Study of Black Liquor Evaporator Fouling at Södra Cell Värö

Master's Thesis within the Industrial Ecology programme

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Cover:
Picture of the new evaporation plant at Södra Cell Värö

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ABSTRACT

The growing concern for global climate change has put pressure on industry to reduce its carbon dioxide emissions by reducing energy use. At a pulp mill the single largest energy consumer is the evaporation plant. If there is unwanted accumulation of unwanted substances on the heat transfer surfaces, referred to as fouling, the efficiency decreases.

This master's thesis aims to investigating possible reasons for problems with black liquor fouling in the evaporation plant at Södra Cell Värö. An evaporation plant consists of several evaporation stages called effects and the effects studied in this thesis are effect 1B and effect 2. The method used consists of studying the flow rate and composition of the black liquor in and out of effect 2 and 1B in the evaporation plant. A study was also made to look at process parameters in the process control system relevant to fouling to find correlation with the fouling problems.

The most apparent findings are that the fouling in effect 1B is rapid and can be explained by salt precipitation of a mixture of burkeite and dicarbonate. As this precipitation takes place, the soap content in the black liquor has often been high. In effect 2 the fouling is not as rapid as in effect 1B. In effect 2 the wetting degree is low and this could be an explanation for the fouling taking place in the effect.

The calcium content of the black liquor is also high but does not seem to be the major contributor to the fouling problems. The results from the process parameter analysis show no clear correlation to the fouling problems.

Key words:

Black Liquor   Fouling   Scaling   Evaporation   Dicarbonate   Burkeite   Calcium   Soap

Undersökning av igensättningar vid svartlutsindunstning på Södra Cell Värö

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SAMMANFATTNING

Den ökande medvetenheten om globala klimatförändringar har satt press på industrin att minska sina koldioxidutsläpp genom energibesparande åtgärder. På ett kemiskt massabruk är indunstningsanläggningen den enskilt största energiförbrukaren. Om värmeöverföringsytorna är nedsmutsade med så kallade inkruster, minskar dess effektivitet.

Det här examensarbetet syftar till att undersöka möjliga förklaringar till svartlutsinkrustering i indunstningsanläggningen på Södra Cell Värö. Metoden som använts bygger på att studera flöde samt sammansättning av luten in och ut ur effekt 1B samt effekt 2 i indunstningsanläggningen. En studie har även gjorts för att undersöka processdata relevant för inkrustering för att se om någon korrelation med inkrusteringen kunde hittas.

De viktigaste upptäckerna är att inkrusteringen i effekt 1B är snabb och att den förklaras av utfällning av en blandning av burkit och dikarbonat. När denna snabba inkrustering skedde var såpahalterna ofta höga. I effekt 2 är inkrusteringen långsammare än i effect 1B. Effekt 2 har en låg vätningsgrad vilket kan vara en förklaring till inkrusteringsproblemen i effekten.

Kalciumhalterna i luten är också höga men verkar inte vara den huvudsakliga förklaringen till inkrusteringsproblemen. När processdata studerades hittades ingen klar korrelation som kan förklara inkrusteringsproblemen.

Nyckelord:

| Svartlut | Inkrustering | Indunstning | Dikarbonat | Burkit | Kalcium | Såpa |

Contents

Preface

This report presents a master thesis project carried out for Södra Cell Värö. The project was done from November 2011 to May 2012 at the Department of Energy and Environment, Heat and Power Technology at Chalmers University of Technology, Göteborg, Sweden.

The aim was to map and analyze possible causes for Södra Cell Värö's problems with fouling in their evaporation plant. The work was carried out at Södra Cell Värö's pulp mill located 65 km south from Göteborg.

I would like to show my gratitude to my examiner Mathias Gourdon and my supervisors Erik Karlsson (Chalmers) and Gustaf Collin (Södra), for their commitment. I would also like to thank the employees at Södra Cell Värö for their time and patience.

Göteborg May 2012

Emil Lagerberg-Nilsson

Notations

Roman upper case letters

WL	Weak liquor with dry solid content of 16%
SL	Seed liquor with dry solid content of 19.5%
IML	Intermediate liquor with dry solid content of 32.1%
$IMTHL$	Intermediate thick liquor with dry solid content of 47.2%
HBL	Heavy black liquor with dry solid content of 68%
$HBCL$	Heavy black crystal liquor with dry solid content of 70%
FBL	Firing black liquor with dry solid content of 75%
A_{1B}^{HX}	Total heat transfer surface area in effect 1B
DS_i	Initial dry solids content of black liquor
DS_t	Dry solids content of black liquor at time t
Q	Heat supplied with fresh steam
S	Supersaturation
S_e	Steam economy
W_L	Total heat transfer lamella width
X_l	Salt concentration
X_l^*	Salt concentration at solubility limit

Roman lower case letters

k_{1B}	Overall heat transfer coefficient in effect 1B
$\dot{m}_{1B}^{KF}$	Mass flow of steam condensing in effect 1B
m_i	Initial black liquor sample mass
m_t	Black liquor sample mass at time t
q	Total amount of water evaporated from liquor in evaporation plant
q_V	Volumetric flow rate
x	Solvent free mole fraction between sodium carbonate and sodium sulfate

Greek upper case letters

ΔH_{vap}^{T}	Heat of vaporisation at temperature T
ΔT_{1B}	Differential temperature between condensing steam and circulating black liquor in effect 1B
Γ	Wetting degree

1   Introduction

1.1 Background

The risk for climate change is a growing concern for the global society. The Intergovernmental Panel on Climate Change provides strong evidence that global warming is caused by human activity. In all models assessed by working group I on Global Climate Projections the projected increase in global mean surface air temperature (SAT) during 2011 to 2030 ranges between +0.64ºC and +0.69ºC, i.e. with a range of only 0.05ºC. This means that the outcome is little dependent on mitigation efforts being made. However in the projection for the late century (2090-2099) there is a large difference between different scenarios and only 20% of the warming taking place arises from climate change that is already committed (Meehl et al, 2007). This gives a large potential for mitigating actions for the remaining 80%.

The amount of carbon dioxide in the atmosphere has increased by 35% since the beginning of the industrial era, and this increase is primarily due to the human activities of combustion of fossil fuels and removal of forests (Le Treut et al, 2007). Since the forest in Sweden has increased its standing volume since 1930 with a projected increase of 300 million forest cubic metres during 2010 to 2030 the focus in the Swedish forest industry should be put on fossil carbon dioxide emissions. In Sweden 3.6% of the total fossil carbon dioxide emissions come from the pulp and paper industry. A lot of these emissions are emissions from trucks and forestry machinery. Of the energy used as heat in the Swedish forest industry today approximately 90% is based on biofuels and has no net contribution to carbon dioxide emissions (Skogsindustrierna, 2011).

Sustainable development can be said to rest on three dimensions; ecological, social and economical. When it comes to the economic and social sustainability the pulp and paper industry can be said to be sustainable since Swedish forest industry accounts for 10-12% of Swedish industry's employment, exports, sales and added value. And since the industry is strongly export-oriented with mainly domestic raw-materials and with a small import of forest industry products it's a large contributor to Sweden's trade balance (The Swedish Forest Industries Federation, 2010). As for the ecological dimension the pulp and paper industry also stands for 36.7 TWh/y of fossil free heat production and 6 TWh/yr of fossil free electricity production (Energiläget, 2010). The raw material for pulp and paper, wood, could be used to produce replacements for fossil based products such as plastics, paints and fuels. If a sustainable society is to be achieved a shift from using the wood for paper production to using it as replacement for fossil based products might be needed.

The production of pulp and paper is an energy demanding process and since the consumption of energy is often closely linked to environmental effects there is a great driving force to optimize the use of energy. Skogsindustrierna, which is the Swedish forest branch organization, has set up a goal of a 15% reduction in energy use per manufactured amount of pulp and paper until the year 2020. The evaporation plant is the single largest consumer of energy in a pulp mill and it's therefore essential that it operates under efficient conditions.

Södra Cell Värö continuously works on optimizing the energy use at their pulp mill. During recent years a number of large investments have been carried out aiming to:

- Increase electricity production

- Decrease the use of oil

- Use more process waste heat

- Maximize the deliveries of bio fuels (e.g. bark, tall oil)

One of the latest investments was the building of a brand new evaporation plant which was launched in 2009. This enables the mill to be free from fossil fuels under normal operating conditions.

During the time since the installation, problems with accumulation of unwanted material on the heat transfer surfaces, so called fouling, have occurred. The most apparent effect of this fouling is that the washing intervals are kept much lower than they are supposed to be, leading to production losses. This also leads to a worse heat economy since a lower average amount of water is evaporated from the liquor per supplied amount of fresh steam. At one time the fouling was so severe that the evaporation plant had to been shut down and washed with acid forcing the rest of the pulp mill to shut down as well. (Södra, 2011)

1.2 Objective

The overall aim of this master thesis is to find ways to operate the evaporation plant at Södra Cell Värö that keeps it free from severe fouling leading to production losses. Free from severe fouling in this context means that the washing intervals are kept above the guaranteed value from the supplier of the evaporation plant of 3.5 days.

More specifically the objective is to analyse different liquor compositions at known problematic positions within the evaporation plant together with logged process data, and information about operating conditions, to see if any correlation can be found regarding problems with fouling of the heat transfer surfaces.

1.3 Scope

The analysis is carried out on different liquors, process parameters and trends within the evaporation plant. This study focus on the evaporation plant itself and therefore variations in other parts of the pulp mill will not be considered. An exception is process data easily extracted via the process control system. The liquors are only analysed for known problematic substances. The effects in the evaporation plant studied are the effects in the heavy liquor end, since this is where problems have occurred. The sampling period is approximately 16 weeks.

1.4 Method

The method consists of analysing black liquor samples taken in and out of two effects in the evaporation plant. Together with process data and discussion with relevant expertise, the analysis serves as feedback for possible new samples. The idea is to get samples from periods with a lot of fouling to see what differs in liquor composition from good periods without fouling.

2 The Kraft Pulping Process

The most common way to produce pulp from wood is the kraft pulping process (illustrated in figure 1.1), which accounts for 70% of global pulp production (Möllersten et al., 2004). This process uses alkaline conditions to liberate the fibres from the wood. In the beginning of the process wood logs are debarked and chipped into wood chips with a uniform geometry. The barking process is of great importance to remove most of the metal ions that are situated in the bark that could have a negative impact on the pulping process. Wood chips are then steamed and impregnated with cooking liquor (often referred to as white liquor) before being introduced to a digester. The cooking liquor consists mainly of sodium hydroxide (NaOH) and sodium sulfide (Na_2S). During the cooking, part of the Na_2S is oxidized to Na_2SO_4 and part of the NaOH is oxidized to Na_2CO_3.

After the digester the fibres are separated from the spent cooking liquor, in the washing process, which is now referred to as weak black liquor (as seen in figure 1). The weak black liquor has an approximate composition as seen in table 1. The fibre sludge, pulp, goes through further washing and in some cases several bleaching stages to achieve a certain brightness by lowering the lignin content of the pulp which is derived from the wood.
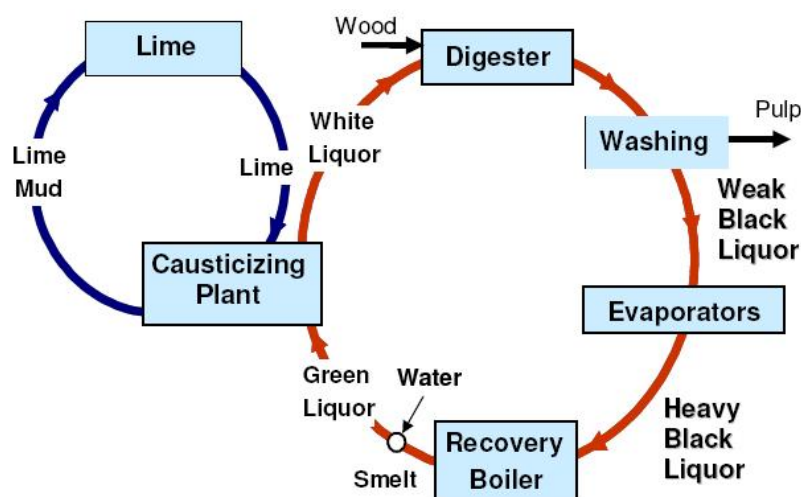
Figure 1   Kraft pulping process (Hajiha, 2009)

Table 1   Chemical composition of dry substance of black liquor (Brelid, 2011)

Element	Amount (mass-%)	Organic material	Amount (mass-%)
Carbon	34-39	Lignin	30-45
Hydrogen	05-mar	Hydroxy acids	
Oxygen	33-38	(Carbohydrate	
Sodium	17-25	related products)	25-35
Sulphur	07-mar	Extractives	3-5
Potassium	0.1-2	Formic acid	~5
Chlorine	0.2-2	Acetic acid	~3
Nitrogen	0.05-0.2	Methanol	~1

The weak black liquor goes to the evaporation plant where the dry solid content is increased. The main reason for this is to be able to burn it in the recovery boiler without the addition of other fuels. In the recovery boiler the organic content of the black liquor is burnt and the heat generated is used to produce steam. The inorganic content, mainly salts, forms a smelt at the bottom of the boiler. In this smelt or char bed Na_2SO_4 is reduced to Na_2S. The smelt which consists of liquid salts are then dissolved to produce green liquor. During the combustion fly ashes containing salts that are wanted in the process are precipitated with the help of an electrostatic precipitator and are returned to the process in the evaporation plant.

To regenerate the NaOH needed in the cooking liquor the green liquor is mixed with burnt lime (CaO) in the causticizing plant to produce white liquor. This mixing results in the formation of lime mud ($CaCO_3$). The lime mud produced is dried and then burnt in a rotating lime kiln. In the lime kiln the CaO used in the causticizing plant is regenerated (Brelid, 2011).

2.1 Black liquor evaporation

The most common way to remove water from a dissolved substance having a boiling point that differs a lot from water is by evaporation. During the evaporation the solution is heated to its boiling point so that the water evaporates to steam that can be condensed elsewhere (Kassberg M., 1994). In industry the heating medium for evaporation of water is almost exclusively steam. There are different types of evaporation equipment used in the pulp industry, but the two most common types are rising film evaporators (Kestner evaporators) and falling film evaporators.

In a rising film evaporator, or Kestner evaporator after its inventor Paul Kestner, the solution is transported upwards by the evaporated water creating vapour bubbles travelling upwards on the vertical heating tubes. Because of this, no pump energy is needed to recirculate the solution over the tubes. A rising film evaporator works well up to a dry solid content of app. 55% but then problems with scaling make operation difficult. (Kassberg M., 1994) For this reason, in new installations, this type of evaporator is not chosen anymore. (Brelid H., 2011)

Today falling film evaporators are the type being built in the pulp industry. Falling film evaporators have heating elements consisting of vertical tubes or lamellas. The heating steam condenses on one side of the tube/lamella heating surfaces. The liquor is situated on the opposite side of the heating surfaces and is not in direct contact with the steam. The liquor is pumped into a distribution box, located at the top of the heat body, which distributes the liquor evenly onto the heating elements. The liquor then flows downwards by gravity on the heating surfaces in the evaporator forming a thin film from which water can be evaporated. To avoid spots from being dried out a surplus of liquor is circulated (Kassberg M., 1994).

The driving force of evaporation is the temperature difference between the heat medium (steam) and the liquor. Different salts in the liquor will interact with the liquor resulting in a boiling point rise which increases with the dry solid content. The total temperature difference in the evaporation train is the temperature difference between incoming live steam and incoming weak black liquor.

An evaporation plant is made up by several evaporation stages or effects. The first stage, which is also the stage having the highest dry solid content of the black liquor,

is fed with fresh steam. Since it is favourable to use the heat in the fresh steam more than once, the water evaporated from the black liquor in this effect is used as heating medium (steam) in the next effect which gives an overall better steam economy. The steam economy(S_e) is defined as

$$S_e = \frac{Q_{supplied}}{q_{evaporated,tot}} = \frac{Q_{supplied}}{\sum_{i=1}^{N}(q_{evaporated,i})} \qquad (1)$$

Where $Q_{supplied}$ (MW) is the heat supplied with fresh steam, $q_{evaporated,tot}$ (t) is the total amount of water evaporated from the liquor and N the number of effects in the evaporation plant. From this definition it is clear that the heat economy is better when the number of effects increases, since this increases the total amount of water being evaporated.

The steam available in the subsequent effect has the saturation temperature of the black liquor in the previous stage. To account for this the pressure needs to be gradually lower in the effects after the first effect to decrease the boiling point of the liquor. In the evaporation train there will also be temperature losses due to pressure drops. The useful temperature difference is the total temperature difference adjusted by removing the temperature losses caused by pressure drops and the boiling point rise in the different effects. (Kassberg M., 1994)

One operating condition that is of interest is the differential temperature in an evaporator effect defined as the temperature difference between the condensing steam and the circulating black liquor. It can be said to represent the heat transfer resistance in the evaporation effect. Another interesting parameter is the overall heat transfer coefficient (k-value) in an evaporator effect expressed in W/m^2,K. To be able to calculate the k-value the flow of condensing steam, the total heat transfer area and the heat of vaporisation for the liquor in the effect have to be known.

2.2 Evaporation train at Södra Cell Värö

The evaporation train at Södra Cell Värö consists of 8 effects of falling film type with lamellas. Effect 4-7 are used to produce intermediate liquor (IML) with a dry solid content of 32.1% from seed liquor (SL) with a dry solid content of 19.5%. Effects 2 and 3 with help of a liquor preheater are used to produce intermediate thick liquor (IMTHL) with a dry solid content of 47.2%. Effect 1B produces heavy black liquor (HBL) with a dry solid content of 68% and effect 1A produces firing black liquor (FBL) with a dry solid content of 75%. An overview of the liquor flow in the evaporation train is illustrated in figure 2 and a principal layout of an effect is shown in figure 3.
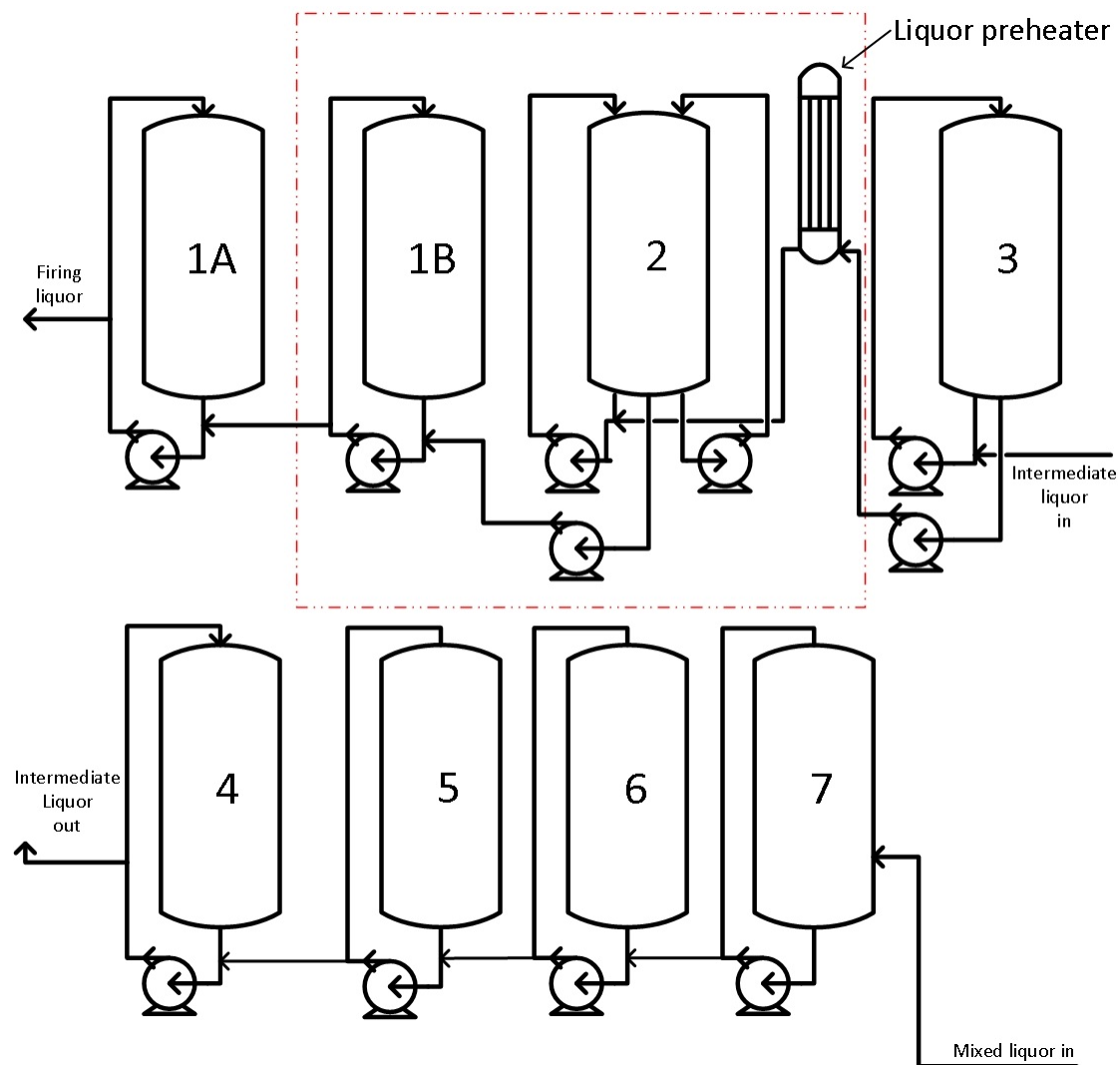

Figure 2   Overview of evaporation train at Södra Cell Värö. For a more detailed version see Appendix A.

Figure 3   Principal layout of an effect in the evaporation train. Brown arrows represent black liquor flow and red arrows represent steam flow.

2.2.1 The system studied in this thesis

In this study there are mainly two effects that have been studied, effect 1B and effect 2. Normally the effects have a distribution box on top of the lamella bundles to distribute the liquor onto the heat transfer surfaces. However if there's a potential that an effect will be fouled this configuration could lead to particles getting stuck on top of the lamellas. Since effect 2 operates in a critical region in terms of dry solids content it is equipped with spray nozzles instead of a distribution box and dual recirculation pipes. Two recirculation pumps carry the liquor to the spray nozzles via the two recirculation pipes. The lamellas in effect 2 are divided into 4 bundles receiving steam from different sources in the evaporation plant. Two lamella bundles receive steam from the stripper column. One lamella bundle receives steam from effect 1A and partly from effect 1B regulated by a valve. The last lamella bundle receives steam from the fresh steam liquor flash tank. The effective heat transfer surface area for effect 2 is 7102 m^2. The temperature of the liquor leaving effect 2 is app. 105°C.

Effect 1B has one recirculation pipe and uses an inlet box to distribute the liquor onto the lamellas. It has one lamella bundle that is heated with fresh steam. The effective heat transfer surface area is 6625m^2. The temperature of the liquor leaving effect 1B is

app. 130$^\text{o}$C. Before the liquor is introduced to effect 1B it is mixed with biosludge, tall oil plant brine and heavy black liquor with ash precipitated from the recovery boiler for reasons further explained in section 3.1.1. The heavy black liquor is mixed with the liquor from effect 2 to increase the dry solids content of the liquor above the solubility limit. The tall oil plant brine (TOP brine) is a by-product from the tall oil plant containing fractioned rosin acids and is added because of its valuable sulphur content. The bio sludge comes from the biological waste water treatment plant and is later burnt in the recovery boiler as a bio fuel. The idea is to add this late in the evaporation plant to cause as little disturbance as possible.

3 Fouling in black liquor evaporators

Fouling refers to accumulation of unwanted material on solid surfaces, often in aqueous solutions. In black liquor evaporation this material can consist of e.g. fibres, soap or matter coming from the biological waste water treatment. Since the material can foul surfaces that are sensitive e.g. heat transfer surfaces this could have a large effect on the operation of industrial processes. The most common fouling in black liquor evaporation is precipitation of different salts called scaling.

3.1.1 Salt scaling

The weak black liquor contains inorganic substances needed in the wood cooking process. These are mainly sodium salts. During the flow through the evaporation train the solubility limit of some of these salts are passed, due to the gradual increase in dry solid content, which will lead to crystallization. However, for crystallization to occur, the salt concentration must exceed its solubility limit and there must also be some particulate matter or surface for the crystals to start to grow on. At the solubility limit the solid phase of the salts is in thermodynamic equilibrium with the salt in solution. If however crystallization does not occur the liquor is said to be supersaturated with respect to the salts in question. Supersaturation (S) is defined as (Mersmann, 1999):

$$S = \frac{X_l - X_l^*}{X_l^*} \qquad (2)$$

Where X_l is the mass fraction of salts in the liquid phase and X_l^* is the mass fraction of salts in the liquid phase at the solubility limit. If the supersaturation exceeds a certain limit, called the metastable limit, crystallization of the salts will occur spontaneously, without any seed crystals. Between the saturation concentration and the metastable limit is a region called the metastable region. Here the solution can remain saturated without any crystallization taking place. When the metastabile limit is passed, crystallisation will occur rapidly due to nucleation and approach the thermodynamic equilibrium (i.e. the concentration of dissolved salt will be at the solubility limit). If the metastable limit is close to the saturation concentration a small crystal mass will form upon nucleation whereas a large crystal mass will form when the metastable limit is greatly separated from the solubility limit (Gourdon et al., 2010).

Primary nucleation occurs in a system not containing any crystalline matter, whereas secondary nucleation occurs when other solute crystals are involved. Different nucleation mechanisms require different level of supersaturation to occur and will therefore have different metastable regions (Gourdon, 2009b). Experimental results by Shi et al. (2003) clearly show that calcium ions inhibit the primary nucleation of burkeite.

The black liquor contains among other salts sodium carbonate (Na_2CO_3) and sodium sulfate (Na_2SO_4) and the ratio between these two salts is an important parameter affecting the crystallization in black liquor (Gourdon et al., 2009). The solvent-free mole fraction can be expressed as:

$$x = \frac{[Na_2CO_3]}{[Na_2CO_3] + [Na_2SO_4]} \qquad (3)$$

Depending on the ratio, x, different salts will form. For a ratio between 0.2 and 0.833 burkeite is formed with the approximate formula $2Na_2SO_4 \cdot Na_2CO_3$. and for $0.833 < x < 0.9$ sodium sulphate dicarbonate is formed with the app. formula $2Na_2CO_3 \cdot Na_2SO_4$. For $x < 0.2$ sodium sulphate will form and for $x > 0.9$ sodium carbonate will form (Shi and Rousseau, 2003). The major variables affecting the solubility limit of these salts are the total sodium content and the liquor dry solids content (Grace, 1975a). Figure 1 shows a comparison of different liquor compositions and the salts formed upon crystallization.

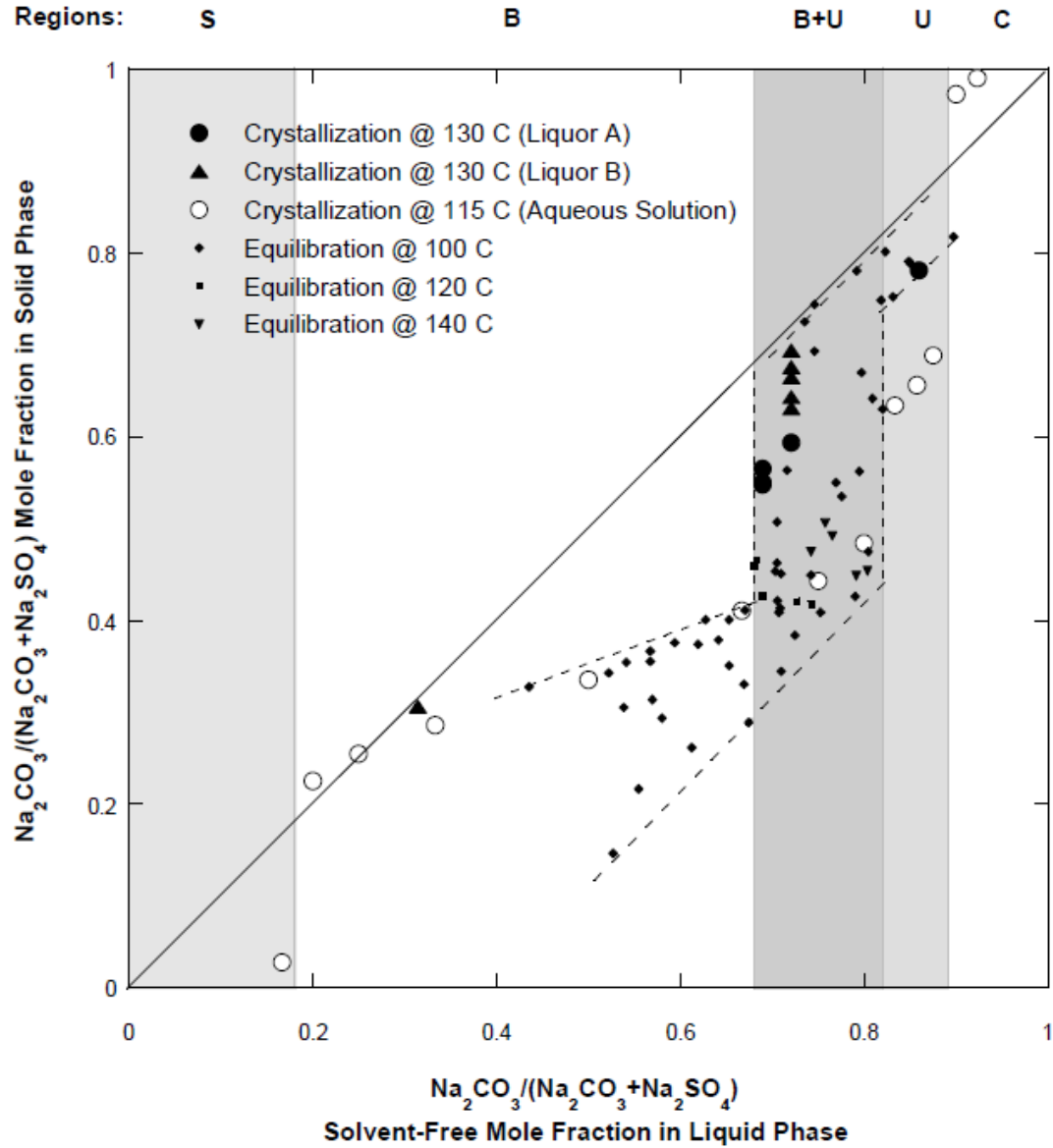*Figure 1*   *Comparison of the crystal compositions obtained from black-liquor crystallization at 130ºC, aqueous-solution crystallization at 115ºC, and equilibrium of solid phases with black liquors at 100, 120 and 140ºC. S denotes sodium sulphate region, B denotes burkeite region, B+U denotes region crystallizing both burkeite and dicarbonate, U denotes dicarbonate region and C denotes sodium carbonate region. (Shi, 2002)*

According to Patel J.-C. (2008) burkeite reaches its solubility limit at a dry solid content of around 50-55% while dicarbonate reaches it a little bit later at 60%. This is due to the fact that burkeite contains approximately 2 sodium sulphate molecules and 1 sodium carbonate molecule, and as the precipitation process progresses, the black liquor will exhaust its supply of sodium sulphate and will subsequently only precipitate sodium carbonate (Golike et al, 1998). This transition point has been given the name "second critical solids" by Golike in 1998. The most severe problems with scaling are considered to be caused in the dicarbonate region or in the region were both burkeite and dicarbonate crystallize (Frederick et al., 2004).

Both burkeite and dicarbonate have reverse solubility with temperature giving them a tendency to precipitate on the hot heat transfer surfaces (Gourdon et al., 2009). One way to avoid this is to mix the black liquor with thick black liquor already containing crystals before it is introduced to the evaporation train where crystallization can occur on the heat transfer surfaces. This is done by mixing ash precipitated from the recovery boiler with black liquor, resulting in crystal liquor, which is introduced to the evaporation plant. It is recommended to add the ash before the final thickening at a dry solid content between 30% and 45% (Haag & Stigson, 2003). However this would produce a risk of dissolving the ash since the black liquor will have a dry solid content below the solubility limit. It would therefore be more suitable to add the ash to black liquor resulting in a dry solids content above 55%.

Sodium salts are often soluble in water and can quite easily be washed away from the heat transfer surfaces. Scales can also form from calcium salts, the most common being calcium carbonate ($CaCO_3$). Calcium carbonate has a very low solubility in water and the solubility also decreases with increased temperature giving it a propensity to precipitate on the hot heat transfer surfaces. To avoid this heat pretreatment (thermal deactivation) of the liquor with live steam can be used before the liquor is introduced to the evaporation train (Frederick and Grace, 1977). One method patented by Eneberg et al (2000) uses a temperature of 110-145ºC and then let the liquor react in a retention tank for 1-20 minutes. Heat pretreatment gives crystallization the opportunity to occur prior to the hot heat transfer surfaces and instead form crystals in the bulk phase. These solid calcium carbonate crystals will then not scale the heat transfer surfaces in the evaporation train.

The dry solid content of the liquor affects the fouling rate of the heat transfer surfaces. However there is no easy relationship between them. According to Gourdon et al. (2010) the fouling rate depends on the concentration and solubility of the different crystallizing salts rather than the dry solid content of the liquor itself. As an example the fouling rate was higher for a dry solid content of 53% than for both 59% and 49%. In an inquiry survey made by Haag & Stigson (2003) about problems with scaling at different pulp mills in Scandinavia, mills with a dry solid content on their medium thick liquor under 47% did not experience any problems with scaling. It is desirable to pass the solubility limit of burkeite by mixing the intermediate thick liquor with thick black liquor to avoid that the solubility limit is reached in an effect.

The influence of the temperature difference between the black liquor and the heating steam on the fouling rate is that there is a tendency for higher fouling rate with greater temperature difference (Gourdon, 2009).

3.1.2 Soap

Wood contains resin acids that are converted to their corresponding sodium salts in the cooking process. These salts and unsaponifiables separate from the spent cooking liquor as black liquor soap. The soap separates as a lamellar liquid crystalline phase. Black liquor soap is skimmed off from a mixture of weak black liquor and medium thick black liquor (called seed liquor). The soap skimming consists of a mixture of fatty and rosin acid salts (i.e. anionic surfactants), fatty and rosin acid esters and neutral components. The predominance of the given constituents varies with tree species, pulping chemistry etc. The neutral fraction, often called unsaponifiables, is a mixture of a variety of substances including phytosterols, fatty and wax alcohols, terpenes and hydrocarbons.

The fatty acid and rosin acid salts form micelles that solubilise the neutral fraction of the extractives. Micelle formation, which indicates the onset of phase separation, depends on a number of factors including e.g. salt content and temperature. Generally, as the salt content increases, the concentration of soap at which micelles form decreases, i.e., the soap is less soluble.

Soap carryover contributes significantly to evaporator liquor carryover and operational problems in the evaporator feed effects. The problems are most obvious in the weak liquor end with foam formation as a result.

When it comes to scaling in black liquor evaporators Grace (1975b) found that an addition of soap to black liquor increased the calcium scaling by about 30 %. Lamy E.J. (1979) has also shown that soap is a significant scale component, particularly in soluble carbonate-sulphate scales in evaporators and concentrators.

3.1.3 Other fouling components

Fibre is not a primary scaling agent but because it can disrupt the falling film flow pattern in the evaporators it can accelerate other scaling mechanisms. Lignin can also foul the heat transfer surfaces. Fouling due to lignin precipitation is dependent on the pH of the black liquor. A target pH for the weak black liquor above 12 is a good general rule. The pH of the black liquor is easily maintained by controlling the residual effective alkali from the digester. Scales can also form from Aluminium and Silicon. These scales are thin and glassy and require hydroblasting for removal (Clay, 2008)

3.1.4 Wetting degree

The wetting degree is an important design parameter for an evaporation effect. If it is too low the risk of dryout increases. Dryout causes dry matter to adhere very strongly to the heat transfer surfaces. The flow pattern get disrupted and slowed down which further increases the risk of fouling. The concentration gradient from top to bottom of the lamella heating surface is also highly affected by the wetting degree. The wetting degree (Γ) is calculated as the circulation flowrate (q_V) in an effect divided by the total lamella width (W_L).

$$\Gamma = \frac{q_V}{W_L} \qquad (4)$$

4 Method

In the early phase of this master thesis a literature study was conducted in order to gain knowledge about parameters and operating conditions in the evaporation plant that causes fouling and scaling. This knowledge was then used to decide upon which liquors to analyse, how often they should be analysed and what they would be analysed for. The liquor samples were taken out in different sample taps in the evaporation plant and taken to the laboratory at Södra Cell Värö for analysis. To ease the work load of the plant laboratory some analysis were carried out at an external laboratory.

Analyses were also performed on samples taken out before this project was initialized at times when the evaporation plant experienced fouling. Since information was missing in order to analyse these samples according to the method developed during this master's thesis, new samples were taken to provide suitable data.

One way to illustrate the workflow is shown in figure 4. At the start of the project the previous samples together with new samples, logged process data and consultation were all used as input to the analysis. The first results from the analysis were then a basis for discussion during consultation with relevant people with knowledge about the evaporation plant. Since the operators and engineers managing the evaporation plant have great knowledge about parameters affecting the operation of the plant their feedback were of great importance during this project. To better understand the chemistry of the analysis, relevant scientists at Chalmers University of Technology were also consulted.

This led to feedback about what new samples to be taken out, what they should be analyzed for, and also what logged process data that were of interest for the analysis. During the project more and more data were gathered where it was needed. As the work progressed and enough data had been collected the analysis would hopefully show some relevant results, i.e. correlation explaining fouling or scaling problems.
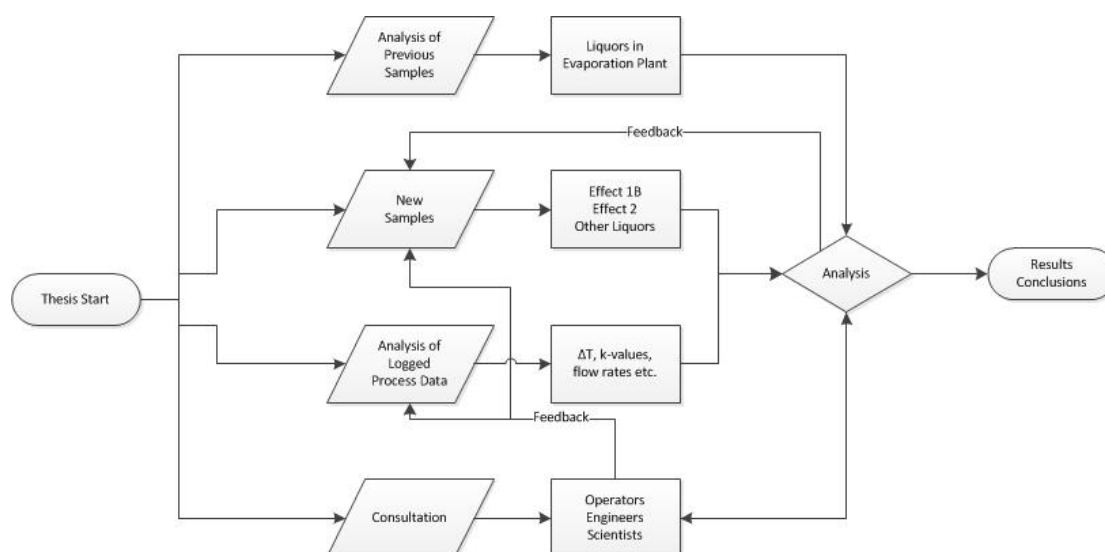

Figure 4   Schematic drawing of the method

Another way to analyse the data was to divide the operating conditions at the evaporation plant into two scenarios. In the first scenario the plant runs well without large fouling or scaling problems and in the second scenario the plant has problems with fouling or scaling leading to short washing intervals. The idea was then to gather as much data as possible about the operating conditions of the evaporation plant, operator input and process data in surrounding parts of the pulp mill and group them into the two different scenarios. These two scenarios could then be compared and any differences could be further investigated.

4.1 Mapping of fouling problems at Södra Cell Värö

To get a clear picture of the experienced fouling problems at Södra Cell Värö a survey was conducted where operators and engineers at the evaporation plant were interviewed. This provided a good basis for hypothesis around what might affect fouling that could be further investigated.

4.2 Sample series of black liquor

The analysed samples were taken out before and after effect 1B and effect 2. This was to see how the composition of the dry solids content of the black liquor changes over the effect. To be able to get a good measurement it is very important to get a clear picture of the time it takes for the black liquor to travel through the evaporation plant. When this was determined one sample could be taken before the black liquor enters the effect of interest and then with help of the residence time another sample could be taken after a certain time had passed on the outflow of the effect.

The samples were analysed for, $[SO_4^{2-}]$, $[CO_3^{2-}]$, $[Na^+]$, $[K^+]$, $[Ca^{2+}]$, [fibres], soap, total organic content (TOC) and dry solids content. This was decided since they are the substances or factors considered to have the largest effect on the fouling and scaling. Potassium is not a scaling component but can be used as a trace element which is useful to calculate the inlet flow to an effect if the outlet flow is known or reverse.

4.2.1 Sample positions

The sample into effect 2 was taken out from valve 204-26 right after the liquor preheater and the sample out of effect 2 from valve 204-22 on the pressure side of the outlet pump. Instead of one sample tap in to effect 1B three samples were used and the composition of the inlet to effect 1B was calculated by analysing the three samples and using their respective volumetric flow rates. One sample of the crystal liquor right before it enters the inlet to effect 1B using valve 208-25. One sample of the bio sludge located on the pressure side of the pump used to pump it to the inlet of 1B using the standard sample tap for bio sludge and the sample out of effect 2. One sample was also taken of the outlet from effect 1B from valve 208-28. The sample layout can be seen in figure 5.
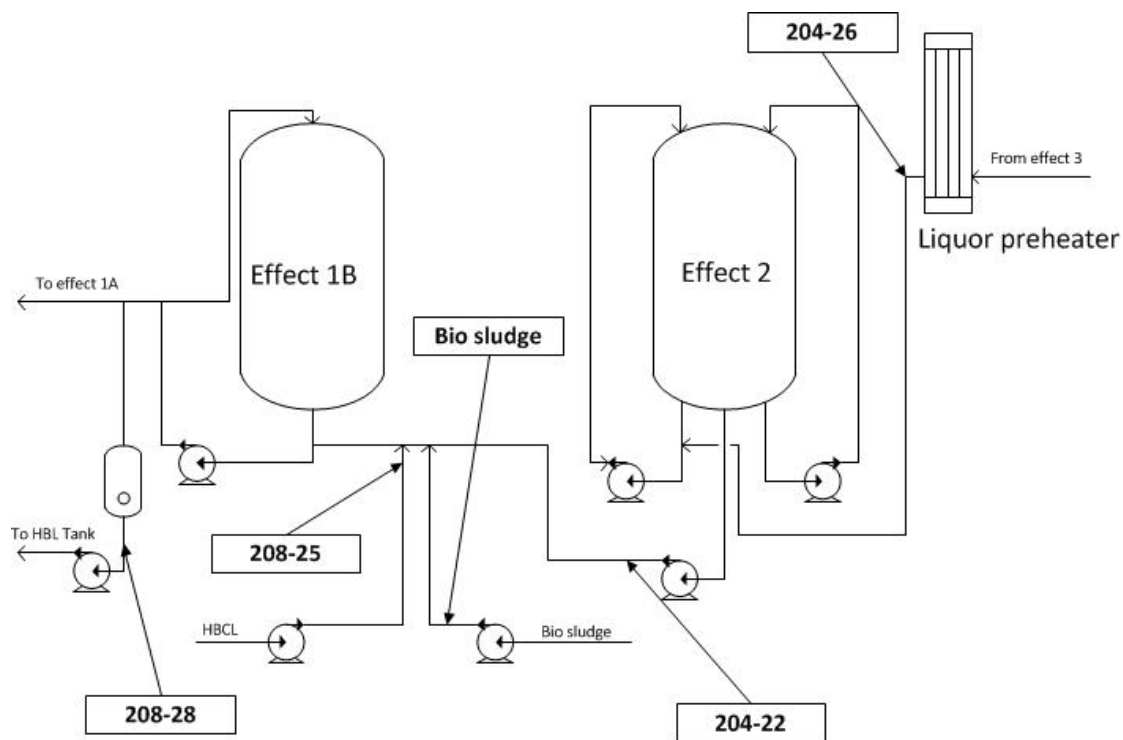
Figure 5   Schematic layout of sample tap positions

In the beginning another sample layout was tested using only in and out samples of the different effects. This configuration did not work because the sample taken out before effect 1B was not considered to be representative for the inlet to effect 1B. The explanation for this is that the sample was taken out on the inlet pipe approximately 1 m after the crystal liquor had entered the pipe. Therefor the inlet sample was not uniformly mixed. The sample before effect 1B was taken out from valve 208-34 right before the liquor enters the suction side of the recirculation pipe on 1B. A schematic layout of the initial sample taps can be seen in figure 6.

Figure 6   Schematic layout of initial sample tap positions

4.2.2 Residence time

In order to analyse the same liquor as it goes in and out of an effect the internal residence time in an effect must be known. The internal residence time in an effect is defined as the total volume of the evaporator effect (which includes the volume of the lower liquor chamber, the flash tank, all the piping and the volume of liquor on the heat 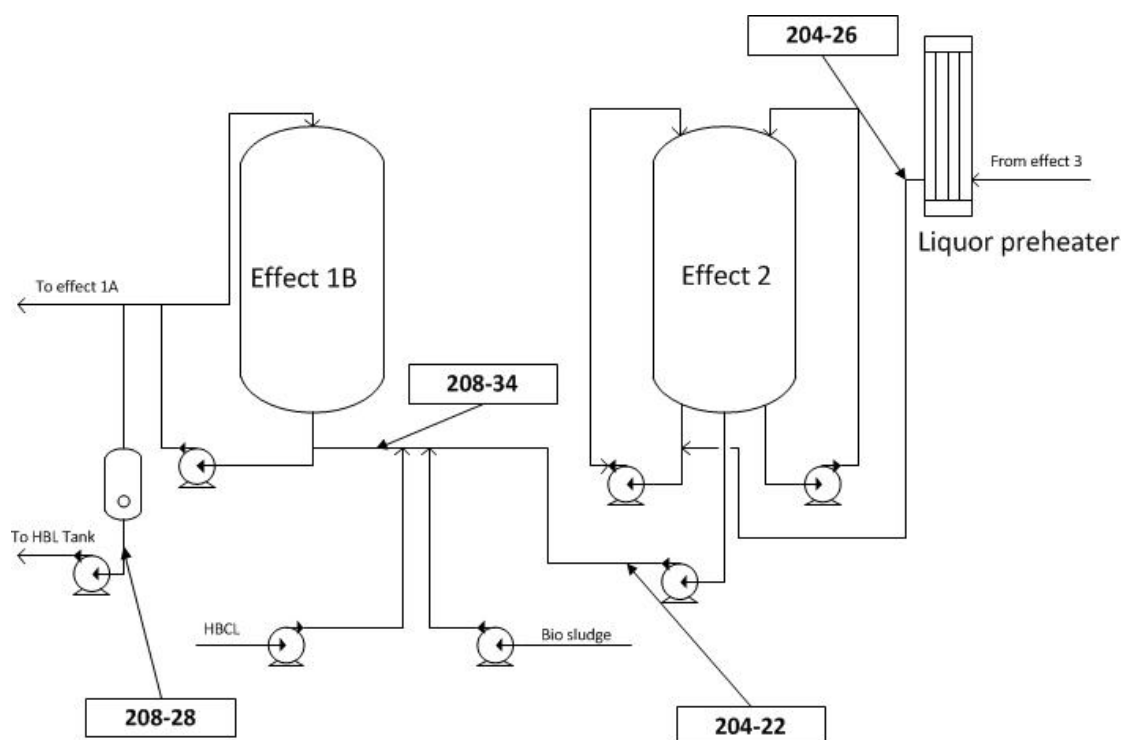transfer surfaces) divided by the volumetric flow rate out of the effect. To determine the volume of the liquor in the lower liquor chamber of the effect the percentage shown in the process control system was used. This percentage is based on a height in the effect which had to be recalculated to a volume. The bottom of the effect consists of an end cap constructed in compliance with a standard for pressure vessels called SS 482 having a certain geometry. The volume of the flash tank was calculated in the same way but because there are insufficient drawings it was assumed to be a vertical cylinder. When it comes to the piping this was calculated with help of pipe isometric drawings where the length and diameter of the pipes are shown. The volume of the liquor on the heat transfer surfaces was approximated with the effective heat transfer area and an average film thickness (Alterby, 2011). For the detailed calculations of the residence time for effect 1B and 2 see appendix 1.

4.2.3 Solubility measurement of black liquor

To measure the solubility limit of the black liquor in the evaporation plant a laboratory setup as seen in figure 7 can be used.
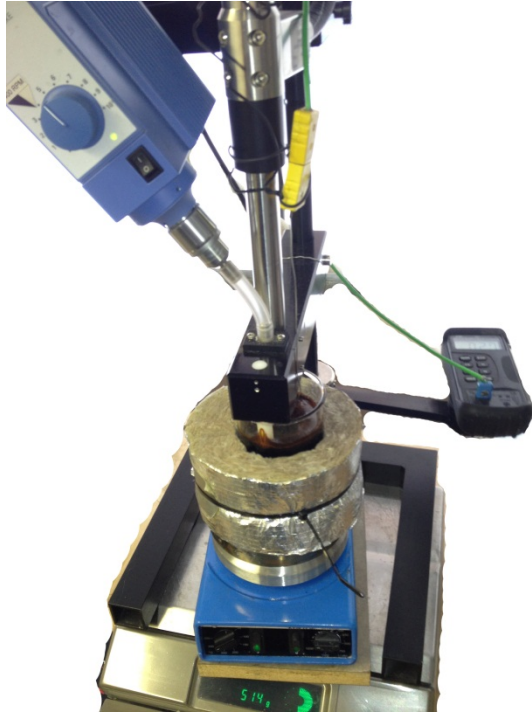
Figure 7   Experimental setup for solubility measurement of black liquor.

The experimental equipment is placed on a scale that was then tarred without the black liquor. Then black liquor with a known dry solid content was poured into the beacon. The initial weight of the black liquor is recorded. The heater and the stirrer were then turned on and eventually water started to evaporate from the sample. The scale was connected to computer software enabling the weight to be logged. As water evaporated the weight decreased and based on the initial dry solid content of the sample the instantaneous dry solid content (DS_t) can be calculated as:

$$DS_t = \frac{DS_i * m_i}{m_t} \qquad (5)$$

Where DS_i is the initial dry solid content, m_i is the initial sample weight and m_t is the weight at time t.

An instrument to monitor particles in the black liquor (Lasentec FBRM) was also used and connected to software which logs the size, distribution and number of crystals in the sample. When passing the metastable limit a large amount of crystals will be formed and detected by the Lasentec. Since the Lasentec uses a laser beam to measure the particles as the cord lengths it is difficult to get reliable results if the black liquor is very dark.

4.3 Method for evaluation of process data to map scaling

To evaluate how often scaling takes place in an effect, process data were imported from the control system to an excel file and analysed. Data points, i.e. time stamps, could then be found and used to gather other process data to see if any similarities could be found between different cases of scaling.

Process data for differential temperatures, k-values and wash liquor flow were imported to an excel file with 2 minutes intervals. Suitable values for the following criteria's were then used to find rapid scaling leading to a wash.

- The k-value should drop by a certain percentage in a certain time (i.e. the value studied should be a certain percentage less than the average value for a number of previous data points)

- The wash liquor flow should be zero at the point studied

- The k-value should be below a certain value not to include declines following a wash when the k-value is very high

- A wash should be carried out within 90 minutes from the studied data point to fulfil that the scaling leads to a wash

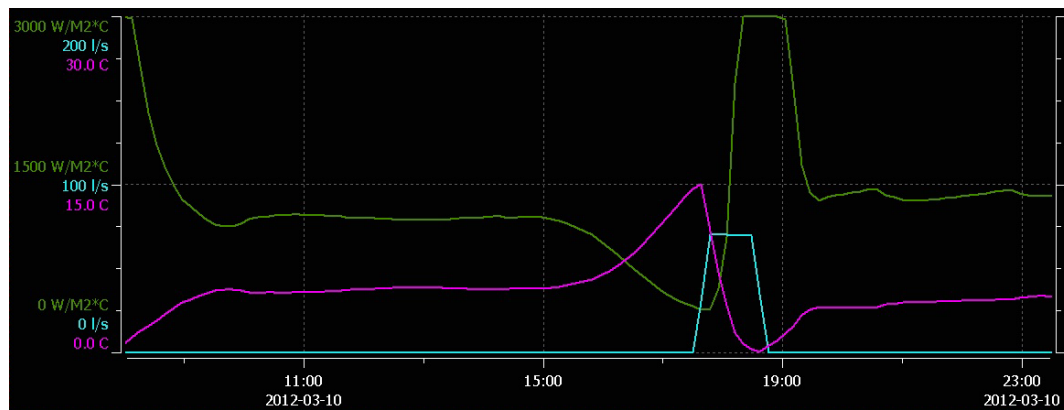Figure 8 below shows what the process data looks like with the above criteria's fulfilled.

Figure 8   *Showing steep decline in k-value(green) for an effect with steep increase in differential temperature(purple) leading to a wash(light blue)*

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5 Results and Discussion

The results presented here begin with the mapping of historical fouling problems at Södra Cell Värö (section 5.1). In section 5.2 the results from the old liquor samples analysis are presented followed by the results from the scale deposit sample analysis in section 5.3. Section 5.4 presents the results from new samples that were taken out to complement the old liquor samples.

5.1 Mapping of historical fouling problems at Södra Cell Värö

Below are the results from mapping of process conditions and interviews with personnel at Södra Cell Värö that was carried out to find possible reasons for the fouling problems in the evaporation plant.

Since the installation of the new evaporation plant in November 2009 some problems with fouling have occurred. During a 2 week period in the beginning of March 2010 the effects 1A, 1B and 2 were repeatedly scaled. Mainly water soluble scales were formed and the problem was resolved by short washing intervals leading to production losses due to lower availability. During this time, the plant operators took out daily samples at 8 different locations in the evaporation plant which were analysed at the plant laboratory for sodium carbonate, sodium sulfate, dissolved calcium, silicon dioxide and aluminium. Throughout the year of 2010 more samples were taken out in some of these sample positions. Samples of scales were also sent to analysis. The scales analysis showed that it was mainly made up by calcium.

In the early operational phase after the installation of the evaporation train there was a problem when effect 1A and 1B were being washed. These effects were being washed at the same time. The fresh steam was kept at the same flow rate as during ordinary operation. The feed to effect 1B is normally intermediate thick liquor coming from effect 2 with a dry solid content of 47.2% but upon switching to the wash sequence the feed is changed to seed liquor with a dry solid content of 19.5%. The normal dry solid content of the firing black liquor out from 1A is 75% and sent to the firing liquor tank but with the change in feed the dry solid content started to drop. When it dropped under 70% it was no longer sent to the firing liquor tank. Instead it was recycled back to the collection tank or the seed liquor tank. This lead to problems with thickening of the seed liquor giving a plug flow of liquor through the system with a too high dry solid content that the control system could not handle. To cope with this today when the dry solid content drops below 70%, the heavy black liquor tank receives the liquor and when the dry solid content drops below 50% the seed liquor tank/collection tank receives the liquor thus avoiding having a high dry solid content in the weak liquor end of the evaporation plant.

The same problems occurred when effect 2 was being washed. Effect 3 is then by-passed and a liquor flow corresponding to 80% of the normal flow coming from effect 2 was fed to effect 1B from effect 3. The fresh steam to effect 1A and 1B was still the same as under normal operation giving lot of steam to effect 2. Since the wash liquor used was in this case as well seed liquor that was being circulated, the dry solid content gradually increased and the intermediate thick liquor tank was eventually filled. The only way to reduce the level in the intermediate thick liquor was to send it back to the seed liquor tank, giving the seed liquor a high dry solid content. When the washing cycle was over, this once again had a negative effect in the form of a plug

flowing through the system. These plug flows of liquor through the system created problems with fouling probably because of the shift in dry solid content making the liquor saturated with salts that could precipitate. The problems occurred in effect 2 since this is the effect that lies in the most critical dry solids content region.

Effect 2 was also at times operated at a high dry solid content because of lacking instructions on how to operate it. Since the plant was new, little experience existed in the matter.

Another problem related to the evaporation plant is the complex system for cleaning the different liquor condensates consisting of a stripper, a methanol column and a turpentine decanter. The problem with this system is that it is hard to control the methanol content of the steam going to the methanol column. The gas phase from the methanol column containing methanol and water goes through a primary condenser where the water is condensed and returned to the methanol column. The remaining gas phase goes to a secondary condenser where the methanol is condensed and taken to the methanol tank. At high loads the primary condenser cannot cope with the high steam flow and water vapour can end up in the methanol tank.

Depending on the wood raw material and the operation of the soap skimming there have been some problems with foaming when the dry solid content has been low in the last effects. The tall oil plant has also experienced problem leading to overbearing of tall oil to the tall oil plant brine that is returned to the evaporation plant. There have also been some problems with the fibre sieve resulting in a high fibre content of the weak black liquor. At times the fibre sieve has been by-passed leading to high fibre content in the black liquor that can foul the heat transfer surfaces.

One thing of interest is also that effect 2 has been more fouled on the side were the inlet stream is located. This has led to speculations about if the steam coming to effect 2 differs in some way on the different sides, but also if there are any differences in the liquor composition in the different recirculation pipes.

The evaporation plant is also highly affected by the caustizing plant which in turn is highly affected by the recovery boiler. One problem here is that the recovery boiler is often optimized for combustion and production of steam/electricity with green liquor as a by-product resulting in poor green liquor quality.

5.1.1 Differential temperature measurements in effect 2

The differential temperature should ideally be measured over the lamella heating surface. In reality this is very difficult so instead the temperature difference between the steam condensate and the circulating liquor is used as an approximation. Effect 1A and effect 1B only has one lamella bundle and one circulation pipe giving a good estimate of the differential temperature.

Effect 2, in contrast to all other effects, has two differential temperatures measured as shown in figure 9. They are meant to represent the differential temperature in each of the two recirculation pipes. The differential temperature for 2A measures the temperature difference between recirculation pipe A and the steam coming from the stripper. The differential temperature for 2B measures the difference between recirculation pipe B and the clean condensate (stemming from the liquor vapor from effect 1A) temperature. In the early operational phase of the evaporation plant there was no other temperature measurement than the clean condensate temperature

(T1AC) and the temperature measurement on recirculation pipe 2B (TR2B). In February 1ˢᵗ 2010 the temperature measurement on the steam coming from the stripper (TS) was installed but there was still no measurement on recirculation pipe 2A so differential temperature 2A represented the difference between recirculation pipe 2B (TR2B) and the stripper steam temperature (TS). On October 12ᵗʰ 2010 the temperature measurement for recirculation pipe 2A (TR2A) was installed and led to today's differential temperature 2A.
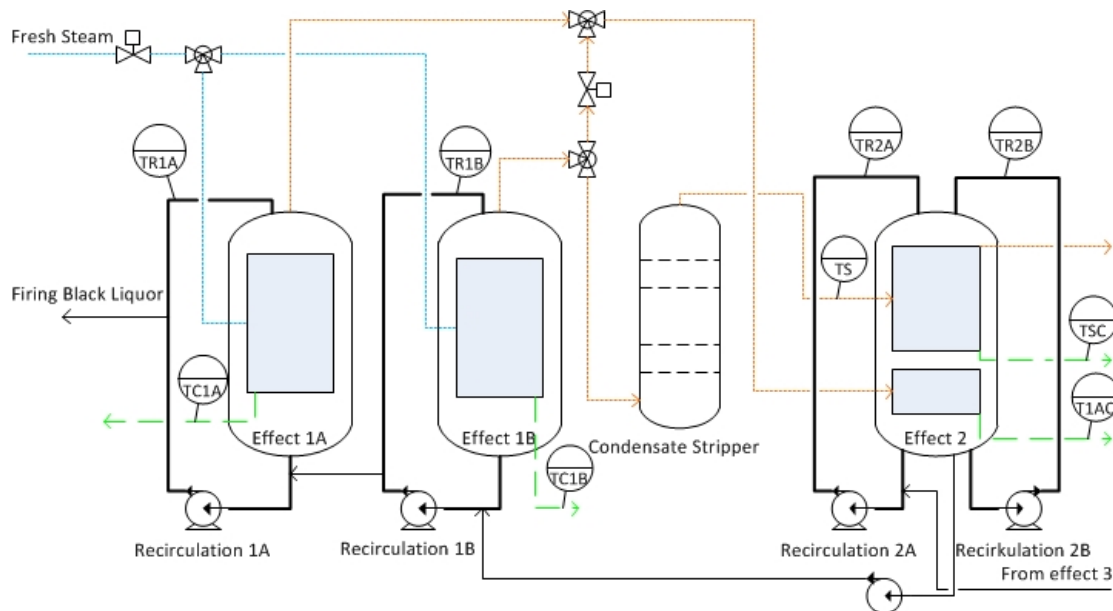

Figure 9   *Illustration of the steam flow and different temperature measurements in the heavy end of the evaporation plant. The temperature sensor TS was added 2010-02-01 and the temperature sensor TSC will be added as a consequence of this master thesis.*

If effect 1B is heavily scaled far less of the fresh steam will condensate in the lamella bundle in effect 1B which increases the steam pressure and forces the steam into effect 1A instead. Under normal operating conditions 1B uses approximately 20 kg/s of fresh steam and effect 1A 5 kg/s. During a period in March 2010 these figures reached 12.3 kg/s for effect 1B and 13.5 kg/s for effect 1A. The amount of produced liquor vapor in effect 1A increased a lot and this steam was condensed in the lamella bundle in effect 2 where the temperature measurement (T1AC) for the differential temperature in effect 2 was situated. Since this lamella bundle normally handles less steam the pressure built up and as an effect the temperature of the steam increased. This led to that each time effect 1B was heavily scaled the differential temperature in effect 2 went up indicating that it was scaled as well. Another consequence occurring when effect 1B is heavily scaled is that the control valve for the fresh steam opens to 100% giving no operational abilities for the steam supply.

The high differential temperature in effect 2 together with the control valve of fresh steam being 100% open led to the decision to shut down the evaporation plant for acidic washing of effect 2 in April 2010. When the evaporation plant was shut down there was not enough sulfamic acid to perform a complete acidic wash of effect 2 and

therefore effect 2 was once again washed with acid during the maintenance stop at the end of April. When effect 1B was inspected at these stops it was very clean.

5.1.2 Differences between side A and B in effect 2

Effect 2 has two recirculation pipes carrying the black liquor onto the lamella bundles on side A and side B in the effect. The mapping showed that these two sides had been unevenly fouled and therefore this was further investigated. Figure 9 below shows the interface for effect 2 in the process control system. The inlet to effect 2 is situated on the left recirculation pipe (pipe A) which is also the side in the effect that has been fouled most. This is contradictory in the sense that this recirculation pipe will have slightly lower dry solids content than the right one implying that it should have lower propensity to foul the heat transfer surfaces. In the bottom of the effect there is a communicating wall separating the two sides. The outlet from the effect is located on the right side of this wall. In the process control system the outlet is located on the left side of the effect as seen in figure 10.
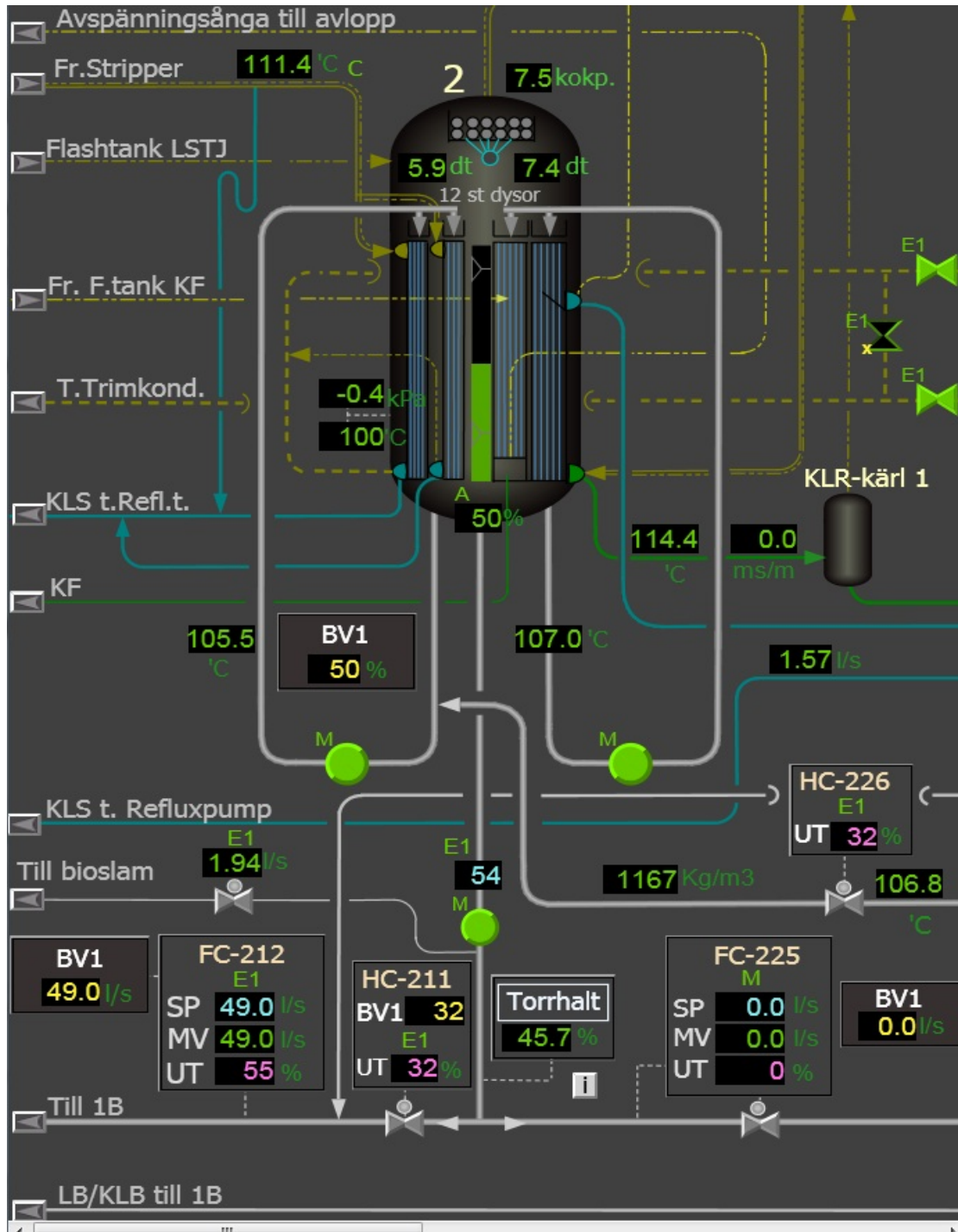
Figure 10   Screenshot from process control system showing effect 2

If the lamella bundles were situated as in figure 10 the different sides (left/right) would have different sources of steam. However this is not the case since in reality the lamella bundles are situated perpendicular to the recirculation pipes. The steam is introduced in the middle or on both sides of the effect and distributed evenly to both sides as seen in the right drawing in figure 11. Another thing of interest is the relative sizes of the lamella bundles. In figure 10 it looks as the two left side lamella bundles receiving steam from the stripper are smaller than the two right ones. In reality it is

the other way around. In the left drawing in figure 11 it is clear that the lamella bundles receiving steam from the stripper are the dominant ones.

Another thing of interest was to investigate if the recirculation flowrate differed between the two recirculation pipes. This was done using a mobile flow meter of the type Fluxus F601. The recirculation flow did not differ much between the two sides but the flow measurement was useful in the sense that it could provide data to calculate the wetting degree in the effect.

The wetting degree for effect 2 with respect to circulation pipe A was calculated to 1.39 m^3/m,h and with respect to circulation pipe B to 1.56 m^3/m,h with help of the measured flowrate. For the detailed calculations see appendix B. In a previous calculation made by ÅF the wetting degree for effect 2 was 3.0 m^3/m,h. They calculated the wetting degree with recirculation flows approximated from pump curves with help of an estimated pressure drop over the piping and spray nozzles. They recommended a wetting degree of 5.0 m^3/m,h if the effect had problems with fouling indicating that the wetting degree for effect 2 is too low. This low wetting degree is something that could increase the fouling in effect 2 since the effect does not operate ideally.
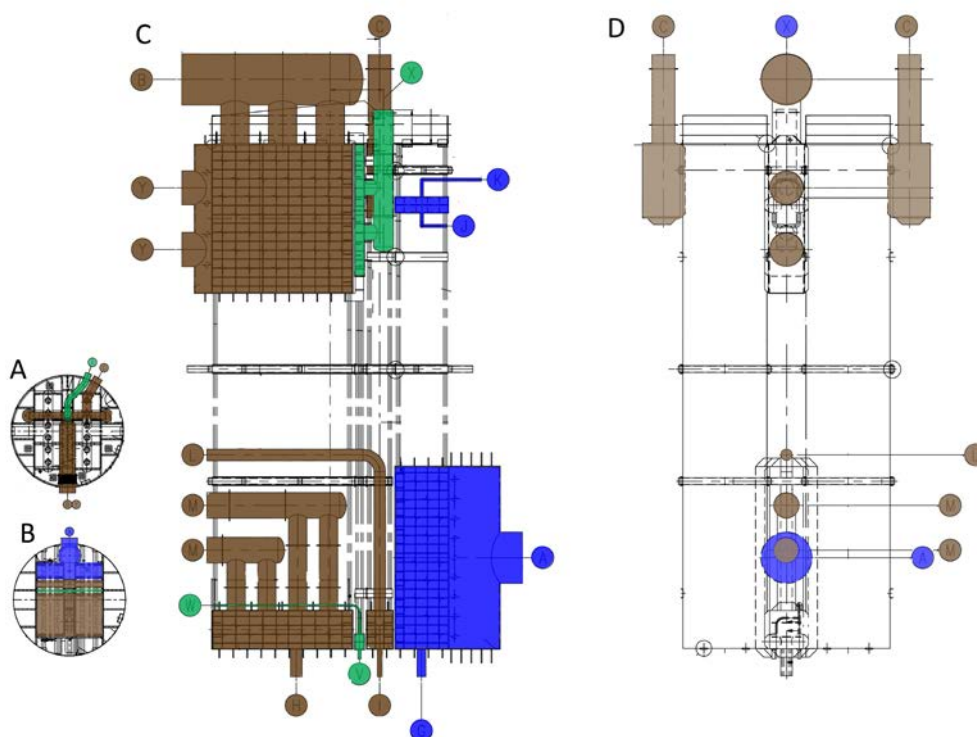

Figure 11   Construction drawings showing steam flow to different lamella bundles in effect 2. A and B shows top view of effect, C shows effect from right side and D shows front side of effect. Brown represents steam from the stripper. Blue represents steam from effect 1A with small addition from effect 1B. Green represents steam from fresh steam condensate flashing.

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5.1.3 Calcium

In the suppliers guarantee for the evaporation plant it is specified that the maximum allowed dissolved calcium content is 200 mg/kg DS in the weak black liquor. This value is often exceeded, however, when using the method of comparing the inlet and outlet of an effect it is not necessary to look at dissolved calcium. If the aim is to see what stays in the effect one can compare the total calcium content in and out of the effect. Analysis investigating dissolved calcium also involves filtering the black liquor and is therefore costly and time consuming. With a calcium content of 200 mg/kg DS rapid calcium scaling should not be a problem. Covering 1% of the heat transfer area in effect 2 with a 1 mm film would take 3 hours if all the calcium was deposited implying that pure calcium scales cannot be the cause. However calcium can still be a problem because it can crystallize as a thin layer that can disrupt the flow pattern on the heat transfer surfaces.

Since the construction of the new recovery boiler in 2002, more ash is precipitated because of better electrostatic precipitators and therefore calcium losses have decreased through the stack. There has also been a shift from using sodium formate as make-up chemical to using Alvamix containing 2000 mg/kg DS of calcium. This could be a source of increasing calcium levels in the black liquor. Since no information exist regarding the calcium content of the black liquor before 2009 it is hard to see any long term trend.

5.1.4 Fibres

Fibres can enter the evaporation plant either via the weak black liquor from the cooking plants washing liquor or via the biosludge. The fibres entering via the biosludge is approximately 500 kg/day. To keep down the amount of fibres entering the evaporation plant via the weak black liquor a fibre sieve is used. On weekdays daily average samples are taken and analysed for fibre content. It is noticeable that the fibre content has increased since 2010 according to these daily samples. The amount of fibres entering the evaporation plant via the weak black liquor can be seen in table 3.

Table 3   Average fibre content in weak black liquor

Year	2010	2011	Goal
Average fibre content [mg/l]	29	46	20

At a plant testing of a new product during this master thesis, the fibre sieve was bypassed. A sample was taken out of the unfiltered weak liquor 8 hours after the bypass and analysed for fibres. The result was 145 mg/l. This shows that a well-functioning fibre sieve is important.

5.1.5 Soap

The mapping of historical mapping problems showed that the soap content in the black liquor has been quite moderate and stable around 0.5% of the dry solids content during 2010 and 2011. At times the soap content has been much higher and could be a

possible cause for the fouling problems. The soap enters the evaporation plant via the weak liquor or via the tall oil plant brine. One reason for high soap content in the weak liquor and seed liquor could be that soap skimming is hindered by density variations caused by the batch cooking. Batch cooking leads to temperature variations in the weak liquor because the process is not at steady state. If the liquor that enters the weak liquor tank have a lower temperature than the liquor in the tank it will have a lower density and does not rise to the surface were it should be skimmed off. In appendix 4 some values for the soap content is summarized.

Since Södra Cell Värö has invested in building a new tall oil plant in April 2012, the amount of soap entering the evaporation plant via the TOP brine will probably decrease. An investment has also been made in a new seed liquor tank that will probably reduce the amount of soap entering the evaporation plant via the seed liquor in the weak liquor end. Therefore the fouling related to high soap contents, if it exists, will hopefully be eliminated once these new installations are in place.

5.1.6 Solubility Measurement of Black Liquor

To measure the solubility limit of the black liquor 8 experiments were performed according to the method described in Section 4.3. Of these experiments 2 results were performed on the same liquor taken out before effect 2 with an initial dry solid content of 34.6%. The results from these experiments can be seen in figure 12 below.
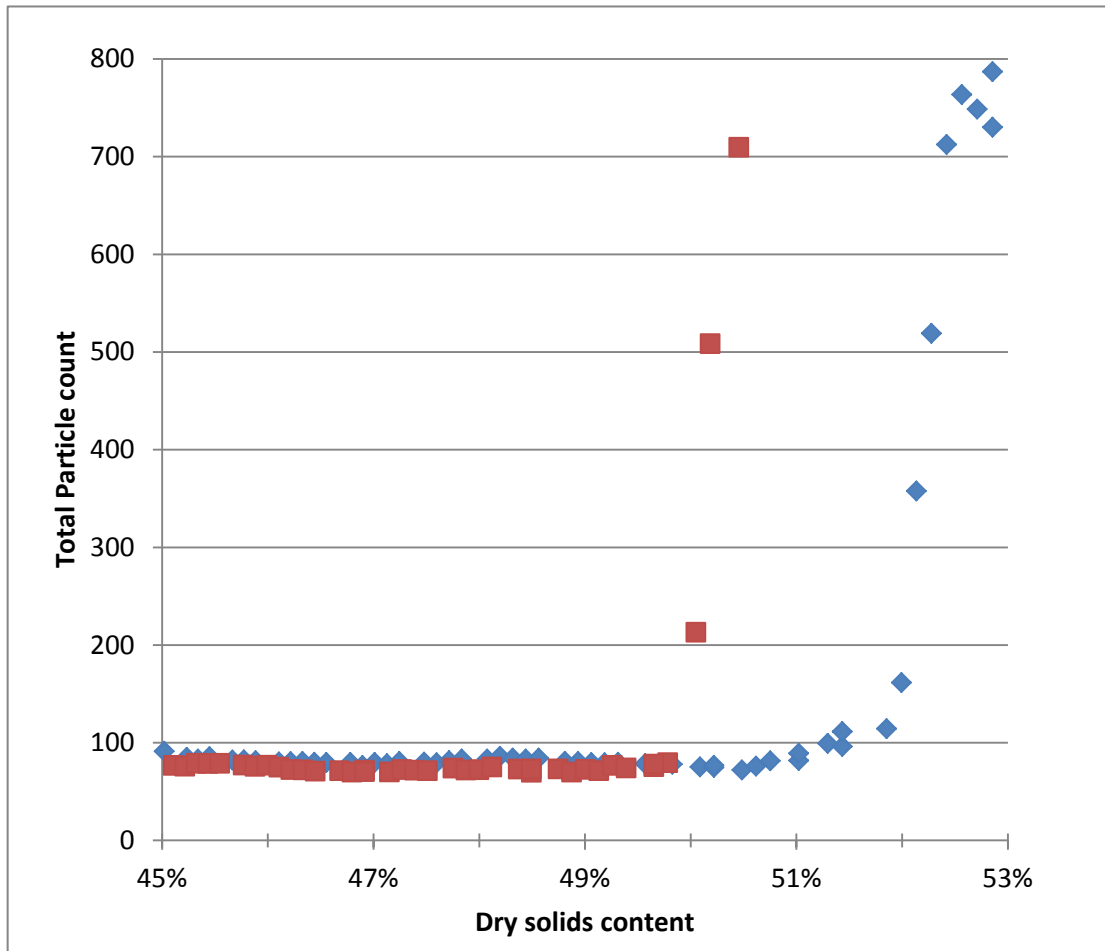
Figure 12   *Solubility results for black liquor taken out before effect 2. X-axis represents dry solid content and y-axis represents total number of particles.*

As seen in figure 12 the metastable limit is passed at a dry solid content somewhere between 50 and 52%. Previous experiments performed by Gourdon(2009C) have shown that the solubility limit lies between 2-3% lower in dry solid content. This gives a solubility limit of the black liquor at Södra Cell Värö between 47 and 50%. This is a very important result for the operation of the evaporation plant since operating an effect to close to the solubility limit could lead to catastrophic fouling caused by rapid precipitation of salts. Therefore this leads to a direct recommendation to operate effect 2 at a dry solids content below 47%.

5.1.7 Process data mapping of scaling in effect 1B

The process data mapping of effect 1B showed that no correlation could be found between the process parameters studied and the fouling taking place in the effect. It is therefore more interesting to study the black liquor composition as the fouling takes place. The effect of liquor composition will be discussed further in section 5.4.1. For all the process parameters studied see Appendix G.

If the load on the evaporation plant increases the operators will increase the supply of fresh steam and if the differential temperature then increases by the same amplitude the k-value will still remain fairly constant. If the heat transfer surfaces are being scaled the differential temperature will go up and the k-value will decrease. If the scaling is rapid the k-value will decrease rapidly. The variation in k-value can therefore be studied to look for rapid scaling more accurately than if the differential temperature was studied.

Data of the k-value in effect 1B was studied for the period 2010-02-02 to 2012-01-26 by importing it to an excel sheet with 2 minute sampling rate together with the wash liquor flow. Then the following conditions were used to study each data point.

- The k-value should drop by 2% in 8 minutes (i.e. the value studied should be 2% less than the average value for the 3 previous data points)

- The wash liquor flow should be zero

- The k-value should be below 1000 W/m^2,K

- A wash should be carried out within 90 minutes from the studied data point

This function found a number of datapoints (i.e. timestamps) indicating a rapid decrease in k-value leading to a wash. The datapoints were then studied visually in the control system to confirm that scaling had occurred. The found times of interest were then used to gather other process data that could affect scaling in order to find similarities between the different cases.

32 cases of rapid scaling were found using this method. The process parameters gathered showed great variance indicating that they had low significance for the scaling.

5.1.8 Process data mapping of scaling in effect 2

During the mapping of scaling it was found that Effect 2 does not suffer from the rapid scaling taking place in effect 1B and therefore the method used for effect 1B could not be implemented for effect 2. The scaling in effect 2 seems to be more long term with a slow build up on the lamella surfaces. Figure 13 shows the process control data for effect 2. Here it is seen that the differential temperature goes up but the time interval is several weeks compared to a couple of hours as was the case for effect 1B. The differential temperature goes up even though the effect is being washed regularly indicating that the wash sequence might work poorly.
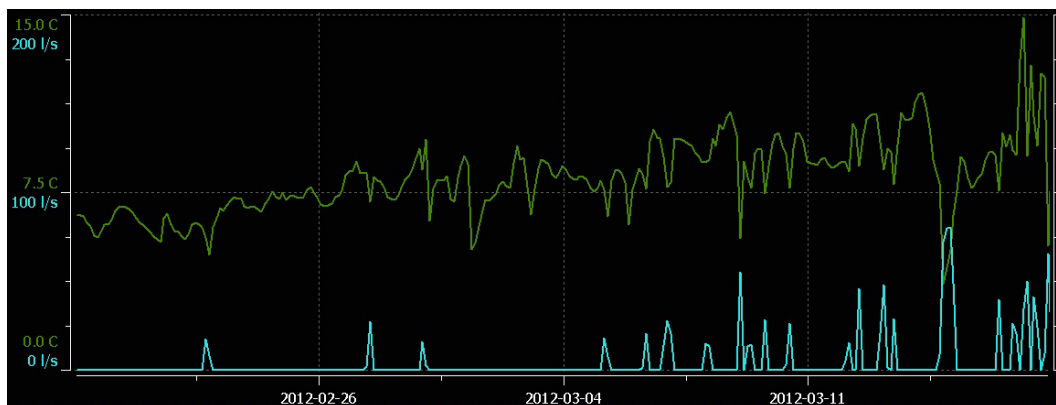
*Figure 13   Showing slow build-up of scales on the lamella surfaces in effect 2
represented by differential temperature (green) and wash liquor flow (light blue)*

5.2 Analysis of old samples

When the problems started with the evaporation plant in early 2010 Södra Cell Värö
started to take out samples at different positions in the evaporation plant. Most of the
samples were taken out during times when the evaporation plant experienced
problems with fouling. Average values from the analysis of these samples that was
taken out during 2010 can be seen in Appendix E.

68 samples of the weak black liquor were taken out. The pH seems to be stable and
over 13 indicating low risk of precipitation of lignin. The scales formed at the
evaporation plant are probably not sodium aluminium silicate since the scales formed
are water soluble. The dissolved calcium levels are high ranging from 107-796mg/kg
DS. 7 samples were analysed for soap content and 6 of these samples had a soap
content under 0.6% DS. One sample had a soap content of 2.4% DS.

The analyses show that the carbonate to sulfate ratio calculated according to eq 5,
ranges from 0.72-0.86 with 12 out of totally 68 samples over 0.83 which is the
theoretical limit for precipitation of dicarbonate.

The carbonate to sulphate ratio for the period in March 2010 when the problems with
fouling started was very high. Between 2010-03-16 and 2010-03-23 the average value
was 0.804 with values ranging from 0.622 to 0.849.

The carbonate to sulphate ratio for the period between 2010-03-16 and 2010-03-23
was even higher out of effect 2 with an average value of 0.833 with values ranging
from 0.704 to 0.911. This could be the result of scaling in effect 2 of burkeite
consuming more sulphate than carbonate ions thereby increasing the carbonate to
sulfate ratio.

The HBCL has a much lower carbonate to sulphate ratio due to the large amount of
sulphur precipitated as ash in the recovery boiler. Besides giving a better carbonate to
sulphate ratio the main task of the HBCL is to provide seed crystals for further
precipitation in effect 1B. These seed crystals must be of the same salt as the one
precipitating and if the ratio is very low the HBCL may lack dicarbonate crystals
(Frederick et al. 2004b).

The most interesting result from old sample analysis is that the carbonate to sulphate
ratio is high and this produces a risk for dicarbonate precipitation.

5.3 Scale deposit samples

The supplier of the evaporation plant and Södra Cell Värö took out samples of scale deposits during the maintenance stop in May 2011. The supplier sent part of these deposits for analysis. Södra Cell Värö also sent part of these scales for analysis. At a short stop in the factory during this thesis effect 2 were opened for inspection. Effect 2 contains two lamella bundles. On the bundle away from the inspection hatchet a lot of char-like thick scaling was found of which some samples were taken. The other bundle were not as severely fouled with seemingly only 5 lamellas scaled in a stroke from top to bottom in line with the inspection hole as seen in Picture 2. A first analysis of the sample taken showed it was easily dissolved in water and contained a lot of fibres. The sample was also sent to KCL in Finland to be analysed in the same way that the earlier scales had been.

The deposit analysis showed that the scales contained a lot of calcium. However it should be noted that the samples were taken of different consistency. $CaCO_3$-scales are very hard and from table 6 below it is clear that of the samples taken by Andritz the one with highest dry solid content also has the highest calcium content. When the dry solid content was lower the sodium content was higher indicating soluble sodium salt scales. The ash content shows how high the inorganic content of the sample is and with a lower dry solid content the organic share of the sample was higher. This could indicate fibres or lignin. The aluminium and silicon content was also as expected quite low. It is notable that the sample taken by Södra contained a quite high share of barium and strontium.

It should be noted that the dry solids content in the deposit samples are very low. One possible reason for this might be that the low wetting degree in effect 2 discussed in section 5.1.2 causes local dry out were liquor can be burnt to the heat transfer surfaces. Before the effect was opened for inspected it had to be washed with water to cool down. This water could then have dissolved the scales to some extent.

Figure 14   Picture of stroke of scales in effect 2 taken at short stop in November 2011. Scales showing as black shiny substance between the vertical lamellas.

Table 6   *Table of the most important findings in the scale deposit samples from effect 2 sent to analysis. Andritz 1-3 and Södra were taken at the maintenance stop in May 2011. The Thesis sample was taken out in November 2011.*

	Unit	Andritz 1	Andritz 2	Andritz 3	Södra	Emil
DS	% DS	64.00	50.10	25.00	72.90	45.10
Ash (550°C)	mass-% in ds.	90.70	88.00	67.50	87.80	66.70
Na	mass-% in ds.	1.57	1.96	7.86	7.45	32.83
SO4	mass-% in ds.	1.31	1.82	8.41	N/A	36.61
CO3	mass-% in ds.	19.38	24.59	72.38	N/A	21.00
Ca	mass-% in ds.	71.31	61.46	7.80	84.72	8.61
Al	mass-% in ds.	0.03	0.06	0.02	0.04	0.15
Si	mass-% in ds.	0.60	1.11	0.34	0.87	2.83

5.4 New Sample series taken out

The old liquor samples could not provide sufficient information to draw any clear conclusions related to fouling. This is because the old samples were not taken out to provide a mass balance over the effects. Therefore it was of interest to take out new samples more suitable for mass balance calculations. These samples were taken out in and out of effect 1B and effect 2.

5.4.1 Sample series of black liquor effect 1B

The approximate residence time for effect 1B was calculated to 25 minutes. The first 4 sample series for effect 1B did not work because of the initial sample layout. The values from the analysis can be seen in Appendix F. The outlet values of calcium, sodium and sulphate were higher in the outlet than the inlet liquor to effect 1B which is very unlikely. And because the inlet sample was taken out in a position where the mixing of the different inlet streams to effect 1B was insufficient the sample layout was changed as an effect of these results.

However a number samples were taken out with the new configuration during rapid declines in the k-value leading to an unwanted wash. Table 8 show values for these 4 cases.

Table 8   *Table showing carbonate to sulphate ratio and rate of scaling for cases with rapid scaling in effect 1B.*

x-ratio in liquor (CO3/(CO3+SO4))	Scaling CO3 [kg/h]	Scaling SO4 [kg/h]	Scaling Ca [kg/h]	Scaling Na [kg/h]	Scales x-ratio (CO3/(CO3+SO4))
0.618	3227	2481	37	3395	0.676
0.575					
0.744	3674	1172	-2	3879	0.834
0.698					
0.681	4241	3217	18	3667	0.679
0.684					
0.709	2406	1908	10	1616	0.669
0.730					

If these values are compared to previous research it is not likely that burkeite crystallizes but rather a mix of burkeite and dicarbonate as seen in Figure 15. Dicarbonate has a higher propensity to crystallize on the heat transfer surfaces than in the bulk phase which can be a reason for the rapid scaling taking place.
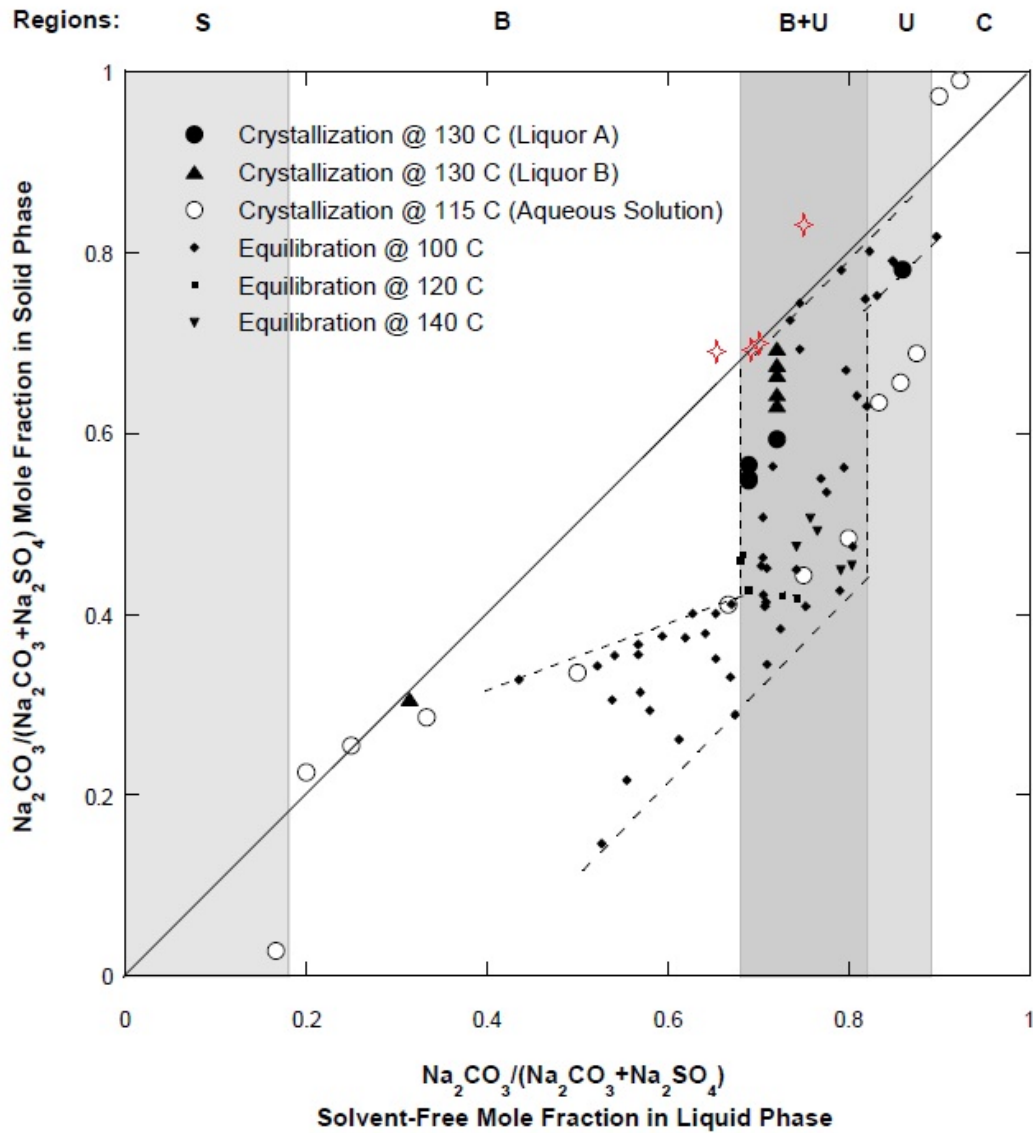
Figure 15   Comparison of the crystal compositions obtained from black-liquor crystallization at 130ºC, aqueous-solution crystallization at 115ºC, and equilibrium of solid phases with black liquors at 100, 120 and 140ºC with the four cases found in this thesis marked with red stars (Shi, 2002) S denotes sodium sulphate region, B denotes burkeite region, B+U denotes region crystallizing both burkeite and dicarbonate, U denotes dicarbonate region and C denotes sodium carbonate region.

5.4.2 Sample series of black liquor effect 2

For the samples taken in and out of effect 2 it is hard to draw any clear conclusions because of the slow fouling process. In some of the samples taken out the total mass decreases and in some of the samples the total mass increases over the effect. Table 9 below shows the values from the samples taken out. The samples show no clear trend except that the carbonate to sulphate ratio is high and lies within the region crystallizing burkeite and dicarbonate for all samples. The calcium scaling is very low and as have been discussed earlier this strengthens the argument that calcium is not

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the main source of the fouling problems in the evaporation plant. It should also be noted that there are uncertainties in the analysis of the samples which could explain the negative values.

Table 9   *Table showing carbonate to sulphate ratio and rate of scaling for samples taken out in and out of effect 2. Positive values in the scaling columns represent accumulation within the effect and negative values represent release from the effect.*

Position	x ratio in liquor [CO3/(CO3+SO4)]	Scaling CO3 [kg/h]	Scaling SO4 [kg/h]	Scaling Na [kg/h]	Scaling Ca [kg/h]
2 IN	0.730				
2 OUT	0.744	220	369	817	3
2 IN	0.680				
2 OUT	0.690	426	459	1166	2
2 IN	0.683				
2 OUT	0.708	335	638	-335	0
2 IN	0.738				
2 OUT	0.740	310	212	743	1
2 IN	0.705				
2 OUT	0.741	-116	449	567	4
2 IN	0.771				
2 OUT	0.799	-1091	-25	1097	2
2 IN	0.743				
2 OUT	0.736	-971	-660	-4401	0
2 IN	0.805				
2 OUT	0.793	-73	-199	-1005	0

6 Conclusions

There are many factors affecting the liquor composition, for example wood raw material, cooking sequence, operation of the caustizicing plant etc. Aside from this, there are variations in temperatures, flow rates and dry solid contents of the black liquor affecting the operation of the evaporation plant.

For the liquor samples, there are difficulties in analysing the samples consistently and repeatedly. The samples need to be diluted for certain analyses further decreasing the accuracy.

All these factors imply that drawing clear conclusions is difficult, and a lot of effort need to be put in the type of analysis made in this project.

In this study it is shown that the fouling has low or no correlation with process parameters collected from the process control system. Therefore studied process parameters do not seem to affect the fouling and the most interesting conclusions can be drawn from the liquor sample analyses.

The carbonate to sulfate ratio in the black liquor is high and in effect 1B this occasionally leads to rapid precipitation of a mixture of burkeite and dicarbonate. As this rapid precipitation of burkeite and dicarbonate takes place the soap content is often high. Measures to improve the carbonate to sulphate ratio and to decrease the soap content are recommended.

The rate of fouling in effect 2 differs from the one in effect 1B. In effect 2 the rate of fouling is slower but the scales formed are not as easily washed away leading to an accumulation of scales on the heat transfer surfaces in effect 2.

The wetting degree in effect 2 is low, especially considering that it is in a sensitive position and has experiences problems with scaling. Future studies should be made in order to investigate the possibilities to increase the wetting degree.

A lot of fibres were found in the scale deposit samples from effect 2. When effect 2 is being washed the fibres are circulated in the evaporation plant leading to accumulation of fibres. These fibres come from the weak black liquor entering the evaporation plant from the cooking plant and therefore it is important with a well-functioning fibre sieve.

The solubility limit for the liquor that enters effect 2 is reached at a dry solid content of approximately 50% based on the experiments performed. This leads to a direct recommendation to operate the effect with a dry solid content out of the effect below this value.

The dissolved calcium content in the liquors throughout the evaporation plant is high compared to the guarantee value of 200 mg/kg DS. This provides favourable conditions for calcium carbonate precipitation. The scale deposit samples from effect 2 also show that they contain calcium but since the scales are easily washed away they are probably not the effect of primary nucleation of calcium carbonate.

7 Recommendations and future studies

It would be interesting for Södra Cell Värö to study the wetting degree in effect 2 further and perform more measurements on the recirculation flow. If the wetting degree continuous to be low an investment in new circulation pumps could enhance the flow pattern on the lamella surfaces and thereby decrease fouling.

It is also important to operate effect 2 at a dry solids content below the solubility limit, which in this thesis was found to be in the range between approximately 47-50%. It would be valuable to perform additional solubility measurements on the liquor entering effect 2 to strengthen the results and be able to give a more exact recommendation. With additional measurements it could also be possible to see how the carbonate to sulfate ratio affects the solubility limit. An interesting idea for Södra Cell Värö is to test operating effect 2 at lower dry solids content, around 45%, and increase the HBCL flow to have a high enough dry solid content of the liquor entering effect 1B. However this would have negative impacts on the capacity of the evaporation plant.

A more challenging task would be to improve the carbonate to sulfate ratio in the liquor. One way to do this is to use pure sulphur as make-up chemical to increase the sulphate content of the liquor. Another way is to decrease the carbonate content by optimizing the caustizicing plant. A high degree of caustizicing gives lower carbonate content in the liquor.

The problem with high calcium levels is also something that is of interest to further study and here a master thesis project investigating the total calcium flow in the pulp mill might bring clarity to means to reduce the calcium content.

To deal with the high soap content it could be interesting to investigate the flow patterns in the tank farm of the evaporation plant. Measures to improve the soap skimming like bubbling could be further investigated.

It is also important to base differential temperature measurements on the best available sensors due to the reasons discussed in section 5.1.1.

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Appendix A – Evaporation Train at Södra Cell Värö

The old evaporation plant at Södra Cell Värö consisted of 3 different lines of which one was made up by Kestner evaporators and the other 2 lines consisted of falling film effects. Installed in 2009 and delivered by Andritz the new evaporation train at Södra Cell Värö consists of 7 falling film effects that raise the dry solid content of the weak black liquor coming from the washing process from 16% to 75%. It is dimensioned to evaporate 550 t/h of water and handle a dry substance weight of liquor of 4425 t DS/d. Each evaporator is equipped with one or two circulation pumps that carry the liquor from the lower liquor container to a distribution box situated above the lamella bundle. From the distribution box the liquor flows downwards on the outside of the heat transfer surfaces, where water is evaporated from the boiling liquor. Steam is condensed on the inside of the heat transfer surfaces. In figure 1.2 a drawing of the completely expanded projected evaporation train is shown. Not all of these effects have been delivered at this time but preparations have been made for future expansion including all effects in the figure. The effects installed to produce liquor with a dry solid content of 32.1% are 4, 5, 6A, and 6B (Named 4, 5, 6 and 7 at Södra Cell Värö). The effects installed to produce medium thick black liquor (47.2% dry solid content) are 3 and 2 and the effects producing the final thick black liquor (75% dry solid content) are 1C & 1B (Named 1A and 1B at Södra Cell Värö).
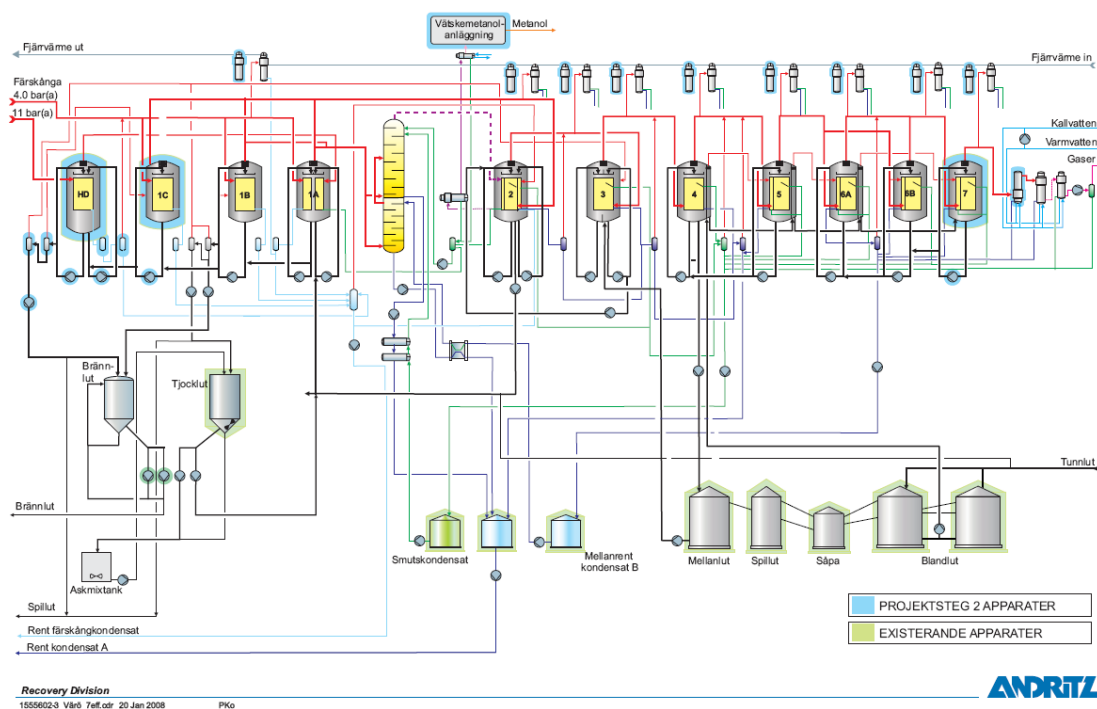

Figure 1.2   Drawing of complete evaporation plant at Södra Cell Värö (Andritz, 2009)

Appendix B – Residence time calculations

A1. Effect 2

Piping volume

Pipe from valve to recirculation suction side 2A 318LM-300:

$L = 244 + 83 + 611 + 1050 + 829 + 900 + 746 + 543 + 400 = 5406$ mm

$D = 305$ mm $= 0.305$m

$$V = \pi \cdot (\frac{D}{2})^2 \cdot L = \pi \cdot (\frac{0.305}{2})^2 \cdot 5.406 = 0.39497 m^3$$

Recirculation pipe suction side 2A 309LMTJ-600:

$L = 1675 + 2235 + 265 + 1467 + 1033 + 800 + 275 + 200 + 700 + 1100 + 358 + 1015 + 600 + 350 =$
$= 11533mm = 11.533m$
$D = 608mm = 0.608m$

$$V = \pi \cdot (\frac{D}{2})^2 \cdot L = \pi \cdot (\frac{0.608}{2})^2 \cdot 11.533 = 3.3484 m^3$$

Recirculation pressure side 2A 308LMTJ-500:

$L = 496 + 6443 + 3394 + 1222 + 13699 + 950 = 26174mm = 26.204m$

$D = 512mm = 0.512m$

$$V = \pi \cdot (\frac{D}{2})^2 \cdot L = \pi \cdot (\frac{0.512}{2})^2 \cdot 26.204 = 5.3951 m^3$$

Recirculation pipe suction side 2B 300LMTJ-600:

$L = 2300 + 1350 + 100 + 750 + 2200 + 775 + 275 + 200 + 700 + 1250 + 208 + 200 + 815 + 600 + 350 =$
$= 12073mm = 12.073m$
$D = 608mm = 0.608m$

$$V = \pi \cdot (\frac{D}{2})^2 \cdot L = \pi \cdot (\frac{0.608}{2})^2 \cdot 12.073 = 3.5052 m^3$$

Recirculation pipe pressure side 2B 306LMTJ-500:

$L = 496 + 6443 + 2970 + 1435 + 13699 + 800 = 25843mm = 25.843m$

$D = 512mm = 0.512m$

$$V = \pi \cdot (\frac{D}{2})^2 \cdot L = \pi \cdot (\frac{0.512}{2})^2 \cdot 25.843 = 5.3207 m^3$$

Outlet pipe suction side of pump 311LMTJ-350:

$L = 200 + 2200 + 2200 + 1100 + 1100 + 866 + 1000 + 1200 + 650 + 1100 + 750 + 350 + 750 + 100 + 490 =$
$= 14056mm = 14.056m$
$D = 355mm = 0.355m$

$$V = \pi \cdot (\frac{D}{2})^2 \cdot L = \pi \cdot (\frac{0.355}{2})^2 \cdot 14.056 = 1.3913 m^3$$

Total volume of piping effect 2: 19.35567m^3

Heating surface volume

Total effective area of effect 2 is:

$$A_{eff} = 7102m^2$$

Film thickness is approximated as thickness given by Ulf Alterby, Andritz (2011):

$$D = 1mm = 0.001m$$

$$V = A_{eff} \cdot D = 7102 \cdot 0.001 = 7.102m^3$$

Lower liquor chamber volume

The formula for calculation of the volume of the end cap is taken from Ekdals Plåt (2011):

$$V = 0.1298 \cdot (D_i)^3 = 0.1298 \cdot (6345)^3 = 33156568070mm^3 = 33.1566m^3$$

However the level indicator is set to approximately 50% corresponding to a height above the bottom of the vessel and not a volume. For simplicity half the volume will be used:

$$V = \frac{33.1566}{2} = 16.5783m^3$$

Flow rate

The outgoing flow from effect 2 varies with production but is approximately $0.046m^3/s$

Residence time

$$\tau_r = \frac{V_{tot2}}{q_{out2}} = \frac{43.03597m^3}{0.046m^3/s} = 936s = 16\min$$

A2. Effect 1B

Piping volume

From sample tap on inlet to 1B to recirculation pipe 301LMTJ-300:

$$L = 500 + 650 + 650 + 1050 + 1800 + 1410 + 200 + 1000 + 1000 + 750 = 9010mm = 9.010m$$

$$D = 305\,mm = 0.305m$$

$$V = \pi \cdot (\frac{D}{2})^2 \cdot L = \pi \cdot (\frac{0.305}{2})^2 \cdot 9.01 = 0.6583m^3$$

From recirculation pressure side 1B to pipe to flashtank 304LTJ-300:

$$L = 1162 + 1872 + 1741 = 4775mm = 4.775m$$

$$D = 323.9\,mm = 0.3239m$$

$$V = \pi \cdot (\frac{D}{2})^2 \cdot L = \pi \cdot (\frac{0.3239}{2})^2 \cdot 4.775 = 0.3934m^3$$

Recirculation pipe suction side 1B 305LTJ-1100:

$V = 10.5m^3$ (From construction drawing)

Recirculation pipe pressure side 1B 306LTJ-1000:

$V = 20.8m^3$ (From construction drawing)

Total volume of piping: $32.3517m^3$

Heating surface volume

Total effective area of effect 1B is:

$$A_{eff} = 6625m^2$$

Film thickness is approximated as thickness given by Ulf Alterby, Andritz (2011):

$$D = 1mm = 0.001m$$

$$V = A_{eff} \cdot D = 6625 \cdot 0.001 = 6.625m^3$$

Lower liquor chamber volume

The formula for calculation of the volume of the end cap is taken from Ekdals Plåt (2011):

$$V = 0.1298 \cdot (D_i)^3 = 0.1298 \cdot (5178)^3 = 18020250790mm^3 = 18.0203m^3$$

However the level indicator is set to approximately 50% corresponding to a height above the bottom of the vessel and not a volume. In this case level 0% corresponds to approximately 25% of the end cup. 100% level corresponds to all of the end cup and the rest is approximated as a straight cylinder. Measure height is 1750mm of which 950 mm is in end cup and the rest is in cylindrical region. For level 50% this gives:

$$V = \frac{344.5mm}{1294.5mm} \cdot 18.0203m^3 + 50\% \cdot \frac{1}{100}(\frac{950mm}{1294.5mm} \cdot 18.0203m^3 + \pi \cdot (\frac{5.178m}{2})^2 \cdot 0,80m) = 19.83m^3$$

Flow rate

The flowrate out of effect 1B varies with production but is approximately $0.040m^3/s$

Residence time

$$\tau_r = \frac{V_{1Binout}}{q_{out1B}} = \frac{58.81m^3}{0.040m^3/s} = 1470s = 25\min$$

Effect 1B from split to flash out

Piping volume

Pipe from split to flash tank LTJ from 1B 83-712-147:

$$L = 536 + 299 + 1074 + 621 + 1567 + 273 + 210 + 212 + 229 = 5021\,mm$$

$$D = 168.3\,mm = 0.1683m$$

$$V = \pi \cdot (\frac{D}{2})^2 \cdot L = \pi \cdot (\frac{0.1683}{2})^2 \cdot 5.021 = 0.1117m^3$$

Volume in flash tank

Based on 50 % level based on height of 800mm and cylinder without end cups 83-712-147:

$$D = 1100mm = 1.1m$$

$$h = 800mm$$

$$V = \pi \cdot (\frac{D}{2})^2 \cdot h = \pi \cdot (\frac{1.1}{2})^2 \cdot 0.8 = 0.7603m^3$$

50 % full gives:

$$V = \frac{0.7603m^3}{2} = 0.3801m^3$$

Flow rate

The out flow from LTJ flash varies with production but is approximately $0.012m^3/s$

Residence time

$$\tau_r = \frac{V_{toflash1B}}{q_{fromflash1B}} = \frac{0.4918m^3}{0.012m^3/s} = 41s = 1\min$$

Appendix C – Detailed wetting degree calculations

C1. Effect 2 circulation pipe A

The flowrate ($\dot{V}_{2A}$) is based on the average value for the period 2012-01-17 14:23 to 2012-01-19 09:55 measured with 10 second intervals. The lamella width (W_L) is 1.5m according to the construction drawings. There are 134 lamellas and the liquor flows on both sides.

$$\Gamma_{2A} = \frac{\dot{V}_{2A}}{W_L} = \frac{9289 l/\min \cdot 60\,\min/h}{1000 l/m^3 \cdot 2 \cdot 134 \cdot 1.5 m} = 1.3864 m^3/m,h$$

C2. Effect 2 circulation pipe B

The flowrate ($\dot{V}_{2B}$) is based on the average value for the period 2012-01-14 11:34 to 2012-01-17 11:23 measured with 10 second intervals. The lamella width (W_L) is 1.5m according to the construction drawings. There are 134 lamellas and the liquor flows on both sides.

$$\Gamma_{2B} = \frac{\dot{V}_{2B}}{W_L} = \frac{10482 l/\min \cdot 60\,\min/h}{1000 l/m^3 \cdot 2 \cdot 134 \cdot 1.5 m} = 1.5645 m^3/m,h$$

Appendix D High Soap Contents in Black Liquor

Table D1   *Soap content in different liquors in the evaporation plant*

Date	Time	Position	Soap [% DS]
2012-02-16	15:00	2 in	2,4
2012-01-19	10:48	2 out	2,3
2012-02-16	09:00	2 out	2,6
2012-03-12	10:00	2 out	1,5
2011-12-03	10:51	1B in	1,5
2011-12-04	11:56	1B in	2,1
2011-12-03	11:12	1B out	0,9
2011-12-04	12:14	1B out	3,5
2012-03-12	10:00	1B out	2,5
2012-01-19	10:47	HBCL	3,3
2012-02-06	14:07	HBCL	3,1
2012-02-01	09:37	WL	2,2
2012-02-01	11:31	WL	2,0
2012-02-01	13:01	WL	2,4
2012-02-01	14:27	WL	1,8
2012-02-01	09:44	SL	3,0
2012-02-01	11:34	SL	2,7
2012-02-01	13:04	SL	2,5
2012-02-01	14:31	SL	2,5

Appendix E Average Old Black Liquor Samples

Table E1   Average values from analysis of liquor samples at different locations at the evaporation plant taken out during 2010.

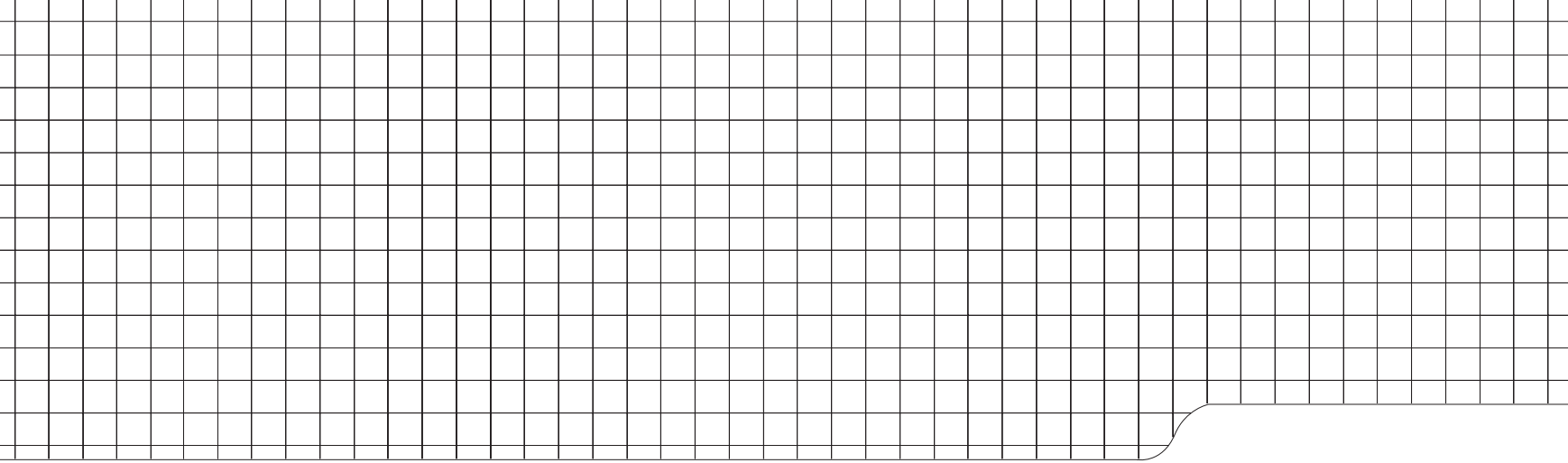|	Unit	WL	SL	Out of effect 4	IML	IMTHL	HBCL	HBL	FBL
Number of samples		68	8	8	28	28	8	10	8
DS	%	17	18	29	29	45	68	66	73
SO_4	g/kgDS	22	22	20	25	25	144	53	53
Na_2SO_4	g/kgDS	33	32	30	36	36	209	76	77
CO_3	g/kgDS	57	51	54	58	61	59	56	49
Na_2CO_3	g/kgDS	101	91	95	102	107	104	99	87
Total Ca	mg/kgDS	266	221	193	229	222	365	N/A	330
Dissolved Ca	mg/kg DS	240	159	170	179	185	319	N/A	264
Al	mg/kgDS	49	40	42	45	43	39	42	48
Si	mg/kgDS	578	306	266	443	450	330	346	298
SiO_2	mg/kgDS	1237	655	570	947	963	706	741	637
Soap	%DS	0.56	0.26	0.18	0.57	0.30	0.51	0.44	0.50
Na2CO3/ (Na2CO3+ Na2SO4)	x	0.755	0.739	0.762	0.736	0.751	0.332	0.565	0.531

Appendix F Initial Samples Effect 1B

Table F1   The initial 4 sample series for effect 1B

Date:	Position	Dry Solid Content [%]	Ca dissolved [mg/kg ds]	Ca total [mg/kg ds]	Na+ [g/kg ds]	CO3 [g/kg ds]	SO4 [g/kg ds]
2011-11-22	1B in	51.5	256	289	200	46.6	41.8
2011-11-22	1B out	67.1	198	262	198	45.0	39.5
2011-11-30	1B in	50.7	247	256	187	27.1	25.1
2011-11-30	1B out	67.1	239	243	218	42.5	48.3
2011-12-03	1B in	48.7	235	242	195	43.7	37.9
2011-12-03	1B out	65.6	350	353	197	47.9	50.7
2011-12-04	1B in	49.0	190	204	186	51.9	28.8
2011-12-04	1B out	65.4	218	276	191	46.5	36.9

Appendix G Process Parameters Studied Effect 1B

Table G1   All process parameters studied in process data mapping of effect 1B

Ash leaching of chloride ions from recovery boiler [yes/no]
Calculated residence time effect 1B [min]
Dry solids content in to effect 1B [%]
Dry solids content out of effect 2 [%]
Flow of biosludge to effect 1B [l/s]
Flow of HBCL to effect 1B [l/s]
Flow of IMTHL to effect 1B [l/s]
Fresh steam flow to effect 1B [kg/s]
k-value effect 1B [W/m2,k]
Liquor level HBL tank 1 [%]
Liquor level HBL tank 2 [%]
Liquor level in effect 1B [%]
Liquor temperature in to effect 1B [C]
Liquor temperature out of effect 1B [C]
Pressure steam room effect 1B [kPa]
Product being produced [black/blue/green]
Temperature fresh steam condensate from effect 1B [C]
Temperature steam room effect 1B [C]