CHALMERS
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Sodium Sulphate and Sodium Carbonate Crystals in Industrial Black Liquor

- New Sampling Method and First Results



Master's thesis in Innovative and Sustainable Chemical Engineering

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Department of Chemistry and Chemical Engineering
CHALMERS UNIVERSITY OF TECHNOLOGY
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Cover: Picture of the black liquor evaporation plant located at Stora Enso Skoghall.

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Abstract

A common problem in black liquor evaporators is unwanted crystalline deposits called scales occurring on heat transfer surfaces. The scales decrease the efficiency and the capacity of the evaporation plant. One of the most problematic scales are caused by precipitation of sodium salts consisting of sodium carbonate and sodium sulphate. The precipitation of the sodium salts can either create scales or free crystals in the black liquor, called bulk crystals. The influence of bulk crystals on scaling is not entirely known. This thesis aims to bring knowledge about crystals in industrial black liquor using a newly developed sampling equipment based on filtration. The crystal sampler enables inline sampling and filtration of black liquor during industrial operation. The work conducted in this thesis revolves around collecting and analysing samples obtained with the crystal sampler at the two Swedish Kraft mills Södra Cell Värö and Stora Enso Skoghall.

Three different samples were obtained at each sampling occasion; one unfiltered and one filtered black liquor sample as well as a filter cake. Measurements of dry solids content (DS), have been performed on the unfiltered and filtered samples. From the results of DS measurements, the amount of crystals in the unfiltered sample has been calculated. The amount of sodium sulphate and sodium carbonate, referred to as salt content, was determined for the filtered samples and a selection of the unfiltered samples. A ratio of sulphate and carbonate was calculated in the filter cake and filtered black liquor to determine crystal species in the filter cake.

The results indicate that the crystal fraction might be overestimated with this method, at least at Skoghall at DS over 64 %. This may indicate that other compounds than the expected sodium salts are captured in the filter in the crystal sampler, or that the crystal sample has some malfunction when sampling liquor with high DS. The results from the salt content analyses are sometimes ambiguous, which raises concerns regarding the reliability of the gained analysis results. Hence, the results regarding crystal species are also uncertain.

The most evident conclusion from the results is that the crystal sampler can be used for sampling of industrial black liquor. However, it has been concluded that the amount of bulk crystals determined from DS measurements should be verified with salt content measurements. A solubility limit for the mentioned salts in the black liquor has been established and is lower than previous findings for both Värö and Skoghall mill.

Keywords: Evaporation, Black liquor, Crystallisation, Scaling, Bulk crystals

Natriumsulfat- och natriumkarbonatkristaller i industriell svartlut - Ny provtagningsmetod och första resultaten

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Sammanfattning

Indunstning av svartlut är en energikrävande process som används på sulfatmassabruk. Ett vanligt förekommande problem är kristallina beläggningar så kallade inkruster, som bildas på värmeöverföringsytor i svartlutsindunstare. Inkrusteringen minskar kapaciteten för indunstningsanläggningen. En av de mest problematiska inkrusteringarna orsakas av natriumsalter bestående av natriumkarbonat och natriumsulfat, som fäller ut i svartluten. Utfällnaden av natriumsalterna kan antingen ge upphov till inkrustering eller fria kristaller, så kallade bulkkristaller. Bulkkristallernas påverkan på inkrustering är inte helt känd. Det här arbetet syftar till att undersöka kristaller i industriell svartlut genom att använda en ny provtagningsutrustning baserad på filtrering. Kristallprovtagaren möjliggör provtagning och filtrering av svartlut under industriell drift. Arbetet som genomförts i denna studie kretsar kring insamling och analysering av prover tagna med kristallprovtagaren på de två svenska sulfatmassabruken Södra Cell Värö och Stora Enso Skoghall.

Tre olika prover erhölls vid varje provtagningstillfälle, ett ofiltrerat prov, ett filtrerat och en filterkaka. Torrhaltsmätningar genomfördes på samtliga ofiltrerade och filtrerade prover. Resultaten från torrhaltsmätningarna användes för att beräkna kristallhalten i svartluten. Mängden natriumsulfat och natriumkarbonat, benämnt som salthalten i provet, bestämdes för de filtrerade proverna och utvalda ofiltrerade prov. En ratio av sulfat och karbonat bestämdes i filterkakan och filtrerad svartlut för att avgöra kristalltyp i filterkakan.

Resultaten indikerar att kristallfraktionen överskattas med den här metoden, speciellt för Skoghalls prover med en torrhalt över 64 %. Det indikerar att andra föreningar än natriumsalter fäller ut och fastnar i filtret i kristallprovinsamlaren eller att kristallprovinsamlaren inte fungerar felfritt vid provtagning av lut med hög torrhalt. Resultaten från salthaltsanalyserna är tvetydiga vilket väcker tvivel för trovärdigheten hos resultaten. Av denna anledning kunde inte kristalltyperna i filterkakorna bestämmas.

Den mest uppenbara slutsatsen är att kristallprovinsamlaren kan användas för provtagning av industriell svartlut. Det har dock blivit konkluderat att mängden bulkkristaller från torrhaltsmätningar bör verifieras med salthaltsmätningar. Löslighetsgränsen för de nämnda salterna i svartluten kunde bestämmas till ett värde lägre än vid tidigare undersökningar för både Värö och Skoghall.

Nyckelord: Indunstning, Svartlut, Kristallisation, Inkruster, Bulkkristaller

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Sofia Bergklint and Ida Blomgren,
Gothenburg, June 2019

Notations

Symbols

m	Mass [kg]
n	Amount of substance [mol]
DS	Dry solids content [kg/kg]
cf	Crystal fraction derived from dry solids content [kg/kg]
cf^*	Crystal fraction derived from salt content [kg/kg]
Rcs	Molar fraction of carbonate and sulphate [mole/mole]
U	Overall heat transfer coefficient [$Wm^{-2}K^{-1}$]
h	Heat transfer coefficient [$Wm^{-2}K^{-1}$]
l	Distance [m]
κ	Thermal conductivity [$Wm^{-1}K^{-1}$]

Subscripts

$unfilt$	Unfiltered
$filt$	Filtered
$diss.fc$	Dissolved filter cake
$cryst$	Crystal
d	Dried
w	Wet
BL	Black liquor
ds	Dry solid
$diss$	Dissolved salt
$water$	Water
tot	Total

Abbreviation

WBL	Weak black liquor of ∼15-20 % DS
$IMBL$	Intermediate black liquor of ∼32 % DS
$IMTBL$	Intermediate thick black liquor of ∼47 % DS
FBL	Firing black liquor of ∼80 % DS

Chemical formulas

Na_2CO_3	Sodium carbonate
Na_2SO_4	Sodium sulphate
$2Na_2CO_3{\cdot}Na_2SO_4$	Approximate composition of dicarbonate
$2Na_2SO_4{\cdot}Na_2CO_3$	Approximate composition of burkeite

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1 Introduction

The growing concerns for climate change have increased the incentives to drive industries towards more energy efficient operations (Ek et al., 2009*a*). In Sweden, the pulp and paper industry stands for more than 50 % of the total energy usage in the industrial sector (Swedish Energy Agency, 2019). The dominating pulping process of wood in Sweden and globally, is the Kraft process (FAOSTAT, 2019). In the Kraft process cellulose fibres are liberated from wood during a cooking process using alkaline chemicals dissolved in water and at elevated temperature. The yield of wood to pulp in the Kraft process is around 45 % on a dry wood basis. In addition to the pulp, the process also generates an aqueous mixture of spent cooking chemicals and dissolved wood material (Sjöström, 1993). This residue stream is called black liquor (Biermann, 1996). The dissolved material in the black liquor is rich in energy and can be incinerated to generate steam and electricity if the water content in the black liquor is decreased (Ek et al., 2009*b*). The water is removed from the black liquor by evaporation carried out in evaporator units which function as heat exchangers where steam is the heating media. This evaporation process is the most energy intensive unit operation in the Kraft process (Darmawan et al., 2017) (Gourdon, 2009).

As a mean to increase the yield from wood in the Kraft process, a biorefinery concept could be implemented with the aim of valorising the components in the wood that do not end up in the pulp (Sjöström, 1993). Some of the wood residues, that currently become a part of the black liquor that is incinerated, could be extracted from the black liquor. This extracted wood material could potentially be used as a renewable raw material for production of products that have a higher value than heat and electricity. However, this would mean less material available for combustion and generation of heat and electricity. Therefore, a more energy efficient evaporation process would be beneficial.

The work presented in this thesis revolves around crystallisation fouling creating unwanted deposits called scales, on heat transfer surfaces in black liquor evaporators. The scales become an isolating layer which decreases heat transfer from steam to black liquor in evaporator effects (Chen and Gao, 2004). Therefore, the scales limit the capacity and productivity of the evaporation operation, leading to a further increase in energy usage (Area and Felissia, 2015). Thus, there are both economic and environmental incentives for gaining more knowledge about scales and enabling improvement in operation of evaporation units in Kraft mills.

One of the most problematic type of scale is caused by crystallisation of sodium salts consisting of sodium carbonate (Na_2CO_3) and sodium sulphate (Na_2SO_4), present in the black liquor. The crystallisation of the sodium salts can create scales or free crystals in the bulk of the black liquor (Karlsson, 2017). Thus, there is a competition between growth of bulk crystals and destructive growth of scales. The

influence of bulk crystals on scaling is not fully understood. A common hypothesis is that the presence of bulk crystals decreases the amount of scaling (Karlsson, 2017). However, more knowledge about the composition and the amount of bulk crystals present in black liquor is required. The focus of the work conducted in this study revolves around a new equipment that enables sampling of black liquor from industrial evaporation processes. This technique is based on filtration and has the advantage of generating three different samples during one sampling occasion; one unfiltered sample, one filtered sample and one filter cake containing bulk crystals. The information gained from analysing these samples can give important insights on the influence of bulk crystals and how to improve the control of scaling. This new sampling technique is a portable version of an equipment developed by Gourdon (2009) used in a pilot evaporation plant, and will from here on be referred to as the crystal sampler.

1.1 Aim and Issue under Investigation

The overall aim with this master thesis is to gain a further understanding of the crystallisation of sodium salts consisting of Na_2CO_3 and Na_2SO_4 in industrial black liquor evaporation. This knowledge could be used to develop operational strategies for pulp mills to decrease the problem with scaling that may arise in evaporators. The main issue to be answered is if the amount of free bulk crystals can be determined using the crystal sampler. Further on, this study aims to determine the crystal species in and the solubility of potential bulk crystals. Samples of black liquor have been collected at two Swedish pulp mills which enabled measurements of fractions of bulk crystals in the black liquor.

1.2 Scope

The project will focus on crystallisation of the sodium salts Na_2SO_4 and Na_2CO_3, other types of scaling will not be considered. The sampling of black liquor is carried out at the evaporation plants at Södra Cell Värö and Stora Enso Skoghall. The positions available for sampling black liquor at the mills are limited due to process conditions and the fact that a too high viscosity of black liquor makes the sampling difficult. The crystals in the black liquor will be analysed by mass fraction, hence no information about crystal size will be given.

2 Background

In the following section the Kraft process is described in short. Thereafter, a theoretical background of the evaporation plant and the evaporation process is presented. Following this, the problematics of scaling and crystallisation of sodium salt scaling occurring in evaporators are presented, highlighting the principles of crystallisation and research results in the field. Finally, the overall layout of the evaporation plants of the mills Södra Cell Värö and Stora Enso Skoghall are introduced.

2.1 Kraft Pulping Process

Wood consists mainly of the three components cellulose, hemicellulose and lignin that together comprises the wood structure. Lignin is often referred to as the glue that keeps the cellulose fibres together. The main aim during a pulping process is to remove enough lignin to liberate the cellulose fibres which can be used for products such as paper and textiles. A number of different processes have been developed to access the fibres and the type of process technologies can be divided into two main groups, chemical and mechanical pulping. The dominating pulping process has since the 1950s been a chemical pulping method called the Kraft process (Ragnar et al., 2014). An alkaline mixture of sodium hydroxide (NaOH) and sodium sulphide (Na_2S), which are often called cooking chemicals, is used to treat the wood in Kraft pulping. This alkaline mixture is called white liquor. Along with the cooking chemicals, other ions such as carbonate (CO_3^{2-}), sulphate (SO_4^{2-}), thiosulphate ($S_2O_3^{2-}$) and chloride (Cl^-) are also present in the white liquor (Dang, 2017). During Kraft pulping, wood chips are boiled along with the white liquor in a digestor, normally at temperatures of 150-180 °C (Aresta et al., 2015). After the cook, the liberated fibres are separated from the residue liquor through washing. The fibres then continue to be processed in several steps, such as further washing and bleaching depending on the product, before the final pulp is produced (Ragnar et al., 2014).

To decrease the consumption of make-up cooking chemicals used at the mills, an extensive recovery cycle for the chemicals is used. A schematic figure of the recovery process is shown in *Figure 2.1*. The black liquor obtained from the outlet of the digestor does mainly consist of water due to the washing procedure, and is called weak black liquor (WBL). The black liquor is therefore evaporated, creating heavy black liquor also called firing black liquor. The evaporation is necessary for the next step in the process; combustion of organic and inorganic compounds left in the liquor in a recovery boiler. The energy released during the combustion is commonly used as a primary source for both electricity and steam to the mill. In addition to this, the spent cooking liquor is converted to a smelt containing Na_2CO_3 and Na_2S, called green liquor (Ek et al., 2009*b*). The green liquor proceeds to the causticizing process that converts Na_2CO_3 into NaOH with usage of lime, another name for calcium oxide (CaO). After the causticizing process new white liquor is generated,

hence the recovery cycle is complete, and the white liquor can once again be used in the cooking process. The calcium oxide has reacted to calcium carbonate ($CaCO_3$) or lime mud (Ragnar et al., 2014). However, due to limitations in the causticizing process, unwanted carbonates will be present in the newly generated white liquor (Chai et al., 2001).

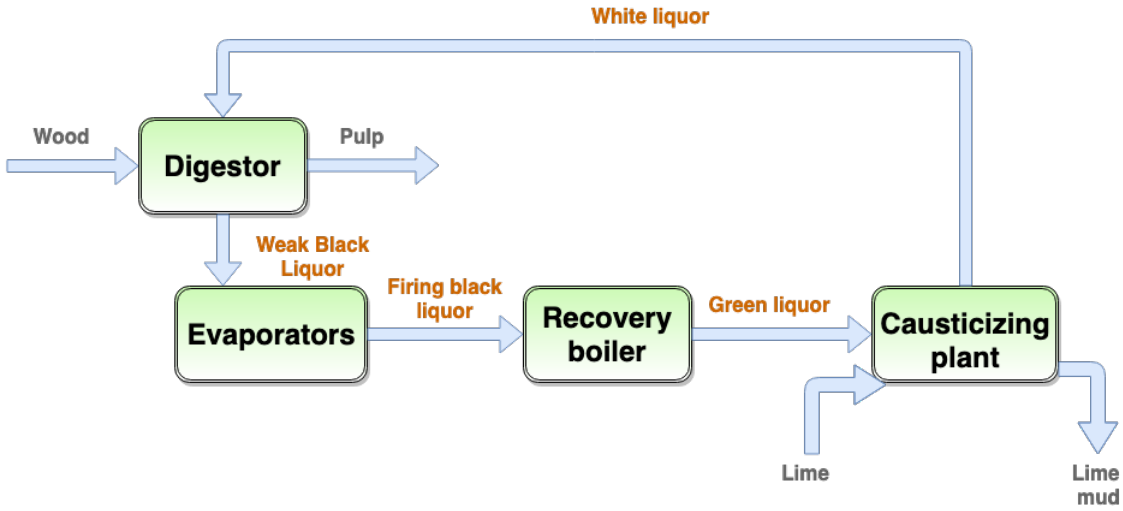


Figure. 2.1: Simplified flow sheet showing the main processing steps for the cooking chemicals in a Kraft process.

2.1.1 Properties of black liquor

The residue stream of black liquor from the digestor consists of a number of organic and inorganic compounds. The compounds mainly originate from wood and cooking chemicals. The composition of black liquor therefore varies depending on the type of wood used as raw material, the amount and composition of white liquor added to the process and the process conditions during the cooking (Ragnar et al., 2014). After the digestor, Na_2SO_4 and $NaCO_3$ are present in the black liquor due to oxidation of Na_2S respectively an incomplete causticizing process. Additionally, black liquor contains unreacted cooking chemicals, and components from wood such as organic carbon, chloride, etc. In *Table 2.1* an average black liquor composition is displayed. The values are based on analyses of black liquor from 19 different mills in North America performed by Schmidl and Frederick (1998).

Table 2.1: Rough representation of the composition of black liquor from analyses performed by Schmidl and Frederick (1998).

Analyte	**Mean**	**Standard deviation**	**Range**
Na_2CO_3 [wt%]	10	2.6	4.77-14.5
Na_2SO_4 [wt%]	6.03	4.18	1.94-16.1
Na_2CO_3/Na_2SO_4 [mole/mole]	2.49	1.67	1.94-16.1
Residual active alkali, [wt%]	5.69	0.92	0.06-12.97
Fibre[a] [wt%]	0.23	0.24	0.04-1.08
Organic carbon [wt%]	33.5	2.5	30.2-39.7
Inorganic carbon [wt%]	1.14	0.30	0.54-1.64
SO_4^{2-} [wt%]	4.08	2.83	1.31-10.9
Cl^- [mg/kg]	4810	3170	1570-12700

a Fibre measurements performed with 30 µm pore size.

Black liquor can be characterised in terms of *dry solids content* (DS). The DS is the mass percentage of dissolved wood products and cooking chemicals in the black liquor (Gullichen and Fogelholm, 1990). Thus, the DS increases as the water content of the black liquor decreases during evaporation. The DS of black liquor can be determined by exposing a sample of black liquor to heat for a certain amount of time (Technical Association of the Pulp and Paper Industry., 1996). The heat treatment results in a drying process where mainly water in the black liquor evaporates. The DS of the black liquor can then be determined by comparing the mass of the dried black liquor sample (m_d) to the mass of the original wet sample (m_w), see *Equation 2.1* .

$$DS = \frac{m_{\mathrm{d}}}{m_w} \qquad [wt\%] \tag{2.1}$$

2.2 Evaporation of Black Liquor

Due to a high heat of vaporisation of water, the latent heat of the dissolved wood and chemical residues in the weak black liquor is not sufficient to enable combustion (Ek et al., 2009*b*). Thus, more energy would be required to burn the weak black liquor than would be generated from the combustion (Gullichen and Fogelholm, 1990). However, the heating value can be drastically increased by concentrating the liquor through evaporation (Ek et al., 2009*b*). The evaporation operation aims to increase the heating value of black liquor by increasing the DS in the liquor from approximately 15-20 % (weak black liquor) to 70-80 % (firing black liquor) (Ek et al., 2009*b*). The dissolved inorganic and organic material can be separated from the water due to their differences in boiling point(Gullichen and Fogelholm, 1990).

Evaporation is accomplished by heating the black liquor to the boiling point of water using steam as heating medium. The driving force for evaporation is the temperature difference between the saturated steam and the black liquor (Gullichen and Fogelholm, 1990). The evaporation operation can be characterised by the overall

heat transfer coefficient U defined in *Equation 2.2*, expressed with the steam condensate flow (Q_{tot}), the area of the heat transfer surface (A_m) and the temperature difference between the steam and the black liquor ($T_{steam} - T_{bl}$) (Gullichen and Fogelholm, 1990). A high heat transfer coefficient indicates that heat is transferred efficiently from the steam to the black liquor.

$$U = \frac{Q_{tot}}{A_m(T_{steam} - T_{bl})} \qquad [Wm^{-2}K^{-1}] \tag{2.2}$$

A problem encountered in many pulp mills is scaling occurring on the heat transfer surfaces, which lowers the overall heat transfer coefficient. The overall heat transfer coefficient can also be expressed as in *Equation 2.3*. The terms in the denominator are expressed using the individual heat transfer coefficients for the steam and the liquor (h_{steam}, h_{liquor}) and the thickness and thermal conductivity of the wall of the heating element (l_{wall}, κ_{wall}) respectively the scales (l_{scale}, κ_{scale}). The thermal conductivity of scales is much lower than the conductivity of the metal in the heating elements (Ek et al., 2009*b*).

$$U = \frac{1}{\frac{1}{h_{steam}} + \frac{l_{wall}}{\kappa_{wall}} + \frac{l_{scale}}{\kappa_{scale}} + \frac{1}{h_{liquor}}} \qquad [Wm^{-2}K^{-1}] \tag{2.3}$$

The most common scaling occurring in Kraft mill evaporators can be divided into three groups; calcium scales, aluminium or silica scales and sodium scales (Karlsson, 2017). *Sodium scales* have been linked to most of the problems arising in evaporators (Gourdon et al., 2008) and are therefore of importance. It is mainly scales consisting of Na_2SO_4 and Na_2CO_3 that have been reported to be a problem, which usually precipitates in two different crystal forms, *burkeite* and *dicarbonate*. However, other types of sodium salts can also cause scaling, such as sodium oxalate ($Na_2C_2O_4$), but these are less common (Schmidl and Frederick, 1998). Another sodium salt called sodium sulphate carbonate was discovered in 2007, however little is known about this salt (Karlsson, 2017) and it will not be discussed in detail further in this report. Throughout this thesis, the terms *sodium salts* and *sodium scales* refer to salts composed of Na_2SO_4 and Na_2CO_3.

2.2.1 Evaporator Equipment

Black liquor evaporators used in kraft mills functionate as heat exchangers that provide indirect contact between hot steam and black liquor (Gullichen and Fogelholm, 1990). There are various designs of evaporators, but common constituents for all types of evaporators are heating elements and a vapour body. The heating elements are normally tubes or lamellas designed to promote heat transfer from the warmer condensing steam to the black liquor. The vapour body is engineered to separate the evaporated vapour from the remaining black liquor (Ek et al., 2009*b*).

There are mainly two types of evaporators used in the pulp industry, the rising film evaporator and the falling film evaporator (Area and Felissia, 2015). The former

is more subjected to unwanted deposits on heat transfer surfaces and is limited to operate at DS less than 50 % (Ek et al., 2009*b*). Since 1985 only falling film evaporators are installed in the pulp industry (Gullichen and Fogelholm, 1990), since it is less sensitive to deposits. The higher resistance to scaling is mainly due to the shorter residence time attained (Gullichen and Fogelholm, 1990).

The falling film evaporator uses either tubes or lamellas as heating elements. A schematic figure of a falling film evaporator with tubes as heating elements is shown in *Figure 2.2*. The black liquor enters the evaporator unit at the bottom where a fixed volume of black liquor is maintained (Gullichen and Fogelholm, 1990). A circulation pump raises some of the liquor from the bottom of the evaporation unit to the top where a distribution system is located (Gullichen and Fogelholm, 1990). The black liquor is then distributed onto the heating elements, flows downwards and forms a thin film that covers the heat transfer surface. Water evaporates from the black liquor film when heat is transferred through the wall of the heating element, from the steam on the other side (Area and Felissia, 2015). In evaporators using tubes as heating elements, the steam can condense on either the inside or the outside of the tubes depending on the DS of the liquor being processed (Ek et al., 2009*b*).

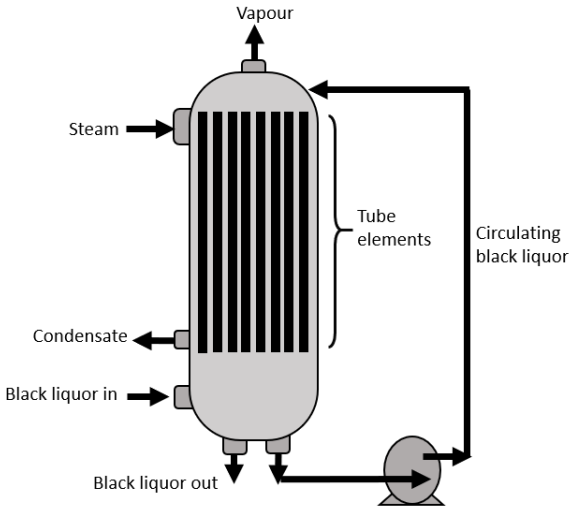


Figure. 2.2: Schematic falling film evaporator reconstructed from Gullichen and Fogelholm (1990)

2.2.2 Design and Operation of Multistage Evaporation Plant

The energy efficiency of an evaporation operation is often characterised by the *steam economy* (Ek et al., 2009*b*). The steam economy is defined as the ratio of the amount of water evaporated to the amount of live steam used (Biermann, 1996). A modern evaporation plant employs *multistage evaporation* and consists of several evaporators placed in series (Billet, 2000). This configuration allows for a better steam economy since the water vapour from one evaporator stage, from here on referred to as evaporator effect, can be used as heating medium in the next stage (Area and Felissia, 2015). Normally, a multistage evaporation plant is composed of seven evaporator

effects together composing an evaporator train (Ek et al., 2009*b*). To improve the steam economy, live steam is normally only used for the evaporator effect producing the firing liquor, this effect is often called concentrator (Gullichen and Fogelholm, 1990). The subsequent evaporator effects are conventionally numbered in their order from the concentrator along the steam flow (Karlsson, 2017). A schematic multiple effect evaporation train is shown in *Figure 2.3*.

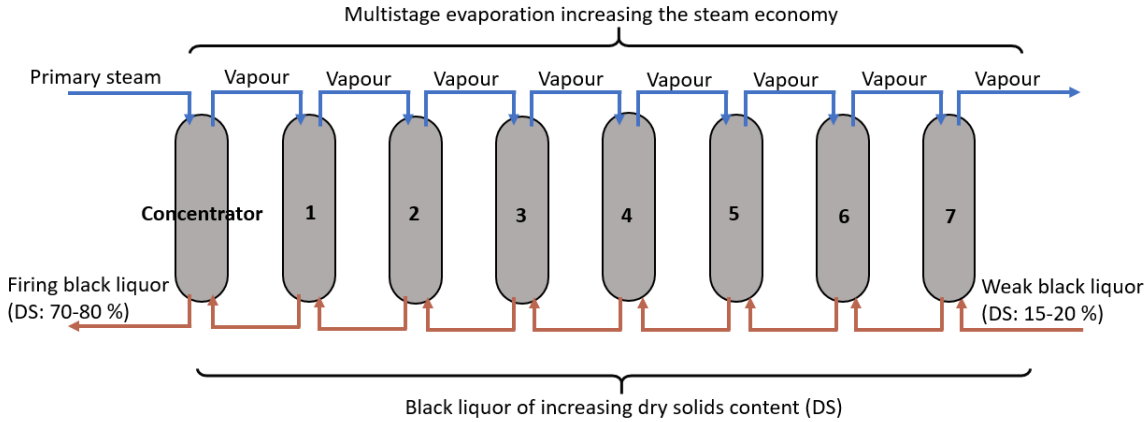


Figure. 2.3: Schematic figure of a multistage evaporation train reconstructed from Gourdon (2009).

A gradual decrease of pressure, lowering the boiling point of water successively in each evaporator effect is required to accomplish evaporation in all units in the evaporation train (Ek et al., 2009*b*). This is required since the steam discharged from one effect has the saturation temperature of the black liquor in the same effect (Area and Felissia, 2015). Thus, the temperature of the steam available for evaporation gradually decreases as the multistage evaporation progresses from the concentrator towards the last effect (Ek et al., 2009*b*).

Important properties of black liquor are viscosity, density, boiling point rise and solubility of the inorganics in the liquor (Gullichen and Fogelholm, 1990). As the DS of the black liquor increases, the viscosity becomes larger and it increases with more than two orders of magnitudes during the evaporation operation (Adams et al., 1997). Black liquor with a viscosity exceeding the pumping limit cannot undergo the evaporation operation (Gullichen and Fogelholm, 1990). However, the viscosity of black liquor is inversely proportional to temperature, and a higher temperature gives lower viscosity. For this reason, the black liquor flow is commonly counter current to the steam in the evaporator train, enabling pumping and processing of the liquor. Using this configuration, the highest DS is attained in the evaporator effect having the highest temperature (Karlsson, 2017). Similar to viscosity, the density of black liquor varies with DS and temperature, among other things. A correlation for density of black liquor at 25 °C with a DS less than 50 % is presented in *Equation 2.4* (Adams et al., 1997).

$$\rho_{25°C} = 997 + 649DS \qquad [kg/m^3] \tag{2.4}$$

2.2.2.1 Washing of Evaporators

Formed scales are removed from the heat transfer surfaces through cleaning procedures (Gullichen and Fogelholm, 1990). Evaporators experiencing sodium salt scaling are commonly washed weekly (Karlsson, 2017). The sodium salt scales are water soluble and a common cleaning strategy is to wash the evaporator with washing liquid consisting of either weak black liquor or condensate. The evaporation effects are commonly washed one at a time or in pairs. During the washing procedure the evaporator effects that are experiencing scaling are bypassed from the evaporation process (DeMartini and Frederick, 2008). This requires the remaining evaporator effects to run at other conditions than standard, to enable production of firing liquor at the end of the evaporation train. For example, the DS in the effects of the evaporator train changes during washing operations.

2.2.2.2 Addition of Residual Streams from Other Parts of the Pulp Mill

The design of black liquor evaporation plants depends on conditions specific for each mill and varies between different industrial sites. Many pulp mills add aqueous streams from other parts of the pulp mill to the evaporation process as a mean to reduce the emissions to the surrounding environment (Foran, n.d.). Evaporation plants are commonly built to allow some variations in the process connections and the positions at which the residual streams are added can vary at the mills. This makes it more difficult to conduct a material balance over process streams and predict the composition of the black liquor. Examples of these residual streams are *fly ash* from the recovery boiler and electric filters, washing water from the wood yard and *tall oil plant alkaline brine* (TOP brine). The addition of these residual streams affects the composition of the black liquor. Consultations with process engineers at the mills estimates an addition of recovery boiler ash to approximately 7 % of the total dry solids content flow to the evaporators. The TOP brine is a residue from the tall oil plant where black liquor soap is converted to crude tall oil using acidulation. The pH of TOP brine is at many mills controlled to exceed 10 to avoid lowering the pH of the black liquor too much. A feed rate of TOP brine of less than 1.5 % of the total liquor feed to the evaporator, is believed to have beneficial effect on scaling (Foran, n.d.).

2.3 Scaling During Evaporation of Black Liquor

Scaling in the evaporators is caused by crystallisation of ions. Therefore, the following section first presents a theoretical background of crystallisation to use as a basis for the following sections presenting crystallisation and behaviour of sodium salts occurring in black liquor evaporators.

2.3.1 Principles of Crystallisation

Crystallisation is a process where a substance, that is homogeneously dissolved in a liquid, transits into a solid phase and creates crystalline particles (Henley et al.,

2011). The molecules, atoms or ions that the crystal consists of are restricted to be positioned in a certain pattern, a lattice pattern. A solution can only contain a certain amount of substance before it becomes saturated. The saturation is a thermodynamic equilibrium between the solid phase and the solution and is dependant on temperature (Mullin, 2003). The limit for saturation also depends on the specific solute and solvent. When a sufficient amount of water evaporates in an evaporator effect, the solution will reach its *solubility limit*. However, it is possible to exceed the solubility limit of a solution, causing it to become supersaturated (Frederick et al., 2004). *Figure 2.4* displays a *solubility-supersolubility diagram* for a salt with an inverse temperature dependence on its solubility. The supersaturated region is divided into a metastable zone and a labile zone which can be described as different levels of supersaturation see *Figure 2.4* (Gourdon, 2009).

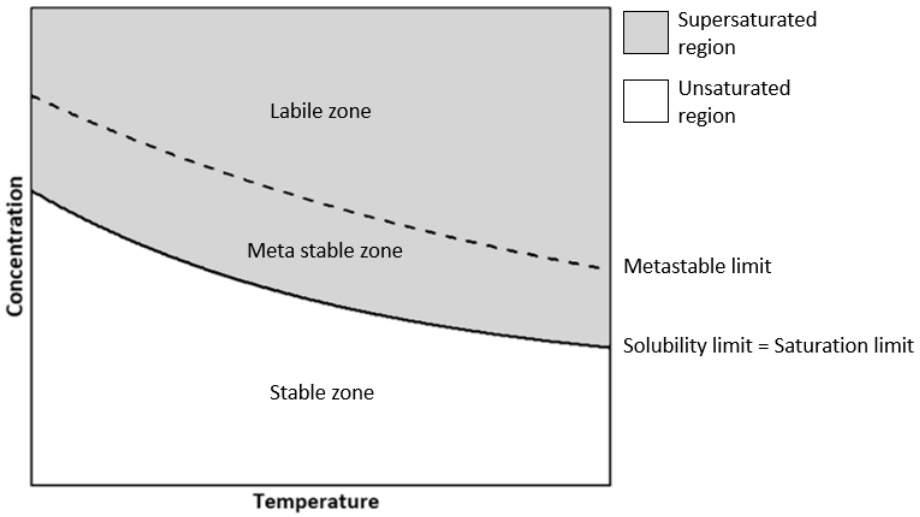


Figure. 2.4: Schematic solubility-supersolubility diagram illustrating the influence of concentration and temperature on the solubility of Na_2CO_3 and Na_2SO_4 reconstructed from Frederick et al. (2004).

The process when new crystalline material is formed in a supersaturated solution is called *nucleation* (Mullin, 2003). Above the saturation limit, in the metastable zone, the solute can crystallise on solid material already present in the liquid (Henley et al., 2011). In this zone, it is possible for so called *secondary nucleation* to occur. Secondary nucleation is created by fractions of crystalline material broken loose from already present crystals due to collisions with other crystals or process equipment. The material that is broken loose creates seeds, nucleation sites where further crystallisation can take place.

If the saturation degree of the solution is increased further into the labile zone, formation of new crystals occurs, a process that is called *primary nucleation* (Henley et al., 2011). Primary nucleation can lead to a rapid increase of new, small, crystals. If a crystal has formed, it will continue to grow as long as the solution is supersaturated. During primary nucleation, a nucleus can start to grow from a cluster of molecules consisting of the same composition as the crystal that later forms on

it, which is called a homogeneous nucleation (Mullin, 2003). If foreign matter is present in the solution, crystallisation can be initiated by this foreign substance with different composition than the crystal species. This is called heterogeneous nucleation.

2.3.2 Burkeite and Dicarbonate Crystals

The crystals that arise during precipitation of sodium salts can take different forms and can be seen as a system that is dependant on temperature and concentration. Two crucial crystals that form during evaporation are called *burkeite* and *sodium sulphate dicarbonate*, often referred to as *dicarbonate*. Burkeite and dicarbonate consists of sodium sulphate ($NaSO_4$) and sodium carbonate ($NaCO_3$) in different ratios (Gourdon, 2009). The approximate composition of burkeite is $2\,Na_2SO_4 \cdot Na_2CO_3$ and of dicarbonate $Na_2SO_4 \cdot 2\,Na_2CO_3$. Which of the crystals that is formed depends on a concentration ratio between sodium carbonate and sodium sulphate in the solution (Frederick et al., 2004). The molar ratio (R_{CS}) defined in *Equation 2.5* will be referred to as the *carbonate sulphate ratio* further on in this report.

$$Rcs = \frac{n_{Na_2CO_3}}{n_{Na_2CO_3} + n_{Na_2SO_4}} \qquad [mole/mole] \tag{2.5}$$

To enhance the understanding of the sodium salt scaling behaviour, studies in both laboratory and pilot scale have been performed by Frederick et al. (2004), Karlsson (2017) and Gourdon (2009) among others. Some studies have been done with aqueous salt solutions with different ratios of Na_2SO_4 and Na_2CO_3 to be able to isolate the scaling of the salts during evaporation. Other studies have been done on black liquor with its more complex composition. However, to the authors knowledge, few studies have been done in an industrial process concerning crystallisation of sodium salts. In *Figure 2.5* data from three former experiments with evaporation of an aqueous sodium salt solution can be seen, displayed as a *phase diagram*. The graphs shows the molar ratio between Na_2SO_4 and Na_2CO_3 for different crystal compositions. The graphs are based on data from experiments from different studies and compiled by Gourdon (2009).

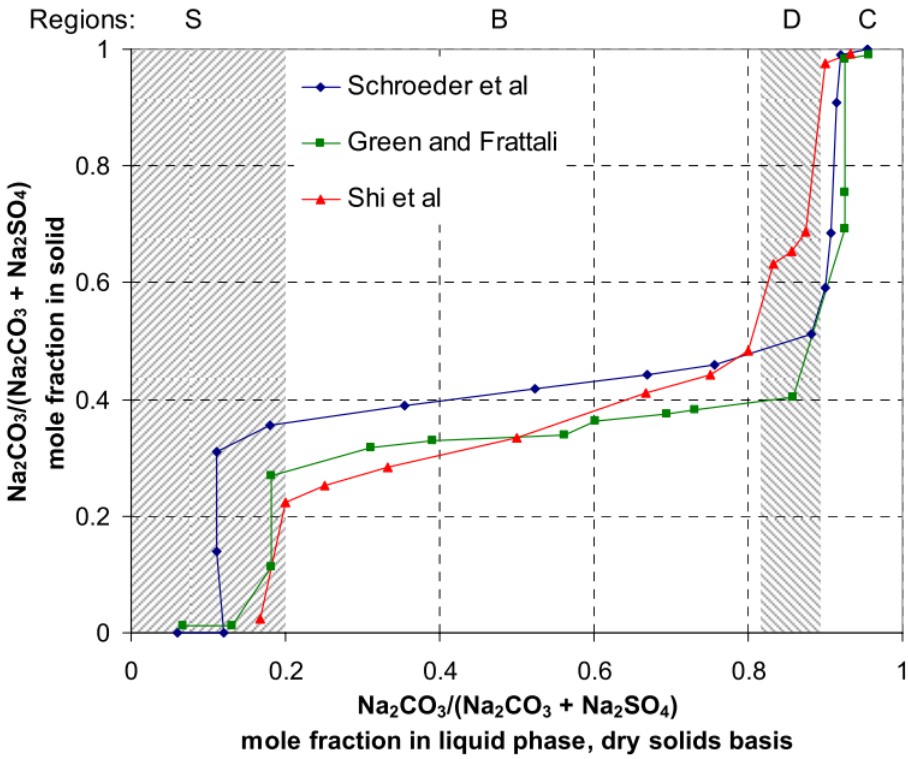


Figure. 2.5: Composition of crystals formed from aqueous solution depending on different ratios of carbonate and sulphate. S = Sodium sulphate, B = Burkeite, D = Dicarbonate, C = Sodium carbonate. Reprinted in courtesy of (Gourdon, 2009).

It can be seen that the crystallisation of burkeite in aqueous solution takes place in a region where there is much sulphate in the solution, R_{CS} is approximately 0.2 - 0.8. For dicarbonate to crystallise, a higher R_{CS} is required, around 0.8 - 0.9. Due to the different compositions of carbonate and sulphate in the crystals, R_{CS} in the solution will change during crystallisation and shift either to the right or left in the phase diagram, depending on what species that crystallises (Shi et al., 2003).

Phase diagrams for black liquor shows a similar behaviour, but has a lower solubility than aqueous solutions of sodium sulphate and sodium carbonate salts (Gourdon, 2009). Since the composition of black liquor changes with process conditions and is dependant on upstream parameters in an industrial process, it is difficult to control what R_{CS} there is in the solution, hence which type of crystal species that will crystallise. A phase diagram for black liquor has been presented by Frederick et al. (2004) who suggest five regions for precipitation of sodium salt species depending on the mole ratio R_{CS} in the solution, see *Figure 2.6*. In the region of 0-0.17 mole % sodium sulphate is expected to precipitate. In the region of 0.17 - 0.68 mole %, burkeite is expected to precipitate. Both burkeite and dicarbonate are expected to precipitate in the region 0.68-0.82 mole %. In the second last region from 0.82-0.89 mole % dicarbonate is expected to precipitate. In the last region ranging from 0.89-1 mole %, sodium carbonate is expected to precipitate.

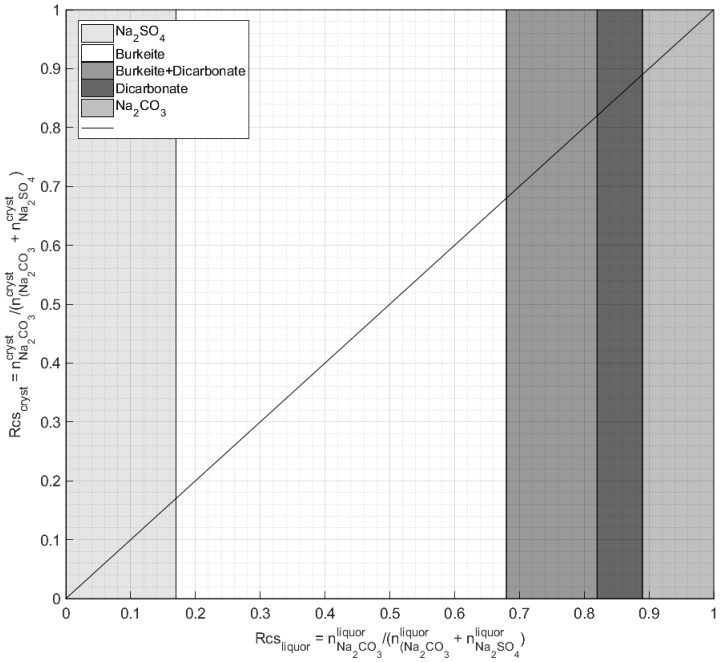


Figure. 2.6: Composition of crystals formed from black liquor depending on the ratios of carbonate and sulphate in the solution.

Further on, studies in a pilot plant have indicated that burkeite and dicarbonate affects the scaling of heat transfer surfaces differently, and that dicarbonate contributes to the more severe ones (Gourdon, 2009). It could indicate that it is preferable to evaporate black liquor at a low R_{CS} to favour the crystallisation of burkeite above dicarbonate. Therefore, it is of interest to understand which type of crystal that causes scaling in an evaporator unit on a mill. From a phase diagram such as *Figure 2.6* it is possible to evaluate what crystals that have formed if the R_{CS} of the crystals and the R_{CS} of the solution are known.

Previous experiments with black liquor in a pilot plant have shown that salts in the black liquor crystallise around 50 - 85 % DS depending on operational conditions. Primary nucleation can take place at two regions, one first at approximately 50 % DS and a second at 65 % DS (Karlsson, 2017). It was shown that the lower region (50 % DS), had a higher scaling rate. It has also been shown that after the point of crystallisation, the rate of scaling does not increase even if the DS is increased (Karlsson et al., 2013). Hence, there are mainly two points in the evaporator train that are critical for scaling, which are in the vicinity of the two primary nucleation regions.

2.3.3 Impact of Bulk Crystals in Falling Film Evaporators

The mechanism of scaling on heat transfer surfaces is believed to be correlated to *bulk crystals* in the black liquor film in evaporators (Karlsson, 2017). A schematic figure of a cross section of a falling film evaporator with a magnified tube with

scaling and a black liquor film with bulk crystals is shown in *Figure 2.7*.

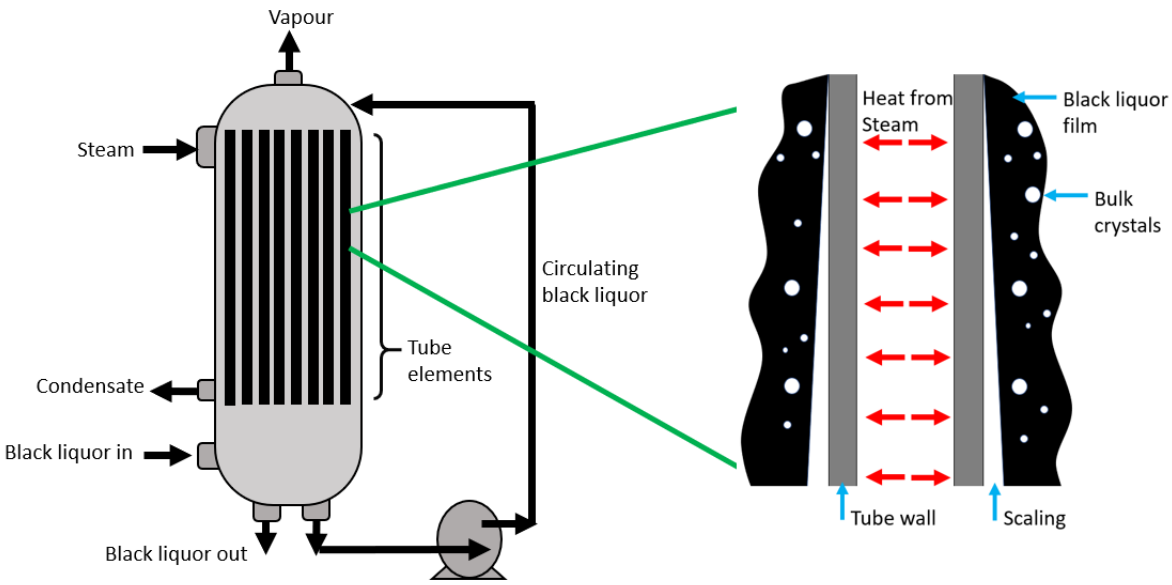


Figure. 2.7: Schematic figure of a falling film evaporator with liquor flowing outside its tubes and a magnified vertical cross section of one of its tubes reconstructed from Gullichen and Fogelholm (1990) and Karlsson (2017)

Black liquor with a DS exceeding the metastable limit usually contains a population of free crystals present in the bulk of the falling film (Zhao and Chen, 2013). The bulk crystals can influence the evaporation process with various severity mainly depending on their size and composition (Frederick et al., 2004). The composition of the black liquor film varies along the axis of the tube as the film is heated and water is evaporated (Gourdon, 2009). Thus, the DS is higher towards the bottom of the evaporator effect. As mentioned earlier, primary nucleation of salts in the black liquor occurs when a higher level of supersaturation is attained due to a concentration and/or temperature increase (Gourdon, 2009). Due to this inverse solubility of the sodium salts, the nucleation will be more severe at the heat transfer surfaces where there is a higher temperature than in the bulk. Therefore, there is a larger tendency for build up of scales on the lower parts of the hot tube walls, see *Figure 2.7*. Thus, bulk crystals may decrease the scale build up as they provide an alternative surface for salts to precipitate on (Karlsson, 2017).

The process in which a scaling layer is created on the heat transfer surface can be divided into two steps; *crystal adhesion* on the heat transfer surface and *growth* of these crystals (Mullin, 2001). Once crystals are present on the tube walls a continual growth of these crystals can occur at lower level of supersaturation, i.e. in the metastable zone see *Figure 2.4* (Karlsson, 2017). Crystals can end up on the tube wall through either primary nucleation or deposition of bulk crystals. The former mechanism requires a high level of supersaturation (Karlsson, 2017). The latter mechanism has been shown to mainly occur for bulk crystals smaller than 50 µm (Karlsson, 2017). These small bulk crystals are likely to cluster together in an

agglomeration process, which enhances the build up of a scaling layer (Mullin, 2001).

It has been concluded that the most severe scaling in the evaporator equipment is caused by primary nucleation (Karlsson et al., 2017). To overcome this issue, one can make sure that there are free crystals present in the bulk in the evaporators to enhance growth of crystals and suppress primary nucleation.

2.3.4 Solubility of Burkeite and Dicarbonate

Several attempts have been made to find a simple way to determine the solubility of burkeite and dicarbonate in industry. As previously mentioned, the amount of sodium sulphate and sodium carbonate in the black liquor will throughout this thesis be referred to as the salt content of black liquor. The solubility of sodium salts in black liquor exceeding the solubility limit can be determined through filtration and measurements of sodium sulphate and sodium carbonate content in the filtered black liquor. When the sample is filtered, bulk crystals present in the black liquor are captured in the filter. The amount of sodium sulphate and sodium carbonate present in the filtered black liquor is consequently the amount of salts that can stay dissolved after crystallisation has occurred, hence the solubility of the salts (Gourdon, 2009).

A correlation between solubility of sodium salts and DS developed by Karlsson (2007) is shown in *Equation 2.6*. The correlation was developed to give practical estimations rather than a definitive solubility and might have to be adjusted somewhat for different black liquors. The correlation gives a solubility curve, x^*, and is based on the solubility limit for the salts in pure water, 0.3283 kg salt/kg total black liquor, and that the solubility is 0 for 100 % DS. Below the solubility curve the salts will stay dissolved and above it the salts will start to crystallise.

$$x^* = 0.2431 DS_{BL}^2 - 0.5711 DS_{BL} + 0.3283 \qquad [kg\ salt/kg\ total\ black\ liquor] \quad (2.6)$$

The solubility limit for a specific black liquor can be determined using the solubility correlation for the liquor. This requires measurements of sulphate and carbonate content, where eventual crystals have been dissolved prior to analysis, and the DS of the unfiltered black liquor. With this information, a salt content line can be plotted assuming that at 0 % DS (pure water) there are no salts in the black liquor. The intersection of the salt content line and the solubility curve gives the solubility limit of the black liquor. However, in an industrial evaporation plant, sulphate and carbonate are added to the black liquor with additionat processing streams during evaporation. Therefore, the total salt content would not be a straight line.

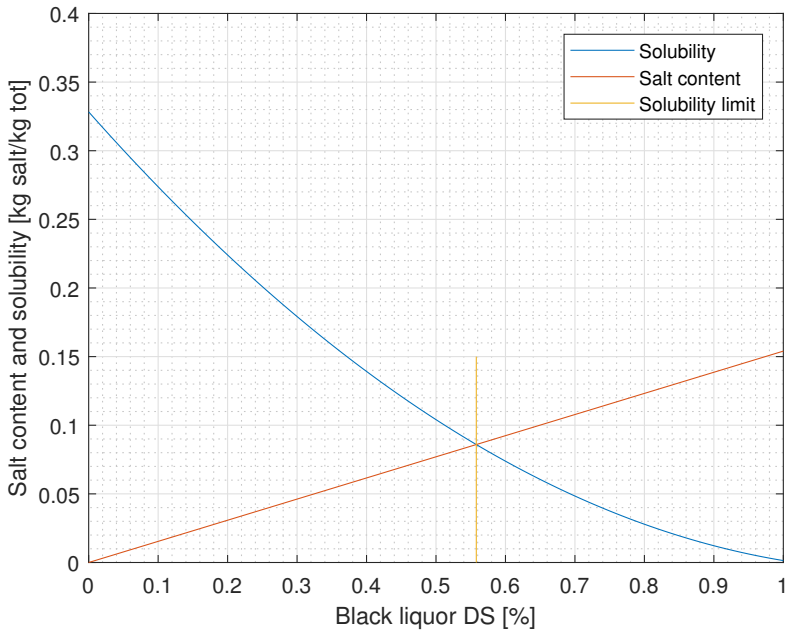


Figure. 2.8: Correlation of the solubility and dry solids content in black liquor developed by Karlsson (2017).

2.4 Evaporation at Södra Cell Värö and Stora Enso Skogshall Mills

There are differences between the evaporation processes at Södra Cell Värö and Stora Enso Skoghall. In the following section simplified flow sheets for each mill are introduced to ease the understanding of the processes and the position at which the black liquor sampling occurred. From here on, the evaporator effects at Södra Cell Värö and Stora Enso Skoghall will be denoted with a V respectively S prior to the effect number.

2.4.1 Södra Cell Värö Mill

The evaporation plant of Södra Cell Värö mill is composed of several evaporator effects, see *Figure 2.9*. The first evaporation effect is composed of three different evaporation units denoted *V-1A*, *V-1B*, *V-1C*. The weak black liquor (WBL) of 15-20 % DS enters a mixing tank where it is mixed with evaporated black liquor of 50 % DS. The black liquor exiting the mixing tank is called *feed liquor* and enters two flash chambers in effect *V-4* and *V-5* before it enters the evaporator effects *V-7* and *V-8*. Thereafter, the liquor progresses through the evaporation train in opposite numerical order. The DS of the black liquor is successively increased during evaporation and intermediate black liquor (IMBL) of approximately 32 % DS is attained in *V-4*. Intermediate thick black liquor (IMTBL) of approximately 47 % DS is attained in *V-2A*.

The evaporator effect experiencing most problems with scaling is *V-1C*. The solubility limit is exceeded somewhere between *V-2B* and *V-1C*. The crystal sampler could be connected to the process at the pressure side of a pump placed at a flash tank positioned after effect *V-1C*, see *Figure 2.9*. The DS of the liquor extracted with the crystal sampler is therefore higher than the DS in effect *V-1C*. The DS in the flash tank is around 63 % while the DS in effect *V-1C* is around 60 % at normal operation. In addition to the flash tank, the crystal sampler can be connected to effect *V-2*, see *Figure 2.9*. Furthermore, unfiltered samples of intermediate thick black liquor, IMTBL, can be extracted from the process at a built-in sampling station at effect *V-2*. The samples received from the sampling station are unfiltered and can provide information about the liquor prior to the sampling station.

Crystal liquor and TOP brine are added separately in the evaporation train. The crystal liquor is attained by mixing the fly ash from the recovery boiler and the electric filters with thick black liquor (TBL). A part of the flow out from effect *V-1C* is led to the flash tank where the crystal sampler can be connected. The flashed black liquor then continues to a thick black liquor (TBL) tank where a subflow of the thick black liquor (TBL) is taken to a mix tank where fly ash and boiler ash is added to the liquor. The mix of the thick black liquor and the ash is called crystal liquor. The crystal liquor is normally added to effect *V-1C*, but can also be added to effect *V-1B* e.g. when washing of *V-1C* is performed.

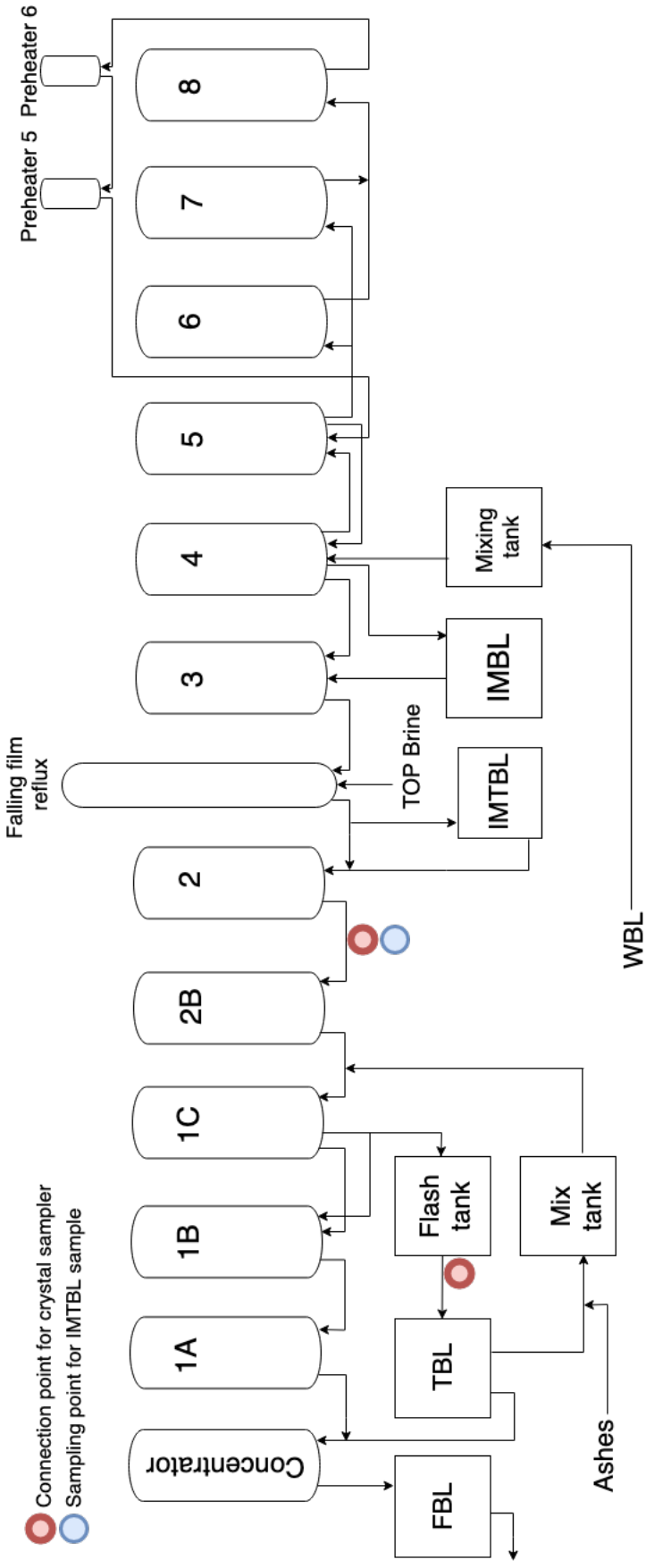


Figure. 2.9: Schematic figure of the evaporator train situated at Södra Cell Värö mill displaying the positions at which the crystal sampler can be connected with a thick solid circle and the IMTBL sampling position with a thin solid circle.

2.4.2 Stora Enso Skoghall Mill

The Stora Enso Skoghall produces Kraft pulp and *chemi thermo mechanical pulp* (CTMP). A simple schematic figure of the evaporator train at Skoghall is shown in *Figure 2.10*. Weak black liquor (WBL) enters mixing tanks where it is mixed with already evaporated black liquor. The attained feed liquor then enters effect *S-5* and proceeds through effect *S-6* and *S-7* which produces intermediate black liquor (IMBL). Thereafter the liquor is preheated before it enters effect *S-4* and proceeds through effect *S-3*, *S-2* where intermediate thick black liquor (IMTBL) is produced. The IMTBL progresses through *S-1* and finally reaches the concentrator. The first evaporator effect *S-1* has four chambers denoted *S-1A*, *S-1B*, *S-1C* and *S-1D* respectively. Both the concentrator and all chambers in the first effect are supplied with live steam.

Crystal liquor is introduced in effect *S-1D*, except when effect *S-1D* is washed, then it is introduced to effect *S-1C*. The crystal liquor is produced by adding fly ash from the recovery boiler to liquor withdrawn from effect *S-2*. Washing water from the CTMP plant with a DS of 0.5 % enters effect *S-9* and is thickened in effect *S-8*. The thicker CTMP washing water is then introduced to *S-1C*. TOP brine is also added in effect *S-1C*.

The concentrator experiences most problem with scaling. However, due to the high viscosity of the liquor in the concentrator, the crystal sampler could not be used to sample its liquor. Instead, the crystal sampler could be connected to all chambers of evaporator effect *S-1*. The connection points for the crystal sampler are marked with a solid thick circle in *Figure 2.10*. In addition to the samples that could be collected using the crystal sampler, samples of IMTBL could be collected from a built-in sampling station at effect *S-2*. The sampling station can only generate unfiltered black liquor samples without addition of crystal liquor.

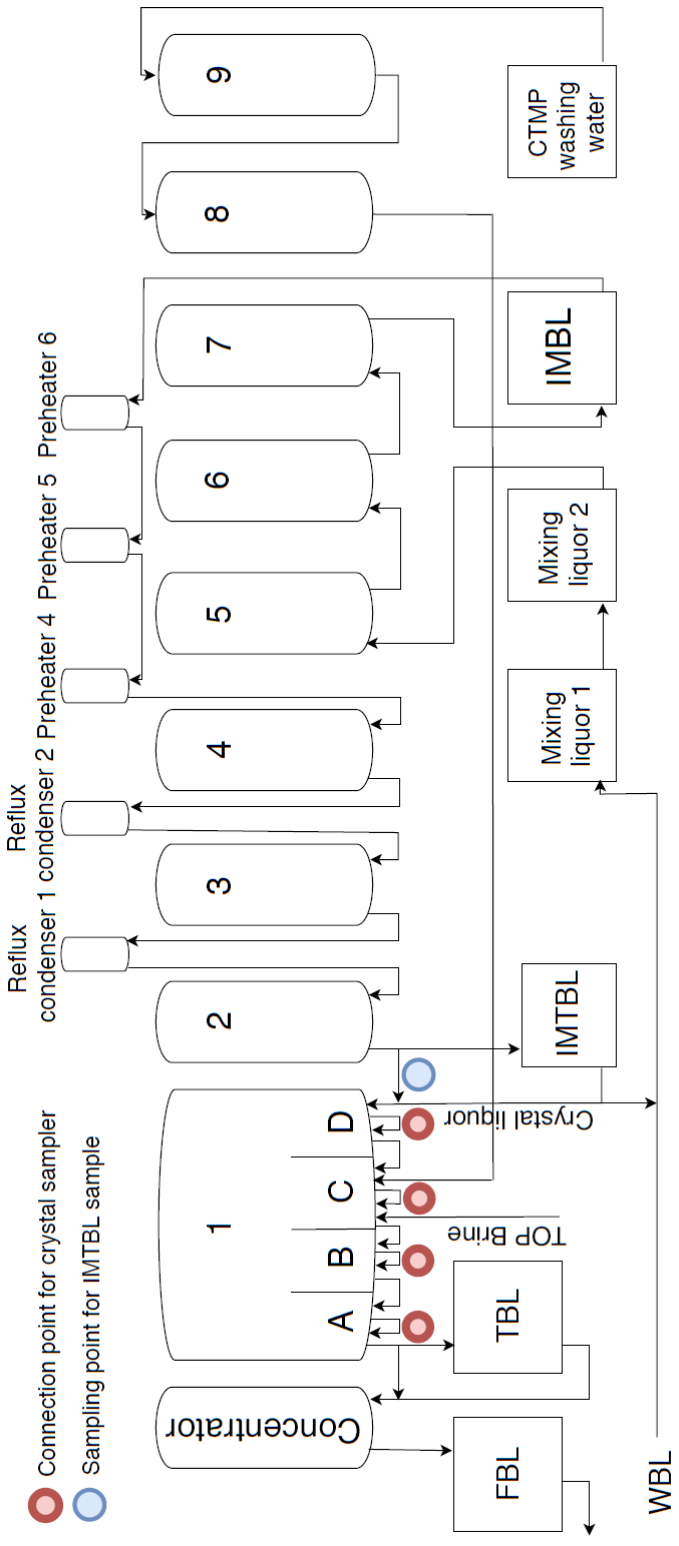


Figure. 2.10: Schematic figure of the evaporator train situated at Stora Enso Skoghall mill displaying the positions at which the crystal sampler can be connected with a thick solid circle and the IMTBL sampling position with a thin solid circle.

3 Methods

As explained earlier, the crystal sampler was used to obtain three different samples at each sampling; one unfiltered sample, one filtered sample and one filter cake containing bulk crystals built up on the filter. The obtained samples were analysed to determine the amount of bulk crystals present in the black liquor and the composition of the captured crystals. The following section presents how the sampling and the experimental work was conducted.

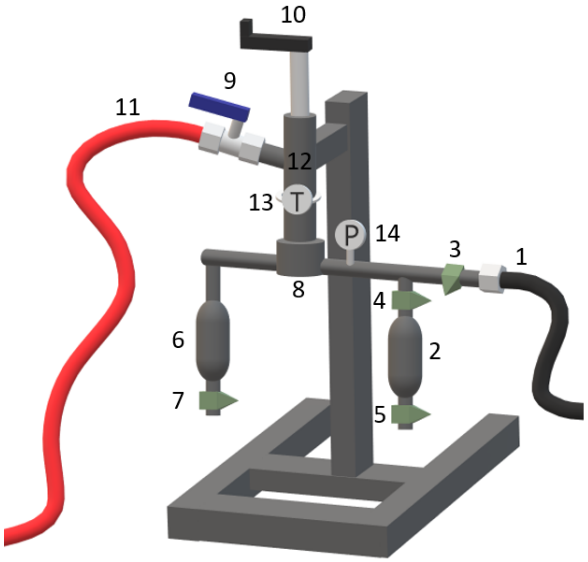
3.1 Sampling Equipment and Procedure

A schematic picture of the crystal sampler is shown in *Figure 3.1* where important parts are denoted with numbers which will be referred to from here on. The crystal sampler could be connected to a black liquor stream as long as the pressure was sufficient (1-2 bar gauge). Sufficient pressure normally prevails on the pressure side of the circulation pumps responsible for circulating black liquor in evaporator effects. Before the sampling procedure, sample bottles with leak proof lids were weighted and their masses were noted. For each sample of black liquor, two bottles of 250 ml for the filtered and unfiltered samples and one 100 ml bottle for the filter cake were required. Before the crystal sampler was connected to the process, all valves (3, 4, 5, 7, 9) on the crystal sampler were closed and the drain hose (11) was placed in a drain. The hose (1) was connected to the specific sampling position on the process line and was flushed through with black liquor to prevent errors in measurements due to old liquor in the hose. The hose (1) was then connected to the crystal sampler which enabled. When valve (3) was opened, the black liquor flowed through the equipment and exited through the drain hose connected to point (9). Before sampling of black liquor in the sample cylinders, the flow-through of black liquor was maintained for a few minutes to heat up the equipment. An approximate temperature was observed from a thermometer (13) attached to the equipment.

When the temperature of the crystal sampler had increased, the sampling was initiated. Firstly, an unfiltered sample of the black liquor was collected in sample cylinder (2) by opening its upper valve (4). When the cylinder was filled, the upper valve (4) was closed again. Immediately after, valve (3) and (9) was closed to start collection of a filtered sample. When the crank (10) at the top of the device was turned the pressure in the equipment increased. The increased pressure forced the remaining black liquor in the equipment through the filter in the filter unit (5). The filtered sample was then collected in sample cylinder (6). The sample cylinders (2) and (6) were allowed to cool down slightly to prevent evaporation of water from the black liquor when the samples were poured into the sample bottles. Evaporation of water from the black liquor could result in an error in the subsequent dry solids content measurements making the black liquor seem to have a higher DS than it

actually had.

The filter cake captured on the filter was scraped off and transferred to the 100 ml sample bottle. Thereafter, the equipment was carefully washed with water and blown dry with grease free compressed air before conducting another sampling procedure. The filter was cleaned in an ultrasonic bath and was then allowed to dry in an oven.



1. Hose connecting crystal sampler to sampling position
2. Sample cylinder unfiltered BL
3. Inlet valve
4. Inlet valve sample cylinder unfiltered BL
5. Outlet valve, sample cylinder for unfiltered BL
6. Sample cylinder filtered BL
7. Outlet valve, sample cylinder filtered BL
8. Filter unit
9. Outlet valve
10. Crank
11. Drain hose
12. Container
13. Thermometer
14. Pressure gauge

Figure. 3.1: Schematic figure of the crystal sampler with its main parts labelled with numbers.

3.1.1 Filter Units and Filters

Several different filters from *Norman filter company* and *Swagelok* have been tested during this thesis work. The filters distinguish from each other mainly in pore size and filtration area. A schematic figure of the different filters and their pore size are presented in *Figure 3.2.* Filter *a*, *c* and *d* are made of porous sintered metal, while filter *b* is made by a woven wire mesh.

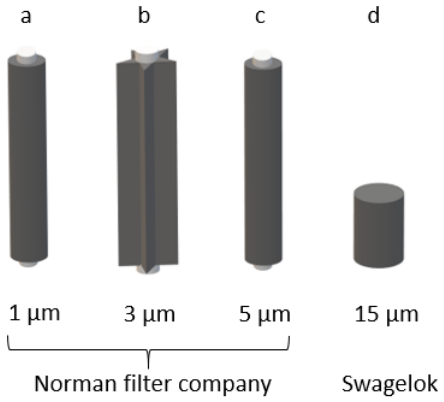


Figure. 3.2: Schematic figure of the different filters from Norman filter company and Swagelok.

Figure 3.3 shows a schematic figure of the crystal sampler with a magnified dismantled filter unit showing a Norman filter company and Swagelok filter. The darker arrows display how the black liquor flows past the filter and fills the container below the crank. The lighter-coloured arrows then indicate how the black liquor is pressed through the pores in the filter when the crank is turned and the pressure increases.

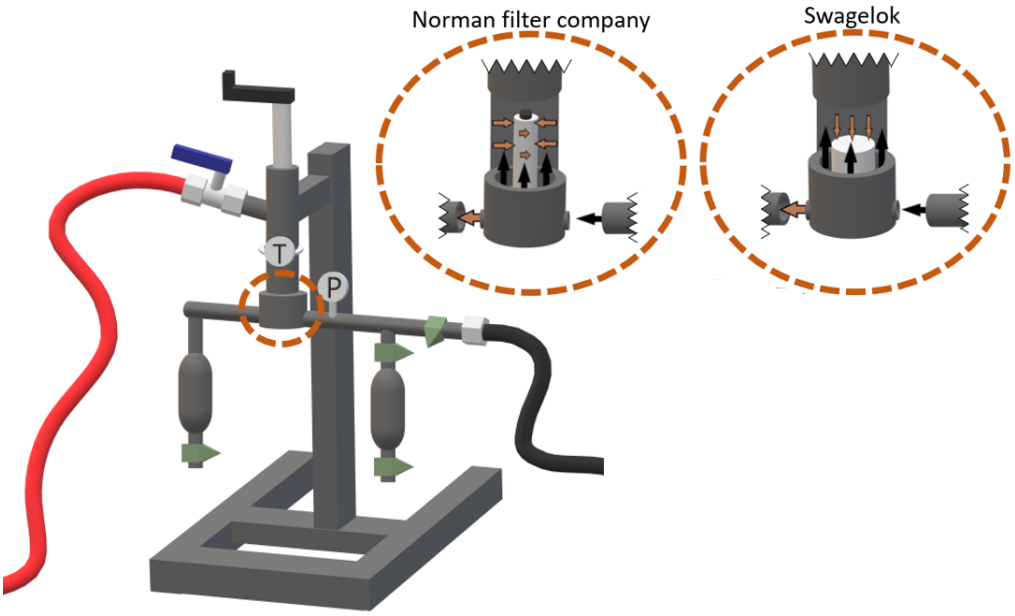


Figure. 3.3: Schematic figure of the crystal sampler displaying the flow of black liquor through the Norman filter company and Swagelok filters.

3.2 Laboratory Analyses

Measurements of the dry solids content were performed for all of the filtered and unfiltered black liquor samples, as well as for the IMTBL samples. Furthermore, analyses of the carbonate, sulphate and chloride content were performed on the majority of the filtered samples and filter cakes, and for a few of the unfiltered and IMTBL samples. Since the analysis was performed by laboratory personnel at the mills, all collected samples could not be analysed. Instead a selected number of samples had to be chosen to not create a too high workload for the personnel. The following sections describe the procedure for the performed measurements and the calculations done to compile the analysis results.

3.2.1 Dry Solids Content Measurements and Calculation of Crystal Fraction

The DS of the black liquor samples collected from the mills was determined by comparing the mass of black liquor before and after it was dried in an oven, see *Equation 2.1*. The DS measurements were carried out for the unfiltered, filtered and IMTBL samples according to the standard TAPPI T 650 om-09 developed by the Technical association of the pulp and paper industry (TAPPI). The samples of black liquor

were diluted prior to the DS measurement. Compared to the TAPPI standard, the dilution conducted in this project was performed directly in the sample bottles, therefore using larger sample volumes than the dilution procedure described in TAPPI T 650 om-09. The dilution was conducted by diluting a black liquor sample of known mass with distilled water giving a final DS of approximately 25 %. After the dilution, the DS measurements were conducted according to the standard.

When pressing the liquor through the filter in the crystal sampler, solids of larger size than the filter pore size was removed. Hence, the DS of the filtered liquor (DS_{filt}) is lower than the DS of the unfiltered sample (DS_{unfilt}). The acronym DS will refer to the dry solids content of unfiltered black liquor (DS_{unfilt}) throughout this thesis if otherwise not stated. If it is assumed that all substance filtered away consists of crystals, it is possible to calculate the mass fraction of free bulk crystals from the DS measurements of the unfiltered and the filtered sample. The total mass of the unfiltered black liquor (m_{tot}^{BL}) can be expressed as *Equation 3.1*, assuming that the mass consists of dissolved dry solid material in the liquor (m_{ds}), mass of the crystals (m_{cryst}) and mass of the water (m_{water}).

$$m_{tot}^{BL} = m_{ds} + m_{cryst} + m_{water} \qquad [kg] \tag{3.1}$$

Employing the expression for dry solids content in *Equation 2.1*, expressions for DS_{filt} and DS_{unfilt} can be established, see *Equation 3.2 and 3.3*.

$$DS_{filt} = \frac{m_{ds}}{m_{water} + m_{ds}} \qquad [wt\%] \tag{3.2}$$

$$DS_{unfilt} = \frac{m_{ds} + m_{cryst}}{m_{water} + m_{cryst} + m_{ds}} = \frac{m_{ds} + m_{cryst}}{m_{tot}^{BL}} =$$

$$= \frac{m_{ds}}{m_{tot}^{BL}} + \frac{m_{cryst}}{m_{tot}^{BL}} \qquad [wt\%] \tag{3.3}$$

A material balance over the filter can be seen in *A.1* in *Appendix A*. When defining the crystal fraction (cf) as the mass of crystals per mass of unfiltered black liquor, an expression for the cf based on the dry solids contents for the filtered sample and the unfiltered sample can be established. Thus, the fraction of bulk crystals can be calculated according to *Equation 3.4*.

$$cf = \frac{DS_{unfilt} - DS_{filt}}{1 - DS_{filt}} \qquad [wt\%] \tag{3.4}$$

If cf and DS_{unfilt} are plotted against each other, DS_{unfilt} can be extrapolated to $cf = 0$ which can give an indication of where the solubility limit for the crystals in the black liquor is located.

Since the water content in the black liquor varies depending on sampling position in the evaporator train, as well as process variations, the amount of crystallised salts will vary with time and position. To compare the salt content required for a certain

cf with the salt content in the corresponding IMTBL or unfiltered black liquor, it is possible to convert the cf to the same unit as the salt content in the different samples so that they are expressed on the same base. This is done by dividing the crystal fraction with the dry solids content of the unfiltered sample obtained at the same sampling occasion.

$$\frac{cf}{DS_{unfilt}} = \frac{DS_{unfilt} - DS_{filt}}{DS_{unfilt}(1 - DS_{filt})} \qquad [wt\%] \qquad (3.5)$$

3.2.2 Salt Content Measurements

The analyses of carbonate and sulphate in the samples made it possible to calculate the sodium salt content by allocating sodium to the analysis results. As previously mentioned, the sum of the resulting concentrations of Na_2CO_3 and Na_2SO_4 is referred to as the *salt content* of the sample. Furthermore, the results from analysis of chloride were used to trace carbonates and sulphates originating from black liquor in the filter cake, as the sodium salt crystals do not contain chloride. The analyses were performed by laboratory personnel at Värö and Skoghall mill and the analysis methods described in the following section were determined in consultations with mill personnel, utilising their competence and techniques. In the standards used for the conducted analysis, no values for measurement errors have been published. It is therefore difficult to estimate the accuracy of the analyses, particularly since the analyses were performed by mill personnel and not an external laboratory.

3.2.2.1 Analysis of Carbonate

The carbonate content in the samples were measured as Total Inorganic Carbon (TIC) using a Total Organic Carbon (TOC) analyser. The standard SS-EN 1484 describes that TIC can be determined with a TOC instrument using UV radiation that oxidises inorganic carbon to carbon dioxide (CO_2) in a TOC analyser. TOC instruments mostly detects CO_2 that originates from carbonates and hydrogen carbonates. It was assumed that all inorganic carbon in the samples was carbonate. For each sample, duplicate readings were performed and a standard carbonate solution was tested prior to each reading. The detailed accuracy of the carbonate measurements is not known.

3.2.2.2 Analysis of Sulphate and Chloride

Analyses of the sulphate and chloride content of the filter cakes, the unfiltered and filtered black liquor and the IMTBL were performed using ion chromatrography (IC). Prior to the IC analysis the filter cake was dissolved in distilled water. Thereafter, the filter cake solution and the unfiltered, filtered and IMTBL samples were diluted with distilled water to a concentration appropriate for detecting the desired chemical species during the IC measurements.

3.2.2.3 Calculation of Carbonate and Sulphate Content in Filter Cake based on Chloride Analysis

The filter cake built up during sampling with the crystal sampler did not purely consist of sodium salts, but did also contain black liquor. The carbonate and sulphate content in the filter cake was of interest to deduce the amount of crystals in the filter cake. However, carbonate and sulphate are also dissolved in the black liquor that the filter cake contains. The carbonate and sulphate in the black liquor are dissolved and do not contribute to the amount of crystals in the filter cake. Therefore, it was needed to determine the amount of sulphate and carbonate originating from the black liquor in the filter cake.

The sulphate and carbonate originating from the black liquor in the filter cake were determined by analysing the amount of chloride in the filtered black liquor, which was later used as a trace element. As can be seen in *Table 2.1*, an average type of black liquor contains around 5000 mg chloride per kg black liquor. Using chloride as an element to base the calculation on, the amount of sulphate and carbonates originating from the crystals could therefore be calculated. All amounts of the respective components from the analysis were converted to moles. A molar balance over the filter was then conducted for chloride. Since chloride is not incorporated in the crystal structure of either burkeite or dicarbonate it was assumed that the chloride content did not change between unfiltered and filtered black liquor. Since crystals composed of sulphate and carbonate are obstructed by the filter, the filtered samples had a lower amount of these compounds than the unfiltered sample. The amount of sulphate and carbonate in the filtered black liquor could be calculated per chloride. It was then assumed that for each amount of chloride in the filter cake, a corresponding amount of sulphate and carbonate would be subtracted from the measured amount of sulphate respectively carbonate in the diluted filter cake.
The quotas $x_{SO_4{}^{2-}}$ and $x_{CO_3{}^{2-}}$ for the molar amount of sulphate ($n^{filt}_{SO_4{}^{2-}}$) respectively carbonate ($n^{filt}_{CO_3{}^{2-}}$) per molar amount of chloride in the filtered black liquor, ($n^{filt}_{Cl^-}$), were calculated, see *Equation 3.6* and *3.7*.

$$x_{SO_4{}^{2-}} = \frac{n^{\text{filt}}_{SO_4{}^{2-}}}{n^{\text{filt}}_{Cl^-}} \qquad [mole/mole] \tag{3.6}$$

$$x_{CO_3{}^{2-}} = \frac{n^{\text{filt}}_{CO_3{}^{2-}}}{n^{\text{filt}}_{Cl^-}} \qquad [mole/mole] \tag{3.7}$$

These quotas were then used to subtract sulphates and carbonates for each mole of chloride in the dissolved filter cake (*diss.fc*), which then is equal to the moles composed by crystals (*cryst*), see *Equation 3.8* and *Equation 3.9*.

$$n^{\text{cryst}}_{SO_4{}^{2-}} = n^{\text{diss. fc}}_{SO_4{}^{2-}} - x_{SO_4{}^{2-}} n^{\text{diss. fc}}_{Cl^-} \qquad [mole] \tag{3.8}$$

$$n^{\text{cryst}}_{CO_3{}^{2-}} = n^{\text{diss. fc}}_{CO_3{}^{2-}} - x_{CO_3{}^{2-}} n^{\text{diss. fc}}_{Cl^-} \qquad [mole] \tag{3.9}$$

The carbonate sulphate ratio for the crystals can then be calculated according to *Equation 2.5* in the above section.

3.2.3 Evaluation of Salt Content

The salt content was determined by allocating two moles of sodium for each mole of carbonate and sulphate measured in the respective samples. The results from analysis of sulphates, carbonates and chlorides were converted from *mole/L of black liquor* to *mole/kg of black liquor*, using the density for black liquor in *Equation 2.4*. From here on the unit for mass of black liquor will be expressed with the notation $kgBL$. The molar masses for the salts were then used to convert the results to $kg\mathrm{Na_2SO_4}/kgBL$ and $kg\mathrm{Na_2CO_3}/kgBL$. The total salt content was then obtained by summing the above giving: $kg\mathrm{Na_2CO_3} + \mathrm{Na_2SO_4}/kgBL$. The salt content was recalculated to be based on different denominators, bases, depending on the usage of the result.

For a comparison between the salt content from the analyses and the concentrations provided by Schmidl and Frederick (1998), the basis of $\mathrm{Na_2CO_3} + \mathrm{Na_2SO_4}/kgBL_{DS}$ was used and attained by dividing the salt content in each sample with the dry solids content of the corresponding sample. The divided crystal fraction cf/DS_{unfilt} is then on the same basis and the salt content in the crystals can be compared with the IMTBL and unfiltered black liquor samples. In theory, cf/DS_{unfilt} should not exceed the amount of salts in the IMTBL together with added salts from ashes and TOP brine, or the amount of salts in the unfiltered black liquor.

The salt content in the sampled IMTBL did not include salt added from the recovery boiler ash and TOP brine. Therefore, salt was added mathematically to the IMTBL using a recommendation of a salt addition corresponding to 7 % of the total dry solids content of the black liquor flow, see the calculation methodology in *A.3* in *Appendix A*. The IMTBL with an average amount of salts added from ashes and TOP brine should represent the salt content in the liquor entering *V-1C*. The salt content in the unfiltered black liquor represents the liquor in the flash tank after effect *V-1C*. Hence, the salt contents should approximately be equal, but eventual scaling in *V-1C* or deviations from an assumed addition of the added salts in IMTBL will give some differences.

The DS of the black liquor decreases during the filtration ($DS_{unfilt} > DS_{filt}$). It is therefore not possible to compare the salt content of filtered black liquor with unfiltered and IMTBL samples of black liquor, even if they are converted to a base of DS. To relate the salt content in the filtered and unfiltered sample sample, it is instead needed to compose a mass balance including either cf or the salt content in both unfiltered and filtered black liquor. However, if the difference between DS_{unfilt} and DS_{filt} not only is a result of precipitating crystals, only the latter alternative of mass balance can be used. Further on, if the salt content in both unfiltered and filtered black liquor are known, it is possible to calculate a cf based on differences of salt content in unfiltered and filtered black liquor, which will be denoted cf^*. It

is then assumed that the lower amount of salts in the filtered sample originates from precipitated crystals.

4 Results

First, some general results valid for both Skoghall and Värö regarding the development and performance of the sampling technique and laboratory analyses are presented in section *4.1*. Thereafter, results from the dry solids content measurements and the salt content measurements specific for Värö and Skoghall are presented. The results will then be further discussed in the *Discussion* in section *5*.

4.1 Development of Equipment and Sampling

The two different filter units, Swagelok and Norman, were tested during sampling at Värö. It was discovered that when using the Swagelok filters, which have a much smaller surface area, there was an increased tendency for plugging of the filter. Plugging occurred even when the largest pore size with the Swagelok filter, 15 µm, was used. The plugging resulted in a smaller amount of filtered black liquor and in some cases not an adequate amount for analysis. Therefore, it was concluded that it was not suitable to conduct sampling with the Swagelok filter unit. Hence, the Norman filter unit was used in the proceeding samplings both at Värö and Skoghall.

The sampling at Värö resulted in 12 successful samples, where 3 samples were done using a pore filter size of 15 µm. The sampling was conducted at two separate occasions with approximately 4 weeks in between. At Skoghall, the sampling resulted in total in 21 samples at the different effects *S-1A*, *S-1B*, *S-1C* and *S-1D*. However, when filtrating black liquor at effects *S-1C* and *S-1D* a filter cake did not always materialise, meaning that no solid phase was visible on the filter and no filter cake sample could be obtained.

4.1.1 Evaluation of the Filtration Procedure

Results of dry solid content measurements of black liquor extracted with the crystal sampler at effect *V-2* in Värö are displayed in *Table 4.1*.

Table 4.1: Dry solids contents and crystal fractions of samples extracted from effect *V-2*.

Sample	$\boldsymbol{DS_{filt}}$ [%]	$\boldsymbol{DS_{unfilt}}$ [%]	$\boldsymbol{cf}$[%]
48	44.4	44.3	−0.2
49	43.8	43.6	−0.3
50	43.0	42.6	−0.7

It can be seen that a negative crystal fraction was obtained for all samples. A crystal fraction equal to zero was expected since the solubility limit not yet is exceeded in effect *V-2*. A crystal fraction close to zero indicates that no substance in the black liquor is filtered away by the crystal sampler below the solubility limit, which is

a presumption for determination of the crystal fraction. Since a negative crystal fraction is not physically possible, the results also indicate a measurement error for the dry solids content measurements. Therefore, the largest obtained deviation from zero will be used as an indication for the measurement error for the crystal fraction. Hence, 0.7 percentage will be the used for vertical error bars in the diagrams displaying crystal fraction.

4.1.2 Impact of Filter Pore Size on Crystal Fraction

The measured crystal fractions, cf, from Varö samples are shown as a function of the dry solids content of the unfiltered sample, DS_{unfilt}, in *Figure 4.1*. The marker type of each data point represents the pore size of the filter used at the sampling. Furthermore, each data point is labelled with the date of sampling.

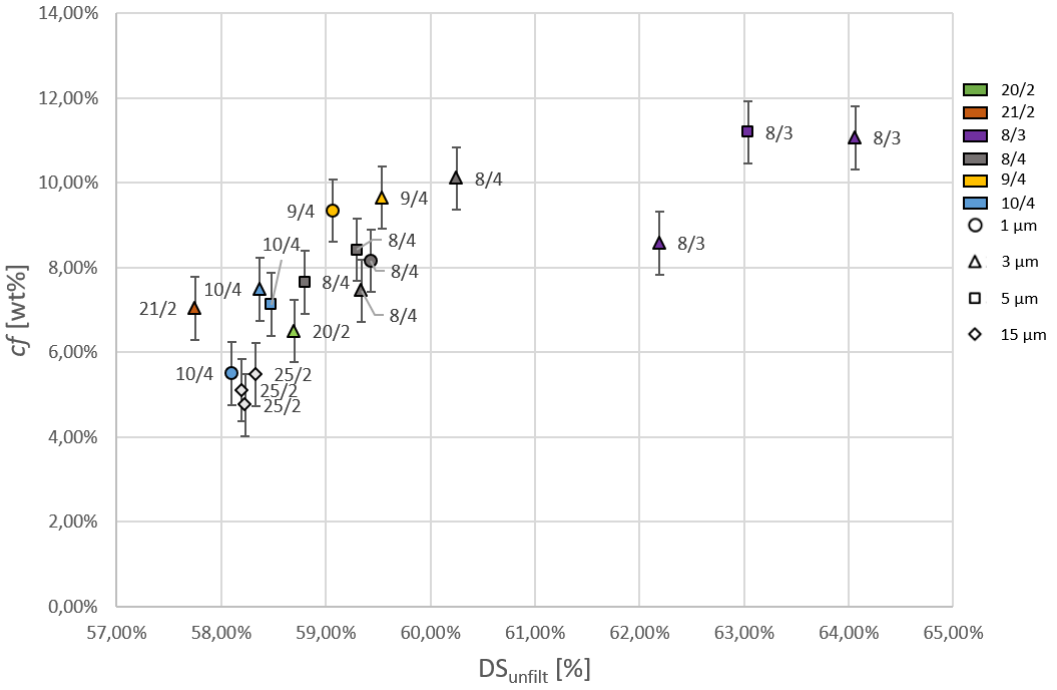


Figure. 4.1: cf against DS_{unfilt} for Värö samples.

It can be seen that there is a stronger tendency for clustering of points due to date rather than filter pore size. This indicates that the process conditions at the time for sampling contribute more to the variety of crystal fraction than the filter pore size. Therefore, no consideration of filter pore size used during sampling will be made when presenting the proceeding results. Further on, the clustering indicates that large errors in the majority of the sampled crystal fractions are improbable. It was expected that process variations would not contribute to a large variation of crystal fraction within a day. However, the three samples obtained using the Swagelok filter unit with 15 µm filter gave the lowest crystal fractions. Since no other filter pore sizes were used for sampling at that date and 15 µm was not used at further samplings, it is hard to conclude that the quite drastically larger filter

size did not affect the crystal fraction. To be consequent in the presentation of the results and consider the eventual effect that the Swagelok filter unit might have, the results gained from the measurements using the Swagelok filter will be excluded further on in the thesis.

A corresponding diagram as *Figure 4.1* for samples from Skoghall can be seen in *Figure B.1* in *Appendix B*. Since each effect only was sampled once a day at the majority of the sampling at Skoghall, it is harder to see a clustering of date in *Figure B.1*.

4.1.3 Comparison of Analysis Results at Värö and Skoghall

Three samples of filtered black liquor were analysed both by Skoghall and at Värö to be able to compare the mills' analysis methods. The results from the analyses are shown in mg/L in *Table 4.2* and in $mg/kgDS$ *Table B.1* in *Appendix B*.

Table 4.2: Comparative testing of salt content in black liquor done by laboratories at Värö and Skoghall mills. Results from sulphate analysis performed at Värö are marked in grey.

	Chloride [mg/L]		**Sulphate** [mg/L]		**Carbonate** [mg/L]	
Sample	**Värö**	**Skoghall**	**Värö**	**Skoghall**	**Värö**	**Skoghall**
10	890	840	3620	3900	11100	7500
21	874	830	2860	4300	10500	5500
42	930	910	5840	3500	7800	4500

It can be seen that both laboratories gave approximately the same chloride content results, while sulphate and carbonate contents deviates much. This suggests that there are differences in how the two mill laboratories perform the analyses and brings uncertainties to the results. Dialogues with mill personnel showed that the Värö laboratory likely had issues with their IC instrument which affected their sulphate analysis. As a result, the sulphate contents measured at Värö are considered as questionable values. In contrast to the sulphate analysis, no explanation for the deviation of carbonate was found despite thorough investigation. Results affected by sulphate analysis results performed by Värö mill will be highlighted in dark grey in the proceedings of this report to be able to distinguish them from analysis made at Skoghall.

4.2 Dry Solids Content and Crystal Fraction

The dry solids content in unfiltered black liquor, DS_{unfilt}, and the calculated crystal fraction, cf, for the samples are presented in the following sections. First are the results for Värö displayed and then for Skoghall.

4.2.1 Värö

Figure 4.2 shows how the crystal fraction varies with dry solids content of the unfiltered sample collected from the sampling point at the flash tank after effect *V-1C*

at Värö. The data points form a cluster that indicates that the conditions in the flash tank varies and give rise to variations in the crystal fraction. It can be seen that sample 6, 10 and 16, which were sampled at the first samples session, (see *Figure 4.1*) deviates somewhat from other samples due to a high DS_{unfilt}. A trend line has been fitted to all the data points. The intersection of the linear trend line composed from the sampling points depicted in *Figure 4.2* has a DS of 48.0 % at zero crystal fraction. However, the solubility limit is a result of extrapolating the trend line relatively far, which could be problematic since a behaviour outside of the data range is assumed.

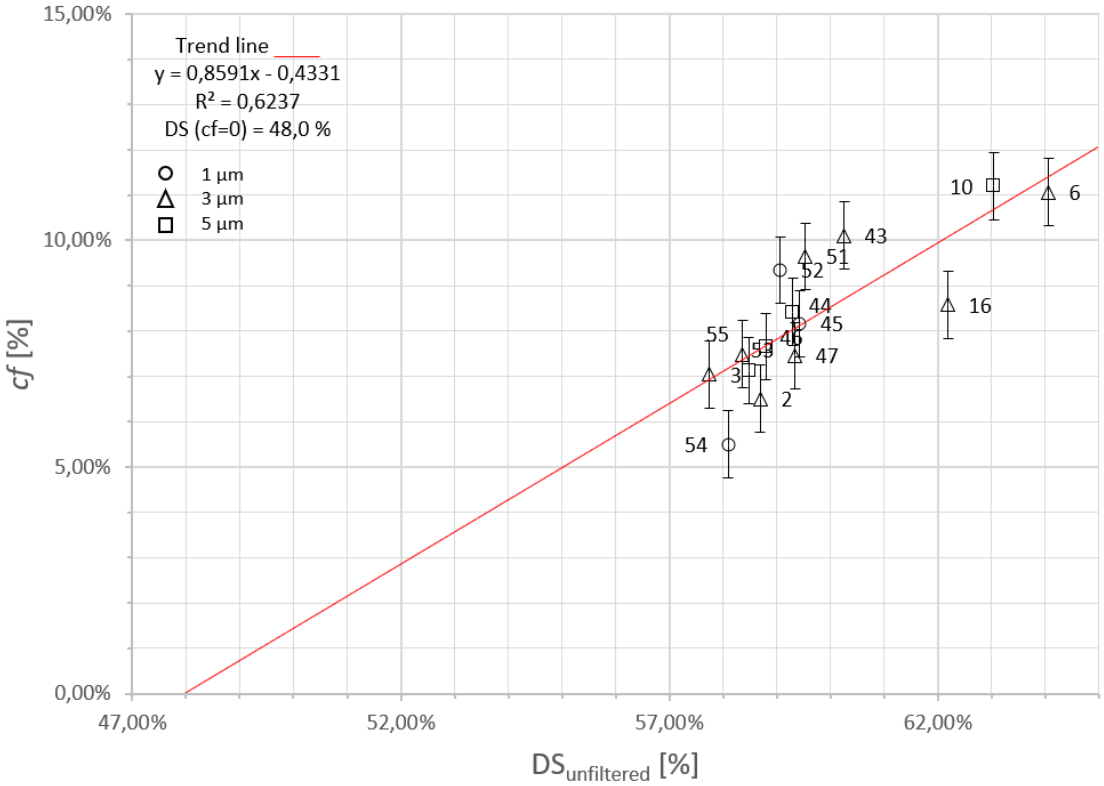


Figure. 4.2: Crystal fraction, cf, against dry solids content in unfiltered samples, DS_{unfilt}, from Värö mill, labelled with sample number.

For all sampling occasions at Värö, a visible filter cake was detected on the filter and sufficient amounts for analyses was obtained. Hence, the lowest crystal fraction that generated a filter cake at Värö was 5.5 %, not including the crystal fraction sampled by the 15 µm Swagelok filter.

4.2.2 Skoghall

The crystal fractions, cf, obtained for sampling at Skoghall are shown against the dry solids content of the unfiltered black liquor, DS_{unfilt}, in *Figure 4.3*. The data labels of the points indicate the sample number. The table to the right in the figure correlates the sample number with the date of the sampling. Sample 29, 35 and 40 deviate much from the linear trend line and could possibly be considered as outliers.

The computed trend line from all samples intersects with zero crystal fraction at a DS of 47.0 %. However, since it is based on eventual outliers, it should not be seen as a certain solubility limit.

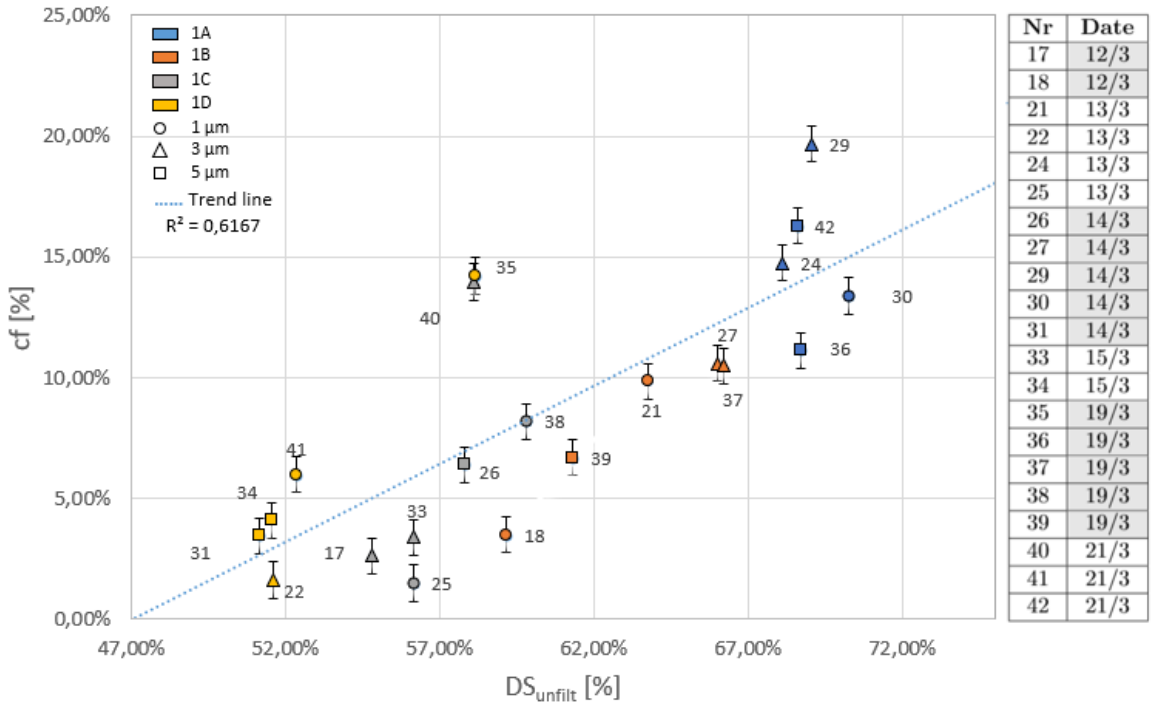


Figure. 4.3: Crystal fraction, cf, against dry solids content in unfiltered samples, DS_{unfilt}, from Skoghall mill. The table incorporated in the figure displays the date of sampling for each sample number.

In *Table 4.3* the average crystal fraction cf for chambers in effect *S-1* is shown. The result shows that the crystal fraction increases as the black liquor progresses in the evaporation train, which indicates that more salt precipitate in the effects operating at higher dry solids content. This compares well with expected results. A visible filter cake was not detected at all sampling occasions performed at Skoghall. The lowest crystal fraction where a visible and sufficient amount of filter cake was attained was at 10.5 %.

Table 4.3: Average crystal fractions and dry solids content of unfiltered samples extracted from the chambers of effect *S-1*.

Effect	**Average cf [%]**	**Average DS_{unfilt} [%]**
S-1A	15.1	69.0
S-1B	8.2	63.3
S-1C	6.0	57.1
S-1D	5.9	53.0

4.3 Evaluation of Salt Content

The following section provides a comparison of the salt content in different samples; the normalised crystal fraction, the unfiltered sample and the IMTBL with addition of salts from recovery boiler ash. It is done to provide a rough indication of what happens with the salts as the liquor proceeds in the evaporation train. Furthermore, the crystal fraction obtained from the dry solid content measurements (cf) will be compared to the crystal fraction based on the salt content measurements (cf^*).

4.3.1 Värö

The salt content measured in the analysed samples of IMTBL and unfiltered black liquor from Värö can be seen in *Table 4.4*. The second column ($IMTBL + ashes$ & $brine$) in the table shows the resulting salt content in the IMTBL when additional salt from the recovery boiler ash and TOP brine has been added according to *A.3* in *Appendix A*. It can be seen that the salt content in the $IMTBL + ashes$ & $brine$ ranges from 21.6- 22.4 $kg/kgBL_{DS}$ while the salt content in the unfiltered samples are slightly higher, 24.3 - 26.0. The results compare relatively well with the numbers presented by Schmidl and Frederick (1998) in *Table 2.1*, where salt content ranged between 6.7- 30.6 with a mean value of 16.0 $kg/kgBL_{DS}$.

Table 4.4: Amount of salts (Na_2SO_4 + Na_2CO_3) in IMTBL with allocated salt from recovery boiler ash and TOP brine and unfiltered black liquor compared with the crystal fraction from dry solid content measurements of Värö samples. Samples marked in grey were analysed by the Värö mill laboratory.

Sample type / Sample nr	**IMTBL + ashes & brine** [wt % DS]	**cf** [wt % DS]	**Unfiltered** [wt % DS]	$\boldsymbol{DS_{unfilt}}$ [wt %]
6	22.4	17.3	-	64.1
10	21.6	17.8	-	63.0
16	21.6	13.8	-	62.2
44	19.5	14.2	24.9	59.3
47	19.6	12.6	24.3	59.3
52	19.6	15.8	26.0	59.1

The difference in salt content between $IMTBL+ashes$ & $brine$ and cf, respectively the unfiltered black liquor and cf, indicates how much of the salt in the liquor that has precipitated as bulk crystals. The difference can therefore give an estimation of the reliability of the cf obtained with the crystal sampler. The comparison of $IMTBL + ashes$ & $brine$ and cf indicates that a large share of the salt content precipitates as bulk crystals, however, none of the cf has salt content exceeding the $IMTBL+ashes$ & $brine$ or the values from unfiltered black liquor. Therefore, there is no indication that the measured cf from Värö is incorrect.

A comparison between the crystal fraction based on the results of dry solid content measurement (cf) and the crystal fraction based on results from salt content measurements (cf^*) is shown in *Table 4.5*. It can be seen that cf^* is slightly higher than

cf for all three samples, but compares rather well.

Table 4.5: Crystal fraction based on salt content measurements and dry solids content measurements for Värö samples. Results from sulphate analysis performed at Värö are marked in grey.

Sample	cf^* [%]	cf [%]
44	9.1 %	8.4 %
47	8.7 %	7.5 %
52	9.8 %	9.3 %

4.3.2 Skoghall

In *Table 4.6* the salt content in IMTBL, unfiltered black liquor and crystals are shown. It can be seen that the salt content in the $IMTBL + ashes$ & $brine$ and unfiltered black liquor correlates with the salt content presented by Schmidl and Frederick (1998) in *Table 2.1.* Sample 21 is the only sample extracted from Skoghall for which the salt content has been analysed in both the IMTBL and the unfiltered sample.

Table 4.6: Amount of salt (Na_2SO_4 + Na_2CO_3) in IMTBL with allocated salt from recovery boiler ash and TOP brine and unfiltered black liquor compared with the crystal fraction from dry solid content measurements of Skoghall samples.

Sample type / Sample nr	**IMTBL + ashes & brine** [wt % DS]	**cf** [wt % DS]	**Unfiltered** [wt % DS]	DS_{unfilt} [wt %]
17	22.4	4.8	-	54.8
21	21.5	15.5	21.1	63.8
22	22.0	3.2	-	51.6
29	-	28.5	22.1	69.1
30	-	19.4	22.0	70.3
34	22.2	8.0	-	51.6
35	-	24.5	18.6	58.2
40	-	24.0	25.8	58.1

A comparison of the salt content in $IMTBL + ashes$ & $brine$ to cf, respectively the unfiltered sample to cf provides a rough indication of the credibility of the crystal fraction, cf obtained from the dry solids content measurements. Sample 17, 22, and 34, which all had a DS_{unfilt} lower than 55 %, has a cf that is clearly lower than the salt content in the respective $IMTBL + ashes$ & $brine$. Sample 21 has a cf slightly lower than the salt content in $IMTBL + ashes$ & $brine$ respectively unfiltered black liquor and was sampled at 64 % DS. Sample 30 and 40 has a cf very close to the salt content in the corresponding unfiltered black liquor, and was sampled at a DS_{unfilt} of 70.3 respectively 58.1 %. Sample 30 and 40 might be considered to have a cf that is unreasonably high. The cf for sample 29 and 35, sampled at DS_{unfilt} of 69.1 respectively 58.2 %, exceeds the salt content in their corresponding unfiltered black liquor, hence sample 29 and 35 have a cf that is not possible which will be discussed further in *Discussion 5* .

The crystal fraction calculated from the salt balance (cf^*) is shown in *Table 4.7* together with the crystal fraction defined from dry solids content measurements (cf).

Table 4.7: Crystal fraction based on salt balance and dry solids content measurements for Skoghall samples.

Sample	$\boldsymbol{cf^*}$[%]	$\boldsymbol{cf}$ [%]
21	10.5 %	9.9 %
29	6.9 %	19.7 %
30	9.2 %	13.4 %
35	6.9 %	14.2 %
40	11.52 %	14.0 %

The calculated cf^* ranges between 6.9 to 11.5 where cf varies more, from 9.9 to 19.7. If the cf was correct it should have approximate the same values as cf^*. It can be seen that cf^* for sample 21 compares quite good with the cf, whereas the other samples deviate. The results from the evaluation of salt content in Skoghall liquor supports the statement made from *Figure 4.3* that sample 29, 35 and 40 are outliers.

4.4 Carbonate and Sulphate Ratio

The following section presents data for the carbonate sulphate ratio Rcs_{cryst} measured in the crystals in the filter cakes, the filtered, Rcs_{filt}, and unfiltered, Rcs_{unfilt}, Värö and Skoghall samples.

4.4.1 Värö

Results of the carbonate and sulphate ratio in the filtered sample and the calculated value in the crystals in the filter cake for the Värö samples are shown in *Figure 4.4*. The shaded regions shown in the figure represent the regions presented by Frederick et al. (2004) for where the salt species sodium sulphate, burkeite, dicarbonate and sodium carbonate are expected to precipitate.

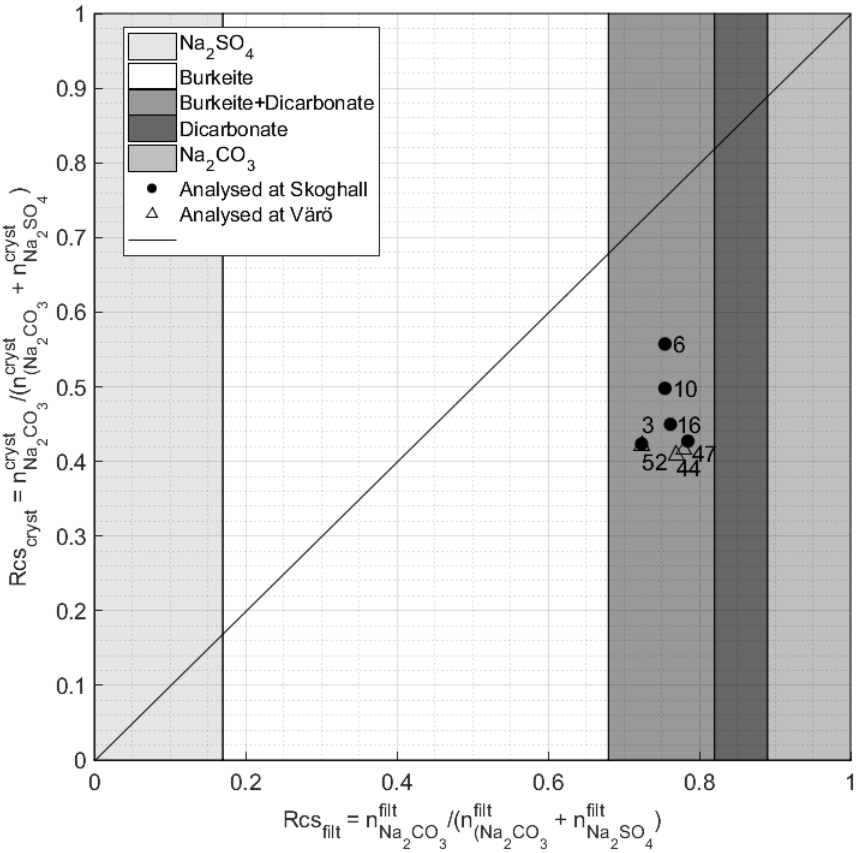


Figure. 4.4: Phase diagram for crystals composed of Na_2CO_3 and Na_2SO_4 in black liquor from Värö, Rcs_{cryst} against Rcs_{filt}.

It can be noted in the figure that the carbonate sulphate ratio is not the same in the crystals and the corresponding filtered black liquor. This suggests that sodium salt crystals have been captured in the filter in the crystal sampler, hence not only black liquor is analysed.

The majority of the carbonate sulphate ratio measured in the dissolved filter cake Rcs_{cryst} ranges between approximately 0.4 and 0.42 mole %. This indicates that the crystals contain slightly less amount of sodium carbonate than sodium sulphate. However, sample 6, 10 and 16 has a bit higher Rcs_{cryst}, 0.43 to 0.55 mole %. It indicates that the filter cakes in these samples consists of approximately equal amounts of sodium carbonate and sodium sulphate. When taking the molar composition of the salts burkeite and dicarbonate into account ($\sim 2Na_2SO_4 \cdot Na_2CO_3$ respectively $\sim 2Na_2CO_3 \cdot Na_2SO_4$), a ratio higher than 0.5 % indicates that the crystals consists of more sodium carbonate than sodium sulphate. It can be seen that majority of the Rcs_{cryst} for Värö indicates that the crystals are on the borderline between burkeite and dicarbonate. The Rcs_{filt} ranges between approximately 0.65 and 0.8 mole % which indicates that the filtered black liquor contains more sodium carbonate than sodium sulphate and places majority of the data points within the burkeite + dicarbonate zone defined by Frederick et al. (2004). Thus, the phase diagram for Värö

indicates that the precipitated crystals probably are both burkeite and dicarbonate, or might be the relatively uninvestigated crystal species sodium sulphate carbonate.

A comparison between the carbonate sulphate ratio in the unfiltered (Rcs_{unfilt}) and the filtered (Rcs_{filt}) liquor was performed for the three samples 44, 47 and 52 . The comparison shows that the carbonate sulphate ratio increases due to the filtration operation. This indicates that the filtration removes materia composed of a higher share of sodium sulphate than sodium carbonate. Thus, the comparison of the Rcs_{unfilt} and Rcs_{filt} indicates that for sample 44, 47 and 52 it is mostly burkeite that precipitates in the liquor. Hence, the results presented in the phase diagram in *Figure 4.4* and in *Table 4.8* indicate the same results.

Table 4.8: Phase diagram for crystals composed of Na_2CO_3 and Na_2SO_4 in black liquor from Skoghall, Rcs_{cryst} against Rcs_{filt}. Values affected by results from sulphate analysis performed at Värö are marked in grey.

Sample	$\boldsymbol{Rcs_{unfilt}}$ [mol %]	$\boldsymbol{Rcs_{filt}}$ [mol %]
44	0.48	0.77
47	0.50	0.78
52	0.51	0.72

4.4.2 Skoghall

The results of the carbonate sulphate ratio in the filtered sample Rcs_{filt} and the calculated value in the crystals in the filter cake Rcs_{cryst} for the Skoghall samples are shown in *Figure 4.5*. The marker for the data points represents the effects where the sample was taken. Since the sampling of black liquor in effects *S-1D* and *S-1C* only resulted in one filter cake in total, the majority of the data points correspond to effect *S-1A* and *S-1B*.

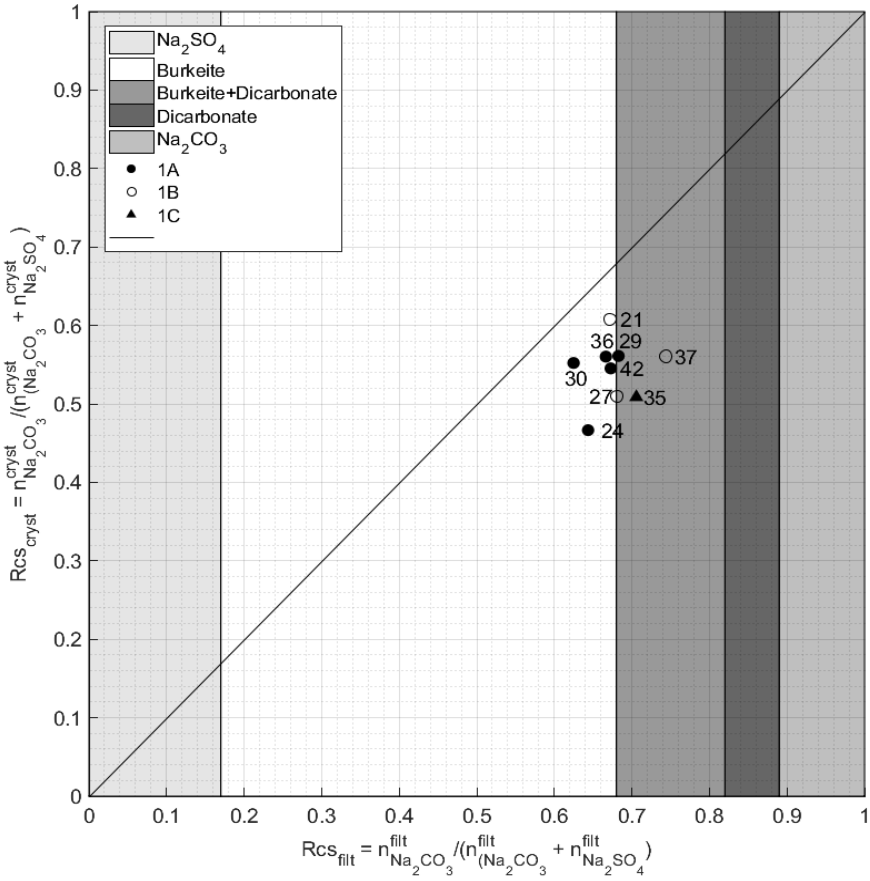


Figure. 4.5: The carbonate sulphate ratio Rcs_{cryst} against Rcs_{filt} for Skoghall samples.

All carbonate sulphate ratios measured in the dissolved filter cake Rcs_{cryst} exceed 0.5 mole %, except sample 24. A ratio higher than 0.3 % indicates that the crystals consist of more sodium carbonate than sodium sulphate. This information together with the approximate composition of burkeite and dicarbonate suggests that the crystals are dicarbonate. However, the Rcs_{filt} ranges between approximately 0.6 and 0.76 and places most of the data points in the burkeite region defined by Frederick et al. (2004). These results are not in agreement with the Rcs_{cryst} results. Furthermore, the figure shows that crystals captured during sampling in *S-1A* has a lower *Rcs* in the filtered black liquor than crystals from *S-1B*. It suggests that the precipitation of crystals results in a shift the *Rcs* in the filtered black liquor, which could indicate that the crystals precipitating consists of more carbonate than sulphates, hence are in form of dicarbonate.

A comparison between the carbonate sulphate ratio in the unfiltered (Rcs_{unfilt}) and the filtered (Rcs_{filt}) liquor shows that Rcs_{filt} is higher, see *Table 4.9*. This indicates that due to the filtration, a substance that is composed of a higher share of sodium sulphate than sodium carbonate, is removed from the black liquor. Thus, the comparison of the Rcs_{unfilt} and the Rcs_{filt} indicates that majority of the precipitated

crystals in the liquor are burkeite. Thus, the results regarding the obtained crystal species gained from Rcs_{cryst}, Rcs_{filt} and Rcs_{unfilt} are ambiguous.

Table 4.9: Carbonate sulphate ratio in unfiltered and filtered sample from Skoghall mill.

Sample	$\boldsymbol{Rcs_{unfilt}}$ [mol %]	$\boldsymbol{Rcs_{filt}}$ [mol %]
21	0.52	0.67
29	0.55	0.68
30	0.59	0.62
35	0.59	0.71
40	0.58	0.72

4.5 Solubility and Salt Content

The following section provides solubility diagrams displaying the results of the salt content measurements performed at Värö and Skoghall. The presented data represents the samples where both the filtered and the unfiltered samples have been analysed. The diagrams provide a comparison of solubility curve fitted to the measured salt content in the filtered samples and the solubility curve developed by Karlsson (2017).

4.5.1 Värö

The salt content in the filtered sample are plotted as data points in *Figure 4.6*, representing dissolved salts in the black liquor. The dotted quadratic graph represents a trend line fitted to the data points for the salt content in the filtered samples, hence a solubility curve specific for the black liquor at Värö. Additionally, averaged salt content of the corresponding unfiltered sample is plotted as a linear graph, which represents a total salt content. Furthermore, *Figure 4.6* displays the solubility correlation from *Equation 2.6* for crystals consisting of the salts Na_2SO_4 and Na_2CO_3.

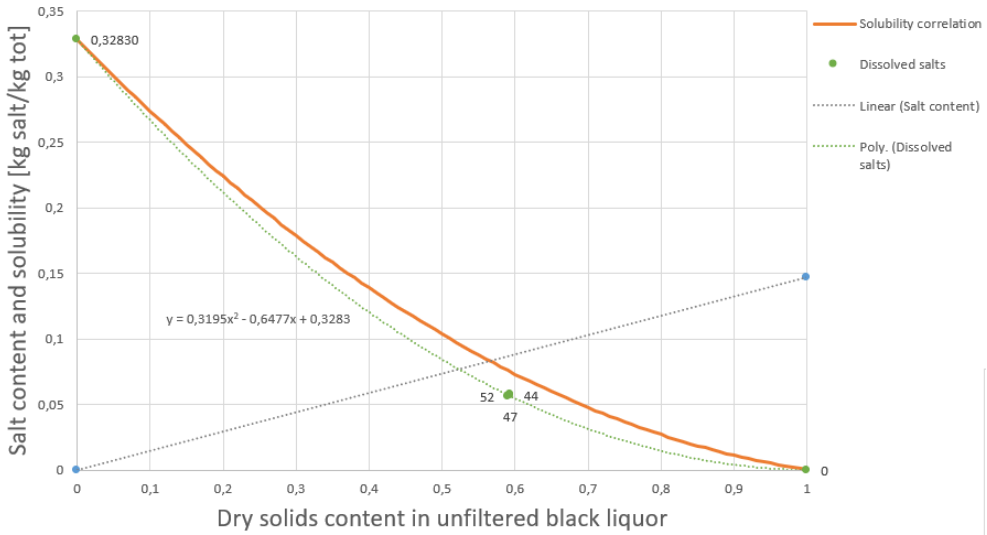


Figure. 4.6: Solubility curve computed from salt content in filtered black liquor at Värö, compared with solubility correlation developed by Karlsson (2017).

It can be seen that the quadratic trend curve deviates from the solubility correlation suggested by Karlsson (2017) shown in *Equation 2.6* and indicates a lower solubility for the salts in the black liquor. The dry solids content at the intersection between the linear curve and the solubility curve represents a solubility limit. Based on the measurements displayed in *Figure 4.6* the solubility of the liquor is at approximately 53 % DS. This value is higher than the solubility limit presented in *4.2*.

4.5.2 Skoghall

In *Figure 4.7* the solubility correlation from *Equation 2.6* is plotted together with data points of the salt content in the filtered black liquor representing dissolved salts. Additionally, the salt content in the unfiltered black liquor samples are plotted as a linear trend line. The quadratic dotted trend line is fitted to the salt content measurement of the filtered samples and represents an adapted solubility curve, specific for the black liquor at Skoghall at the time for sampling.

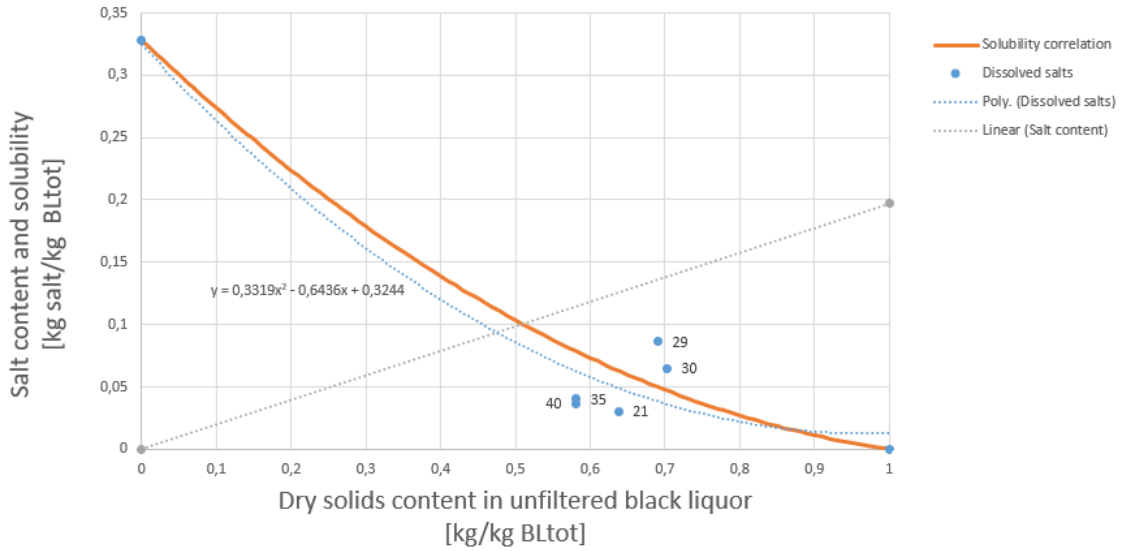


Figure. 4.7: Solubility curve computed from filtered black liquor at Skoghall, compared with solubility correlation developed by Karlsson (2017).

It can be seen that the dotted solubility curve lies below the solubility curve suggested by Karlsson (2017) shown in *Equation 2.6*. The intersection between the solubility curve and the salt content curve gives the solubility limit for the crystals which is approximately at 48 % DS for these measurements. This compares well with the results seen in *Figure 4.3*.

5 Discussion

There are several deficiencies with the data presented in this study that need to be considered when determining the validity of the results. The salt content analysis performed at Värö seems questionable when comparing the results with Skoghall results for the same samples. Furthermore, the number of samples for which the salt content has been analysed in unfiltered black liquor is insufficient to provide information that can be used to draw any definitive conclusions. However, this work has still provided new results and offers valuable guidance for future studies using the crystal sampler. The following sections provide a discussion following the disposition in the results section.

5.1 Development of Equipment and Sampling

The crystal sampler has been upgraded and improved during the work presented in this thesis. The final construction of the crystal sampler could successfully be used for sampling of black liquor. However, during a few samplings at Skoghall mill a problem arose during the sampling. Even though there were no signs of plugging of the equipment and the pressure did not increase significantly while turning the crank, an insufficient amount of filtered sample was obtained. As a consequence, a few of the samplings had to be discarded as failed ones. One explanation to this phenomena could be that the crystal sampler at the moment of sampling partially contained a gaseous phase, e.g. vapour due to flashing of the liquor. If so, the amount of black liquor in the equipment would have been less, which would explain a smaller amount of filtered sample. Further on, the difference in DS for when a filter cake appeared during sampling at Värö and Skoghall mills is interesting (5.5 respectively 10.5 %). It indicates that there are differences in the black liquor obtained at the two mills. Skoghall has an additional residue stream of CTMP washing water compared to Värö which might influence the black liquor. Another process difference that might impact is that the main sampling point at Värö is located after a flash tank unlike sampling at Skoghall. At the sampling points at Skoghall, the the liquor saturation pressure is above atmospheric pressure which gives a risk of flash boiling.

5.1.1 Comparison of Analysis Results at Värö and Skoghall

The comparative analysis of salt content measurements, where samples were analysed both at Skoghall and Värö, showed errors in sulphate and carbonate analysis. Since the laboratory personnel at Värö suspects error with their sulphate measurements, the analysis performed at Skoghall is regarded as more accurate. Furthermore, there were shortcomings regarding the handling of samples that potentially could have caused errors in the salt content analyses. During this work it was not possible to store the black liquor samples below 8 °C after the sampling. Storing

the samples in a refrigerator prior to analysis could have slowed down any eventual oxidation reactions. Since less time had passed between sampling and the subsequent analysis at Skoghall, these values would be more accurate concerning sample handling as well.

The results from Värö are considered as uncertain but may still provide information about the crystallisation of sodium salts and the outcome of the sampling at Värö. From *Table 4.4* it could be easy to draw the conclusion that the salt content in the black liquor analysed at Värö (marked in grey) deviates much from the samples analysed at Skoghall. However, one should also bear in mind that the six samples were taken at two different sampling occasions with quite a large time span in between which also can be seen since they differentiate much in DS. Hence, it is probable that some of the variations in salt content also originate from process variations, not only errors in laboratory analysis. Therefore, the analysis results from Värö will not be entirely rejected, but considered as a rough indicator, which can give information on how to proceed to develop a credible method for determination of bulk crystals.

Additionally, some of the results for Skoghall are also contradictory. This might be a result of black liquor being a complex mixture where different compounds could interfere and affect the analysis performance. Furthermore, the standard SS-EN 1484 used for the carbonate analysis, is mainly used for analysis of water from waste water treatments, which is not ideal. It is possible that sending the samples to an external lab for analysis could have led to more trustworthy results.

5.2 Dry Solids Content and Crystal Fraction

The figures where cf is plotted against DS for the two mills (*Figure 4.2 and 4.3*) shows that there is a tendency for a linear relationship between cf and DS. Furthermore, the trend line is fitted to a data set where it is probable that several outliers are included. However, since process variations, such as washing of an effect and adding residual streams from other parts of the mill, contribute to variations in dry solids content in the black liquor, it is difficult to determine which data points that are outliers due to measurement errors and which that reflect the dynamics of the process. Furthermore, the trend line is fitted to black liquors with a high DS and the solubility limit is obtained by extrapolating to obtain an intersection between the trend line and the x-axis. It is possible that this extrapolation does not reflect the reality. Consequently, the solubility limit computed by the trend lines in *Figure 4.2 and 4.3* should not be interpreted as completely true. However, since cf does have a tendency for linearisation and does cluster as a result of sampling date, it indicates that the sampled cf is good as a rough measurement. However, both Skoghall and Värö results indicate that the sodium salts in their industrial black liquor have a lower solubility limit than presented earlier in literature. This could be reasonable since it in previous studies not has been a clear distinction between the solubility limit and the meta stable limit (Schmidl and Frederick, 1998).

5.3 Evaluation of Salt Content and Validation of Crystal Fraction

In the evaluation of salt content in black liquor from Värö, no results indicate that the measured cf is higher than what could possibly be generated from salts in the black liquor. On the contrary, the cf^* in *Table 4.5* implies that cf is in line with the decrease of salts between unfiltered and filtered black liquor samples. However, since cf^* originates from the salt content analysis made by Värö, the cf^* cannot be considered as completely valid. Nonetheless, at Värö, there are no indications that something else than bulk crystals is filtered away by the crystal sampler. However, since no samplings have been done for black liquor with a DS higher than 64 %, no conclusion can be made for black liquor of high DS.

From the results in the salt content evaluation of black liquor from Skoghall, it was concluded that some of the measured values of cf exceed the salt content in the black liquor, hence are impossible. From *Table 4.6* it was concluded that for collected samples with a DS above ∼64 % there is not enough salt in the black liquor to supply for the measured cf. Since the accuracy of the analyses is unknown it is difficult to determine if the results from the salt content analysis lie within measurement errors. However, the average salt content in the unfiltered black liquor, where sampling was made after the point where streams of TOP brine and ash had been mixed in, at Skoghall was 22 $kg/kgBL_{DS}$. Even if all of these salts would crystallise in evaporator 1 (which is unlikely, since scaling is also occurring in the concentrator), the highest possible cf would be of 16 % at a DS of 70 %. Therefore, it is unlikely that the measured cf is correct, even if measurement errors are considered. It can therefore be concluded that, during sampling at Skoghall, the crystal fraction based solely on dry solids content measurements (cf) did not result in a correct crystal fraction at high dry solids content. However, since no measurements of salt content in unfiltered black liquor have been made for samples with a DS lower than 58 %, it is not possible to say where cf starts to be invalid. Therefore, a larger number of analyses of unfiltered black liquor would be required to make a more thorough assessment of the cf method.

When regarding the crystal fraction calculated from salt differences in unfiltered and filtered black liquor from Skoghall, cf^*, some interesting results can be noted. cf^* implies that a crystal fraction of about 11 % at high dry solids is more likely than the values of 15 to 19 % that the cf imply. In table *Table 4.3* it can be seen that the average cf in effect *S-1A* is 15.05 %. Hence, it is probable that in effect *S-1A* cf from dry solids measurements will always be overestimated.

There are a few possible explanations to why the dry solids content analysis might give faulty values of cf. To begin with, the DS measurements might have been wrong. However, after studying the results of the dry solids content measurements made, it seems unlikely that error in measurements there would contribute to the large deviations in cf. Furthermore, it is a possibility that the high viscosity of the liquor and high DS bring some unpredictable difficulties in filtration. Lastly,

one explanation could be that some other solid substance, than crystals, are filtered away by the crystal sampler.

If there is a solid phase in the black liquor that not consists of sodium sulphate and sodium carbonates, it most likely consists of an organic material, such as fibres or lignin, hemicellulose or cellulose. If fibres would be present in the black liquor it is probable that it would contribute to more severe fouling than reported at Skoghall. Furthermore, if fibres were present they would probably be visible when diluting the filter cake, which was not the case in any of the samplings. Additionally, no measurement in effect *S-2* was made, but if the result made in *V-2* at Värö could be considered valid for Skoghall as well, it means that no solid substance is filtered away below a DS of 44 %. Hence, it is not fibres that are filtered off. To fully exclude this possibility, a filtration of liquor from effect *S-2* could be made. Further on, it is unlikely that the pH in the black liquor falls below 11 in the evaporation trains, hence a precipitation of lignin is improbable. However, while the liquor is evaporated the concentration of salts, ions, increases. This increased ionic strength could impact the dissolution of organic compounds.

5.4 Ratio of Carbonate and Sulphate

From the phase diagram for samples from Värö, *Figure 4.4*, it is seen that the majority of the samplings indiates that the precipitating crystal species is burkeite, which is also confirmed by the calculated Rcs_{unfilt}.

The phase diagram from samples at Skoghall, *Figure 4.5*, shows more unexpected results which do not correlate with the results in *Table 4.9*. The cause for this is difficult to narrow down. It might be due to some uncertainties in analysis, it is the only result where analysis of the filter cake is involved. If the filter cake for e.g. consist of something else than crystals this could have an impact in the results.

5.5 Solubility and Salt Content

Both solubility curves computed for Värö respectively Skoghall samples seen in *Figure 4.6* and *4.7* display a lower solubility than the solubility correlation developed by Karlsson (2017). However, a lower solubility is not unlikely since the experimental analysis providing the data for the correlation developed by Karlsson (2017), was performed on a black liquor lacking ashes and TOP brine. However, since both of the solubility curves are composed by few data points, it would have been interesting to have a larger collection of data. Due to low amount of data points, the curves presented in this work should be viewed as valid only for the black liquor present at time for sampling, rather than as a general solubility correlation. Especially the curve from Skoghall is not very well fitted to the data points and is mainly based on samples that most likely are outliers. However, if a larger number of samples would be gathered, spread out over a large time span, it might be possible to generate a general solubility curve for black liquor at each mill.

6 Recommendations and Future Research

There are still many knowledge gaps that need to be filled to gain a further understanding of the influence of sodium sulphate and sodium carbonate crystals and how they can be studied. It should be prioritised to further investigate how the salt balance between cf and unfiltered black liquor adds up, especially for black liquor at low DS to be able to see where the two crystal fractions starts to deviate. When a reliable method for determination of bulk crystals has been confirmed, further sampling to investigate bulk crystals behaviour can be done, which then could be related to scaling in the evaporators.

It would be interesting to further investigate the possibility that other compounds than sodium salts precipitate in the black liquor and are captured in the crystal sampler. This could also be done by analysing the amount of organic carbon in the filter cakes and the filtered black liquor on a base of chloride, similar to the calculation of sulphate and carbonates in the filter cake conducted in this thesis work. Measurements of cf should also be done in effect *S-2* at Skoghall to exclude that any solids are present already at low DS.

To further enhance the understanding of crystallisation of sodium salts, a complete analysis of all major anions and cations present in black liquor should be performed. Since the crystallisation is an equilibrium process dependant on the solution, varying ion concentration could also give rise to a varying solubility of the sodium sulphate and sodium carbonate salts.

7 Conclusion

- A general sampling procedure for filtering and collecting industrial black liquor has been developed. However, when measuring the crystal fraction it is clear that, at high dry solids content, the crystal fraction calculated solely from dry solids content measurements is overestimated. The reason for this is still uncertain, but it is probable that it is due to difficulties with sampling at high dry solids contents, or that another substance than sodium sulphate and sodium carbonate precipitates in the black liquor.

- This work has shown that the solubility limit for the sodium salts in the black liquor at Södra Cell Värö and Stora Enso Skoghall is around 47-50 %. This is lower than the solubility values for burkeite and dicarbonate shown in literature, which can be explained with that in previous literature it has not been a clear distinction between the solubility limit and the metastable limit of the salts.

- With measurements of salt content in filtered and unfiltered black liquor it would be possible to estimate a solubility limit for the crystals precipitated in the black liquor. To be able to make a general conclusion for the black liquor, a larger number of samplings spread over time would be required.

- The crystal species obtained in the filter cake could not be determined within this work due to ambiguous results from salt content analysis. However, with accurate measurements of the sulphate and carbonate content in the filtered, unfiltered and filter cake it is believed that the carbonate sulphate ratios Rcs_{filt}, Rcs_{unfilt} and Rcs_{cryst} could be used to determine the crystal species in the filter cake.

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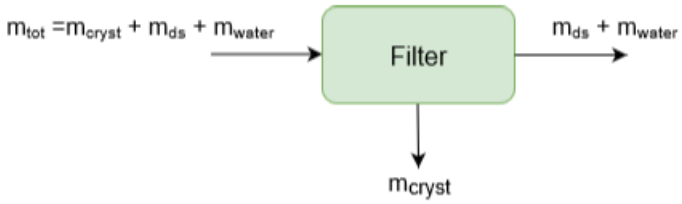
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A Appendix A

The following sections provide derivations of the crystal fraction (cf) from dry solids content measurements and the crystal fraction (cf^*) from salt content measurements. Furthermore, the calculation methodology for the allocation of salt to IMTBL due to addition of recovery boiler ash and TOP brine is presented.

A.1 Derivation of Crystal Fraction Based on Dry Solids Content Measurements



$$m_{tot}^{BL} = m_{cryst} + m_{ds} + m_{water} \tag{A.1}$$

$$DS_F = \frac{m_{ds}}{m_{ds} + m_{water}} \tag{A.2}$$

Solve for $m_{ds} + m_{water}$.

$$m_{ds} + m_{water} = \frac{m_{ds}}{DS_F} \tag{A.3}$$

Substitute A.3 into A.1.

$$DS_{OF} = \frac{m_{ds} + m_{cryst}}{m_{ds} + m_{water} + m_{cryst}} \tag{A.4}$$

Solve for $m_{ds} + m_{water} + m_{cryst}$ in A.4 which gives a new expression for m_{tot}^{BL}.

$$m_{ds} + m_{water} + m_{cryst} = \frac{m_{ds} + m_{cryst}}{DS_{OF}} = m_{tot}^{BL} \tag{A.5}$$

Let A.1 equal A.5.

$$\frac{m_{ds} + m_{cryst}}{DS_{OF}} = m_{tot}^{BL} \tag{A.6}$$

Multiply with DS_{OF}.

$$m_{ds} + m_{cryst} = m_{tot}^{BL} \cdot DS_{OF} \tag{A.7}$$

Solve for m_{cryst}.

$$m_{cryst} = (m_{tot}^{BL} \cdot DS_{OF}) - m_{ds} \tag{A.8}$$

From A.3, solve for m_{ds}.

$$m_{ds} = \frac{m_{water}}{\frac{1}{DS_F} - \frac{1}{1}} \tag{A.9}$$

Substitute m_{ds} in A.8 with A.9

$$m_{cryst} = m_{tot}^{BL} \cdot DS_{OF} - \frac{m_{water}}{\frac{1}{DS_F} - \frac{1}{1}} \tag{A.10}$$

Divide everything with m_{tot}^{BL}.

$$\frac{m_{cryst}}{m_{tot}^{BL}} = \frac{m_{tot}^{BL} \cdot DS_{OF}}{m_{tot}^{BL}} - \frac{\frac{m_{water}}{\frac{1}{DS_F} - \frac{1}{1}}}{m_{tot}^{BL}} \tag{A.11}$$

This gives:

$$\frac{m_{cryst}}{m_{tot}^{BL}} = DS_{OF} - \frac{m_{water}}{m_{tot}^{BL}(\frac{1}{DS_F} - 1)} \tag{A.12}$$

From the definition of dry solids content in equation 2.1:

$$\frac{m_{water}}{m_{tot}^{BL}} = \frac{m_{wet} - m_{dry}}{m_{wet}} = 1 - DS_{OF} \tag{A.13}$$

$$\frac{m_{cryst}}{m_{tot}^{BL}} = DS_{OF} - \frac{1 - DS_{OF}}{\frac{1}{DS_F} - 1} \tag{A.14}$$

Prolong the first term with the numerator of the second term.

$$\frac{m_{cryst}}{m_{tot}^{BL}} = \frac{DS_{OF} \cdot (\frac{1}{DS_F} - 1)}{\frac{1}{DS_F} - 1} - \frac{1 - DS_{OF}}{\frac{1}{DS_F} - 1} \tag{A.15}$$

$$\frac{m_{cryst}}{m_{tot}^{BL}} = \frac{\frac{DS_{OF}}{DS_F} - DS_{OF} - 1 + DS_{OF}}{\frac{1}{DS_F} - 1} \tag{A.16}$$

Multiply with DS_F

$$\frac{m_{cryst}}{m_{tot}^{BL}} = \frac{(\frac{DS_{OF}}{DS_F} - \frac{1}{1}) \cdot DS_F}{(\frac{1}{DS_F} - \frac{1}{1}) \cdot DS_F} \tag{A.17}$$

The definition of crystal fraction from dry solids content measurement is obtained in *Equation A.18.*

$$cf = \frac{m_{cryst}}{m_{tot}} = \frac{DS_{OF} - DS_F}{1 - DS_F} \tag{A.18}$$

A.2 Derivation of Crystal Fraction Based on Salt Content Measurements

The salt content in the unfiltered sample is known from analysis and is expressed in A.19.

$$\frac{m_{tot}^{s}}{m_{tot}^{BL}} = \frac{m_{diss} + m_{cryst}}{m_{tot}^{BL}} \tag{A.19}$$

The salt content in filtrated sample is known from analysis and is expressed in A.20.

$$\frac{m_{diss}}{m_{tot}^{BL} - m_{cryst}} = F_{salt} \tag{A.20}$$

The difference between the salt content in the unfiltered sample and the filtered sample should be the crystal fraction.

$$\frac{m_{cryst}}{m_{tot}^{BL}} = \frac{m_{diss} + m_{cryst}}{m_{tot}^{BL}} - \frac{m_{tot}^{S}}{m_{tot}^{BL}} = \frac{m_{tot}^{s}}{m_{tot}^{BL}} - \frac{m_{diss}}{m_{tot}^{BL}} \tag{A.21}$$

The above balance can be expressed in terms of the salt content in the unfiltered sample and the filtered sample by using A.19 and rearranging A.20.

$$\frac{m_{cryst}}{m_{tot}^{BL}} = \frac{m_{tot}^{S}}{m_{tot}^{BL}} - \frac{F_{salt}(m_{tot}^{BL} - m_{cryst})}{m_{tot}^{BL}} \tag{A.22}$$

$$\frac{m_{cryst}}{m_{tot}^{BL}} = \frac{m_{tot}^{s}}{m_{tot}^{BL}} - \left(\frac{F_{salt} \cdot m_{tot}^{BL}}{m_{tot}^{BL}} - \frac{F_{salt} \cdot m_{cryst}}{m_{tot}^{BL}}\right) \tag{A.23}$$

$$\frac{m_{cryst}}{m_{tot}^{BL}} = \frac{m_{tot}^{s}}{m_{tot}^{BL}} - F_{salt} + \frac{F_{salt} \cdot m_{cryst}}{m_{tot}^{BL}} \tag{A.24}$$

$$\frac{m_{cryst}}{m_{tot}^{BL}} - \frac{F_{salt} \cdot m_{cryst}}{m_{tot}^{BL}} = \frac{m_{tot}^{s}}{m_{tot}^{BL}} - F_{salt} \tag{A.25}$$

The final crystal fraction expressed with the salt content measured in the filtered and unfiltered samples is displayed in *Equation A.26*.

$$cf^{*} = \frac{m_{cryst}}{m_{tot}^{BL}} = \frac{m_{tot}^{s}}{m_{tot}^{BL}(1 - F_{salt})} - \frac{F_{salt}}{(1 - F_{salt})} \tag{A.26}$$

A.3 Allocation of Salt to IMTBL Due to Addition of Ash

The salt content in IMTBL without ash is defined in *Equation A.27* and is known from analysis results.

$$\frac{m_{salt}}{m_{BL}} \tag{A.27}$$

Assuming that 7 % of the $\frac{m_{DS}}{m_{BL}}$ is added ash to the IMTBL, and that all ash is salt with a dry solids content of 100 % the salt content in the IMTBL can be calulated according to *Equation A.28*.

$$\frac{m_{salt}^{IMTBL+ash}}{m_{BL}} = \frac{\frac{m_{salt}}{m_{BL}} + \frac{m_{DS}^{IMTBL} \cdot 0.07}{m_{BL}}}{m_{BL} \cdot 1.07} \tag{A.28}$$

B Appendix B

B.1 Supplementary Data

B.1.1 Comparison of Salt Content Analysis Performed by Värö and Skoghall Mill Laboratories

Table B.1: Comparative testing of salt content in black liquor done by laboratories at Värö and Skoghall mills, results displayed as mg/kgDS of black liquor. Results from sulphate analysis performed at Värö are marked in grey.

Sample	**Chloride** $[mg/kgDS]$		**Sulphate** $[mg/kgDS]$		**Carbonate** $[mg/kgDS]$	
	Värö	**Skoghall**	**Värö**	**Skoghall**	**Värö**	**Skoghall**
10	3100	2900	12 000	13 000	38 000	26 000
21	3000	2900	9800	15 000	36 000	19 000
42	3200	3100	20 000	12 000	27 000	16 000

B.1.2 Crystal Fraction against Dry Solids Content for Skoghall Samples

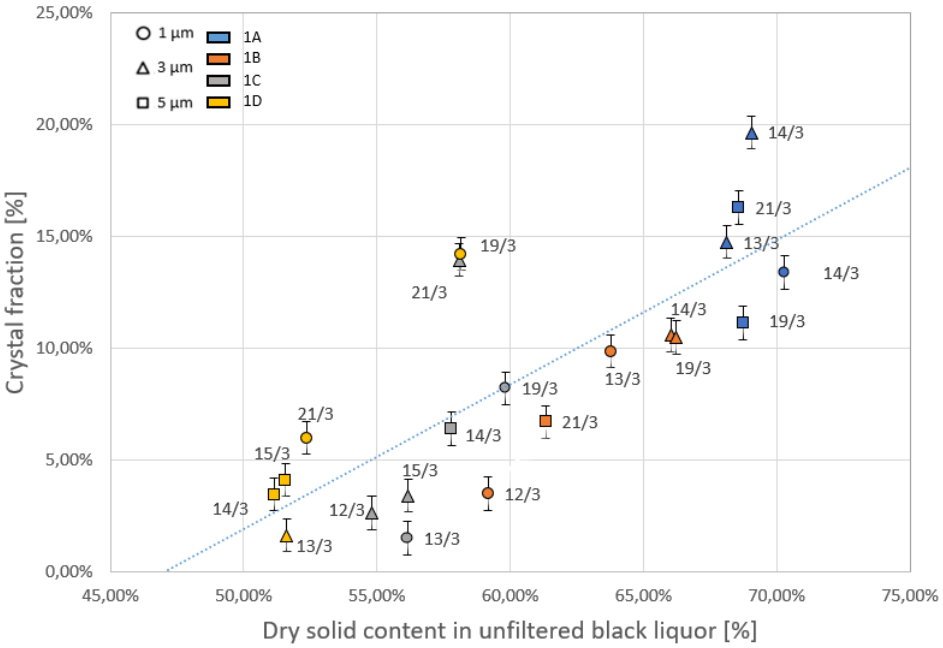


Figure. B.1: Crystal fraction against DS_{unfilt} for Skoghall samples where the date is displayed as data labels and filter pore size displayed as legends. Error bars are based on a fixed value of 0.738 % of the crystal fraction.

B.1.3 Salt content in IMTBL after Accounting for Salt Added with Recovery Boiler Ash and TOP Brine

Table B.2: Amount of salts (Na_2SO_4 + Na_2CO_3) in Värö IMTBL without and with allocated salt from recovery boiler ash and TOP brine

Sample type / Sample nr	**IMTBL** [wt % DS]	**IMTBL + ashes & brine** [wt % DS]
6	17.0	22.4
10	16.1	21.6
16	16.1	21.6
44	13.7	19.5
47	13.8	19.6
52	13.8	19.6

Table B.3: Amount of salt ($Na_2SO_4 + Na_2CO_3$) in Skoghall IMTBL without and with allocated salt from recovery boiler ash and TOP brine.

Sample type / Sample nr	**IMTBL** [wt % DS]	**IMTBL + ashes & brine** [wt % DS]
17	17.2	22.4
21	16.1	21.5
22	16.4	22.0
29	-	-
30	-	-
34	18.5	22.2
35	-	-
40	-	-