h	348
Totalt temperaturområde, °C	145 – 60 = 85
Luttorrhalter, blandlut-tjocklut °C	20 – 72
Färskångförbrukning, mättad, t/h	75
Varmvattenproduktion (23 – 45 °C)	1700

ångt = 75/348 = 0.216

Lutångkondensatflöden (och temperaturer)	
Effekt 1+2+3 (86 °C), t/h	190
Effekt 1+2+3+4 (73 °C), t/h	50
Effekt 5+ytkond (65 °C), t/h	100
Effekt 4, t/h	8
Summa	348

3.2 Cisternpark för svartlut

Cisternparken för indunstningen är byggd 1975 och kompletterades 1996 med en smutskondensatcistern. Cisternparken har följande huvuddata.

Huvuddata för indunstningens cisternpark

	Dia. m	Höjd m	Volym m^3
Blandlutcistern 1, avsåpning	16	17,5	3 500
Blandlutcistern 2, avsåpning	16	17,5	3500
Mellanlutcistern, avsåpning	15	10	1 700
Såpacistern	10	10	700
Mellantjocklutcistern	6	17,5	500
Spillutcistern	12	22,5	2 500
Smutskondensatcistern	6	9	250
Tjocklutcistern 1, i sodahus 7	6	14	400
Tjocklutcistern 2, i sodahus 7	6	14	400

Figure A.6: Summary report for Skutskär evaporation plant pt.3

B

Appendix 2

Known: DS_{in} (%) A m^2

DS_{out} (%) $\dot{q}_{BL}$ m^3/h (Black ligour flow)

T_{cond} °C ΔH_{vap}

T_{BL} °C p bar (in effect)

$$DS\% = \frac{\text{kg dry content}}{\text{kg dry content} + \text{kg water}}$$

$$\rho_{in} = (997 + 649)\left(\frac{DS_{in}}{100}\right)(1 - 0{,}00036\,(T_{BL} - 25) - 0{,}00000194\,(T_{BL} - 25)^2$$

$$\text{Black ligour mass flow} = \dot{m}_{BL,in} = \frac{\dot{q}_{BL} \cdot \rho_{in}}{3600} \qquad \left(\frac{m^3/h}{3600} \cdot kg/m^3 = kg/s\right)$$

$$DS_{flow} = \dot{m}_{BL} \cdot DS_{in}/100 \qquad (kg/s)$$

Water evaporated in effect in kg/s = water that comes in in BL flow − water that co out in BL flow

$$Water_{in} = \text{[illegible]}\ DS_{flow} - \dot{m}_{BL,in}$$

$$Water_{out} = \frac{DS_{flow}}{\frac{DS_{out}}{100}} - DS_{flow}$$

$$dT = T_{cond} - T_{BL}$$

$$Q = \Delta H_{vap} \cdot \text{water evap} \qquad \left(= \frac{J}{kg} \cdot \frac{kg}{s} = W\right)$$

$$U = \frac{Q}{A\,dT}$$

C

Appendix 3

Table C.1: The number of washes with associated information for effect 3C, year 2020

Number of washes	Date and time	Duration	dT before	dT after	Difference in dT	dT commutes between	dT increases next time
1	23/4 11:30-17:00	5,5 h	8.9	7.2	1.7	5.6-8.4	29/4 06:00
2	2/5 8:30-11:00	2,5 h	11.0	10.0	1	9.8-8.8	3/5 08:00
3	7/5 00:30-04:30	4 h	11.4	10.6	0.8	10.5-11.0	7/5 14:00
4	8/5 20:30-23:00	2,5 h	13.4	11.9	1,5	11.7-12.4	9/5 11:30
5	12/5 10:00-13:00	3 h	14.7	11.5	3.2	10.8-12.7	14/5 01:30
6	14/5 15:00-18:00	3 h	13.6	11.3	2.3	11.0-12.3	16/5 17:30
7	17/5 07:30-14:30	7 h	12.6	6.4	6.2	4.1-7.6	23/5 04:00
8	2/6 08:00-17:30	9,5 h	9.9	6.4	3.5	4.6-7.5	7/6 23:00
9	20/6 14:00-17:00	3 h	11.2	8.9	2.3	8.0-10.4	26/6 01:00
10	30/6 21:30-08:00	10,5 h	11.2	8.8	2.2	7.8-9.9	9/7 11:00
11	29/7 21:30-00:30	3h	12.2	8.3	3.9	8.2-10.7	1/8 19:00
12	4/8 09:00-11:30	2,5h	11.3	10.7	0.6	9.8-10.9	direct
13	10/8 05:00-08:30	3,5h	10.7	10.3	0.4	10.0-10.9	direct
14	12/8 14:00-17:00	3h	11.6	10.2	1.6	10.4-8.6	-
15	14/8 21:00-01:30	4,5h	9.7	9.0	0.7	8.3-9.6	-

Table C.2: Continuation of the number of washes with associated information for effect 3C, year 2020

Number of washes	**Date and time**	**Duration**	**dT before**	**dT after**	**Difference in dT**	**dT commutes between**	**dT increases next time**
16	18/8 10:00-14:30	4,5h	8.5	8.4	0.1	7.0-9.4	22/8 10:00
17	29/8 14:30-17:00	3,5h	13.3	12.2	1.1	11.7-13.0	31/8 05:00
18	1/9 14:00-16:00	2h	13.6	12.7	0.9	11.8-13.2	3/9 12:00
19	5/9 06:00-08:30	2,5h	13.5	12.8	0.7	11.0-13.4	direct
20	8/9 13:00 – 17:00	4h	13.7	8.6	5.1	8.2-10.5	11/9 08:30
21	15/9 06:00-08:30	2,5h	13.0	11.4	1.6	11.3-12.0	16/9 17:00
22	19/9 22:30-01:00	3,5h	14.9	12.3	2.6	11.8-12.9	20/9 17:30
23	3/11 00:30-04:30	4h	10.2	9.3	0.9	9.2-9.9	4/11 15:30
24	12/11 17:00-20:00	3h	12.4	10.0	2.4	9.4-10.6	13/11 12:30
25	15/11 01:30-14:30	13h	11.6	7.7	3.9	7.4-9.4	17/11 05:30
26	26/11 05:30-11:00	4.5h	10.3	7.9	2.4	6.8-8.4	27/11 13:30
27	30/11 13:00-16:30	3,5h	11.3	9.0	2.3	8.1-10.2	1/12 12:00
28	2/12 11:30-16:30	5h	11.5	8.6	2.9	7.6-9.4	10/12 11:30

Table C.3: The number of washes with associated information for effect 3C, year 2021

Number of washes	Date and time	Duration	dT before	dT after	Difference in dT	dT commutes between	dT increases next time
1	2/1 12:00-14:30	2,5h	14.0	9.9	4.1	9.3-11.3	5/1 05:00
2	7/1 06:00-12:30	6,5h	12.0	9.8	2.2	8.7-10.6	9/1 07:00
3	14/1 09:00-12:00	3h	11.5	11.8	-	At once	-
4	11/2 06:30-13:00	6,5h	13.0	9.9	3.1	9.1-11.1	14/2 06:00
5	23/2 05:30-14:30	9h	11.9	8.6	3.3	7.4-9.9	25/2 11:30
6	13/3 21:30-00:30	3h	10.7	10.2	0.5	8.7-10.6	18/3 07:30
7	1/4 03:00-06:00	3h	11.8	10.0	1.8	10.0-11.1	2/4 04:30
8	7/4 22:00-01:30	3,5h	13.6	10.6	3.0	9.8-12.0	13/4 14:00
9	15/4 23:30-05:00	5,5h	14.7	11.0	4.7	10.1-12.2	18/4 16:30
10	21/4 15:00- 19:00	4h	15.4	12.1	3.3	11.8-13.2	24/4 11:30
11	25/4 19:00-22:00	3h	15.1	12.2	3.2	11.2-13.4	27/4 14:30
12	29/4 13:30-18:00	5h	15.2	11.5	4.7	8.9-11.5	-
13	3/5 22:00-10:30	12,5h	11.5	14.3	-	-	direct
14	5/5 17:00-00:15	7 h	14	9.3	4.7	8.9-11.6	12/5 07:30
15	14/5 06:40-09:00	2 h	14.5	9.5	5	9.5-10.2	15/5 13:30
16	18/5 04:40-20:00	15 h	12.5	6.7	5.8	4.5-8.7	21/5 20:20

Table C.4: Continuation of the number of the washes with associated information for effect 3C, year 2021

Number of washes	Date and time	Duration	dT before	dT after	Difference in dT	dT commutes between	dT increases next time
17	25/5 23:50-00:45	1 h	12.3	9.2	3.1	8.8-11.0	28/5 16:00
18	31/5 05:50-08:30	2 h 40 min	13.0	10.5	2.5	9.2-12.0	3/6 02:00
19	4/6 00:00-01:45	1 h 45 min	12.7	10.5	2.2	10.3-10.9	5/6 15:30
20	6/6 19:45-22:00	2 h 15 min	13.7	10.1	3.6	9.6-10.6	8/6 02:30
21	9/6 11:45-12:40	1 h	15.0	10.1	4.9	9.2-11.0	10/6 14:00
22	11/6 18:00-23:45	5 h 45 min	12.5	9.1	3.4	8.4-10.2	12/6 17:00
23	16/6 07:30-11:30	4 h	13.0	8.5	4.6	8.0-10.0	22/6 7:30
24	29/6 15:10-17:20	2 h 10 min	11.0	8.9	2.1	7.6-9.8	-
25	6/7 22:20-02:10	3 h 50 min	9.6	8.4	4.7	7.5-9.1	10/7 10:00
26	15/7 19:30-22:30	3 h	9.0	8.6	3.3	8.2-9.5	-
27	25/7 00:40-03:20	2 h 40 min	9.6	8.4	3.2	8.0-9.3	-
28	1/8 01:30 03:10	1h 40 min	8.9	8.9	4.7	7.8-10.1	-
29	31/12 09:00-11:30	2.5h	5.6	5.2	-	-	-

Table C.5: The number of washes with associated information for effect 3C, year 2022

Number of washes	Date and time	Duration	dT before	dT after	Difference in dT	dT commutes between	dT increases next time
1	6/1 09:00-10:30	1.5h	5.7	5.4	-	-	-
2	16/1 12:00-14:30	2.5h	5.9	5.7	-	-	-
3	25/1 15:30-17:30	2h	6.1	5.9	-	-	-
4	15/2 06:30-12:00	5.5h	5.4	5.0	-	-	-

D

Appendix 4

Table D.1: The number of washes with associated information for effect 2C, year 2020

Number of washes	**Date and time**	**Duration**	**dT before**	**dT after**	**Difference in dT**
1	23/4 11:30-16:00	4.5h	5.6	5.4	-
2	2/5 09:00-11:30	2.5h	5.5	5.4	-
3	7/5 00:30-04:00	3.5h	4.5	4.9	-
4	8/5 21:00-23:00	2h	5.1	5.1	-
5	12/5 10:00-13:00	3h	4.7	4.8	-
6	14/5 15:00-18:00	3h	5.2	5.2	-
7	17/5 08:00-14:30	5.5h	5.5	5.2	-
8	2/6 08:30-18:00	9.5h	5.2	4.8	-
9	20/6 14:00-17:00	3h	5.2	5.0	-
10	30/6 21:30-08:00	10.5h	5.4	5.2	-
11	29/6 23:30-03:00	3.5h	5.7	4.9	0.8
12	4/8 09:00-11:30	2.5h	5.4	5.2	-
13	10/8 05:30-09:00	3.5h	5.1	5.2	-
14	12/8 14:00-17:00	3h	5.2	5.2	-
15	14/8 21:30-01:30	3h	5.1	5.2	-
16	18/8 10:00-14:30	4.5h	5.0	5.0	-
17	29/8 14:30-17:00	2.5h	4.8	4.9	-
18	5/9 06:00-09:00	3h	4.7	5.2	-
19	8/9 12:00-17:00	5h	5.1	5.2	-
20	11/9 23:30-01:30	2h	5.2	5.0	-
21	15/9 06:00-08:30	2.5h	5.3	5.1	-
22	31/10 13:30-16:00	2.5h	5.0	4.9	-
23	3/11 00:30-04:30	4h	4.8	5.0	-
24	12/11 17:00-20:30	3.5h	5.1	4.9	-
25	15/11 02:00-15:00	11h	4.9	5.0	-
26	26/11 05:30-11:30	6h	5.2	5.2	-
27	30/11 12:30-17:30	5h	5.4	5.2	-
28	2/12 11:30-16:30	5h	5.2	5.3	-

Table D.2: The number of washes with associated information for effect 2C, year 2021

Number of washes	**Date and time**	**Duration**	**dT before**	**dT after**	**Difference in dT**
1	7/1 06:30-12:30	6h	4.9	5.1	-
2	14/1 08:00-13:00	5h	5.3	4.9	-
3	30/1 21:30-00:30	3h	4.9	4.9	-
4	11/2 06:30-13:30	7h	4.8	4.8	-
5	23/2 05:30-14:30	9h	4.7	4.7	-
6	13/3 21:00-00:30	3.5h	4.9	4.8	-
7	1/4 02:30-06:30	4h	4.4	4.3	-
8	7/4 22:30-04:00	5.5h	4.2	4.3	-
9	15/4 23:30-05:30	6h	4.4	4.4	-
10	21/4 15:00- 19:00	4h	4.0	4.2	-
11	25/4 19:00-22:00	3h	4.1	4.3	-
12	29/4 15:00-18:30	3.5h	4.3	4.8	-
13	3/5 21:30-11:00	13.5h	4.1	4.2	-
14	5/5 17:00-23:30	6.5h	4.2	4.5	-
15	14/5 05:30-09:30	4h	4.3	4.3	-
16	18/5 05:00-19:30	14.5h	4.5	4.5	-
17	25/5 23:00-02:00	3h	4.9	4.8	-
18	31/5 06:00-09:00	3h	4.4	4.7	-
19	4/6 00:30-02:00	1.5h	4.5	4.6	-
20	6/6 19:30-23:30	4h	4.6	4.7	-
21	10/6 18:00-00:30	6.5h	4.8	4.6	-
22	16/6 07:30-11:30	4h	4.5	4.4	-
23	18/6 21:30-13:00	15.5h	4.4	4.5	-
24	29/6 15:00-17:30	2.5h	4.7	4.8	-
25	5/7 22:00-00:30	2.5h	4.7	4.6	-
26	25/7 00:30-04:00	3.5h	5.0	4.9	-
27	31/12 09:00-11:30	2.5h	6.0	5.7	-

Table D.3: The number of washes with associated information for effect 2C, year 2022

Number of washes	**Date and time**	**Duration**	**dT before**	**dT after**	**Difference in dT**
1	6/1 09:00-10:30	1.5h	6.2	5.9	-
2	16/1 12:00-14:30	2.5h	6.0	5.7	-
3	25/1 15:30-17:30	2h	5.8	5.8	-
4	15/2 06:30-12:00	5.5h	6.0	5.5	-

Table D.4: The number of washes with associated information for effect 1C, year 2020

Number of washes	Date and time	Duration	dT before	dT after	Difference in dT
1	23/4 12:00-18:00	6h	8.4	8.0	-
2	2/5 09:00-11:30	2.5h	8.2	8.1	-
3	7/5 00:30-04:00	3.5h	7.3	7.4	-
4	12/5 22:00-01:30	3.5h	7.2	7.9	-
5	14/5 15:30-18:30	3h	7.8	8.1	-
6	17/5 08:00-15:00	7h	8.1	7.7	-
7	2/6 08:30-18:00	10.5h	8.2	7.7	0.5
8	20/6 14:00-17:00	3h	8.5	8.0	0.5
9	30/6 22:00-08:30	10.5h	7.8	7.7	-
10	29/7 00:30-03:30	3h	8.5	8.2	-
11	4/8 08:00-12:00	4h	7.6	7.9	-
12	10/8 05:30-09:00	3.5h	8.0	7.9	-
13	12/8 14:30-18:00	3.5h	8.0	7.6	-
14	14/8 22:00-02:00	4h	7.7	8.2	-
15	18/8 10:00-15:00	5h	8.2	7.6	-
16	1/9 14:00-17:00	3h	7.5	7.2	-
17	5/9 06:00-09:00	3h	7.2	7.8	-
18	8/9 13:00-17:00	4h	7.5	7.8	-
19	15/9 05:30-09:00	3.5h	7.8	7.6	-
20	31/10 14:00-16:00	2h	7.8	7.1	-
21	12/11 17:30-20:30	3h	7.7	7.2	-
22	15/11 02:00-15:30	13.5h	7.9	7.3	-
23	26/11 06:00-12:00	6h	7.9	6.3	1.6
24	2/12 11:30-16:30	5h	8.7	8.4	-

Table D.5: The number of washes with associated information for effect 1C, year 2021

Number of washes	Date and time	Duration	dT before	dT after	Difference in dT
1	7/1 06:30-13:00	7h	7.9	8.1	-
2	14/1 08:00-13:00	5h	8.7	7.9	0.8
3	30/1 22:00-01:00	3h	8.0	8.3	-
4	11/2 07:30-13:30	6h	7.5	6.6	0.9
5	23/2 05:30-14:30	9h	6.3	7.1	-
6	13/3 21:00-00:30	3.5h	7.5	7.5	-
7	1/4 03:30-07:00	3.5h	7.5	7.7	-
8	7/4 22:30-04:30	6h	6.9	7.1	-
9	16/4 23:30-05:30	6h	7.5	7.3	-
10	21/4 15:30-19:30	4h	7.2	7.1	-
11	29/4 16:00-18:30	2.5h	7.1	7.5	-
12	14/5 06:30-10:00	3.5h	7.3	7.6	-
13	25/5 23:30-02:30	3h	7.8	7.7	-
14	31/5 06:00-09:00	3h	7.4	7.9	-
15	3/6 23:30-02:30	3h	7.3	8.0	-
16	10/6 18:00-01:30	7.5h	8.0	7.8	-
17	16/6 07:00-12:30	5.5h	7.3	7.6	-
18	29/6 15:00-18:30	3.5h	8.2	8.0	-
19	5/7 22:00-02:00	4h	7.8	8.2	-
20	25/7 01:30-04:30	3h	8.6	8.2	-

Table D.6: The number of washes with associated information for effect 1C, year 2022

Number of washes	**Date and time**	**Duration**	**dT before**	**dT after**	**Difference in dT**
1	6/1 09:00-10:30	1.5h	6.5	6.2	-
2	16/1 12:00-14:30	2.5h	7.0	6.5	-
3	25/1 15:30-17:30	2h	7.9	7.4	-
4	15/2 06:30-12:00	5.5h	8.0	7.4	-

DEPARTMENT OF CHEMISTRY AND CHEMICAL ENGINEERING
CHALMERS UNIVERSITY OF TECHNOLOGY
Gothenburg, Sweden
www.chalmers.se

CHALMERS
UNIVERSITY OF TECHNOLOGY