THESIS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY

The Formation and Dissolution of Sodium Salt Scales in Black Liquor Evaporators

ERIK KARLSSON

Department of Chemistry and Chemical Engineering
CHALMERS UNIVERSITY OF TECHNOLOGY
Gothenburg, Sweden
2017

The Formation and Dissolution of Sodium Salt Scales in Black Liquor Evaporators
ERIK KARLSSON
ISBN 978-91-7597-533-7

© ERIK KARLSSON, 2017

Doktorsavhandlingar vid Chalmers tekniska högskola
Ny serie nr 4214
ISSN 0346-718X

CHALMERS UNIVERSITY OF TECHNOLOGY
Department of Chemistry and Chemical Engineering
SE-412 96 Gothenburg
Sweden
Phone: +46 (0)31-772 10 00

Cover: Photographs of sodium salt scales produced from sodium carbonate solution (left) and black liquor (right) in the pilot evaporator.

Printed by Chalmers Reproservice
CHALMERS UNIVERSITY OF TECHNOLOGY
Gothenburg, Sweden
2017

The Formation and Dissolution of Sodium Salt Scales in Black Liquor Evaporators

ERIK KARLSSON

Forest Products and Chemical Engineering
Department of Chemistry and Chemical Engineering
Chalmers University of Technology

ABSTRACT

The evaporation of black liquor is an important and energy intense unit operation in the chemical recovery cycle of a Kraft pulp mill. Black liquor has a high content of sodium carbonate and sodium sulphate and, as the liquor becomes concentrated to above about 50% dry solids content, these salts start to crystallize and can form scales on the heat transfer surface, thereby decreasing the performance of the evaporator. Process disturbances due to sodium salt scaling are common and regular cleaning is normally needed to maintain the operation.

In this thesis, the formation of sodium salt scales has been studied experimentally on a pilot scale (using one 4.5 m long evaporator tube), with the focus placed on investigating the influence of the dry solids content and the bulk crystal population. A method for separating crystals (using a hydrocyclone) was developed so that the changes that were required in the studies could be made to the bulk crystal population in the evaporator. The dissolution of scales was also studied experimentally and an evaporator cleaning model was developed to simulate and evaluate industrial cleaning.

The measurements showed that the scaling rate is tenfold greater during primary nucleation of the sodium salts compared with continuous crystallisation (when crystals are available). This is mainly due to the high degree of supersaturation in the former, which causes a rapid initiation of scaling on the majority of the heat transfer surface. Bulk crystals are required to stop the high scaling rate during primary nucleation: all crystallization will otherwise take place on the heat transfer surface. It is therefore important to feed the evaporator with crystals during start-up after cleaning in order to minimize the risk of substantial scaling occurring before it is even back in normal operation.

Provided that a minimum amount of bulk crystals is available during normal operation (continuous crystallization), it was found that a further increase in the amount of bulk crystals will not decrease the scaling rate. The larger crystals contribute to a lower degree of scaling and are therefore more important in the system than the smaller crystals. It was also found that scaling is not a substantial problem when operating at a very high dry solids content (70-90%), which is probably due to the high content of bulk crystals.

The capacity of the evaporator can be improved by avoiding unnecessary and inadequate cleaning. Cleaning can be improved by taking a systematic approach: the overall heat transfer coefficient can be used to decide when cleaning is necessary, and the boiling point rise is a good measure for monitoring the performance of the cleaning operation and to decide when the evaporator is clean.

Keywords: scaling, crystallization fouling, black liquor, sodium carbonate, sodium sulphate, falling film evaporation, evaporator cleaning, solid dissolution.

To those before me

Appended Papers

This thesis is based on the work contained in the following papers:

I. **Karlsson, Erik; Gourdon, Mathias; Olausson, Lars; Vamling, Lennart** (2013)
Crystallization fouling of sodium salts in black liquor falling film evaporators
– Development of experimental method and first results.
Nordic Pulp & Paper Research Journal, 28 (4): 506-513.

II. **Karlsson, Erik; Gourdon, Mathias; Vamling, Lennart** (2014)
Solid dissolution into a vertical falling film under industrial-like conditions.
Industrial & Engineering Chemistry Research, 53 (22): 9478-9487.

III. **Karlsson, Erik; Gourdon, Mathias; Vamling, Lennart** (2014)
Cleaning of water-soluble scales in black liquor evaporators
– A modeling approach.
Industrial & Engineering Chemistry Research, 53 (50): 19600–19611.

IV. **Karlsson, Erik; Vamling, Lennart; Gourdon, Mathias; Olausson, Lars** (2015)
Modelling and evaluation of evaporator cleaning.
Journal of Science and Technology for Forest Products and Processes, 4 (6): 23-33.

V. **Karlsson, Erik; Gourdon, Mathias; Vamling, Lennart** (2016)
Separation and recirculation of bulk crystals to potentially mitigate sodium salt scaling in black liquor evaporators.
Nordic Pulp & Paper Research Journal, 31 (4).

VI. **Karlsson, Erik; Gourdon, Mathias; Vamling, Lennart** (2016)
The effect of bulk crystals on sodium salt scaling in black liquor evaporators.
Submitted to *Nordic Pulp & Paper Research Journal.*

Contribution Report

The author of this thesis has made the following contributions to these papers:

I. Main author. Majority of the planning and performance of the experiments, analysis and evaluation of the results; writing the paper with the support of the co-authors.

II. Main author. The experimental work and the development of the dissolution model were conducted by two Master's students who the author was co-supervising. The model was then refined further and the work on the heat transfer analogy was added by the author; writing was a joint effort with one of the co-authors.

III. Main author. The experimental work was conducted by two Master's students who the author was co-supervising. Modelling, analysing the results and writing the paper were conducted by the author with the support of the co-authors.

IV. Main author. Performing simulation, analysing and evaluating the results and then writing the paper, with the support of the co-authors.

V. Main author. Planning and performing the experiments, developing the implementation concept, analysing and evaluating the results; writing the paper with the support of the co-authors.

VI. Main author. Planning and performing the experiments, analysing and evaluating the results before writing the paper with the support of the co-authors.

Related work not included in this thesis

Karlsson, Erik; Gourdon, Mathias; Olausson, Lars; Vamling, Lennart (2013), Heat transfer for falling film evaporation of black liquor up to very high Prandtl numbers. *International Journal of Heat and Mass Transfer*, 65 s. 907-918.

Karlsson, Erik; Broberg, Anna; Åkesjö, Anders; Gourdon, Mathias (2013), Dissolution rate of sodium salt scales in falling film evaporators. *Conference Proceeding, Heat Exchanger Fouling and Cleaning*, June 09-14, Budapest.
(This is a conference version of Paper II)

Karlsson, Erik; Vamling, Lennart; Gourdon, Mathias; Olausson, Lars (2014), Modelling and Evaluation of Evaporator Cleaning. *Proceedings of the 2014 International Chemical Recovery Conference,* s. 234-247.
(This is a conference version of Paper IV)

Gourdon, Mathias; Karlsson, Erik; Innings, Fredrik; Jongsma, A.; Vamling, Lennart (2016), Heat transfer for falling film evaporation of industrially relevant fluids up to very high Prandtl numbers. *Heat and Mass Transfer*, 52 (2) s. 379-391.

Table of Contents

1

Introduction

Nowadays, all sectors of industry compete in a global market, which means that productivity and product value must be improved continuously to avoid risking failure. Simultaneously, environmental issues exert pressure emissions to be minimized and resource efficiency improved. In common with other industries, the pulp and paper industry has developed towards fewer and larger mills. These factors, combined with rapid technical development, have resulted in the process equipment now being larger, more complex and more efficient. The operation of the processes, in turn, becomes more complex and there is a smaller margin for failure or disturbances. It is very important that all process equipment has high availability and low maintenance costs to maintain a high level of productivity.

The same driving forces, i.e. productivity levels and environmental issues, also favour increased energy efficiency. Selling more of the energy or material streams in the form of products allows less to be used internally; the alternative of buying (more) fuels instead of improving efficiency is less attractive from an environmental perspective. These techno-economic systems are of course very complex and hard to predict. However, the general trend remains: the driving force is for the process equipment to have greater efficiency and availability. This thesis addresses one of the most important issues that affects the black liquor evaporation plant, one of the most steam-consuming units of a Kraft pulp mill.

1.1 Background

The pulp and paper industry is an important actor on the global market (Diesen, 1998). Generally speaking, this sector is comprised of companies using wood to produce cellulose-based materials such as paper and boards. This conversion is energy intense but, due to utilization of residual streams, including bark and black liquor, pulp and paper mills can not only satisfy at least a part of their own energy needs but also sell energy or fuels at times. In 2005 the pulp and paper industry was the fourth largest sector in the world in terms of energy (IEA, 2008). From a Swedish perspective, the forest industry has been important to the economy for a long time: the pulp and paper industry here uses 52% of the total amount of energy consumed in the industrial sector (Energimyndigheten, 2013).

The pulp and paper industry is searching for new opportunities to increase product value and income in order to improve competitiveness. The sector is also aware of the possibility of offering a renewable alternative to all products and fuels that are currently produced from fossil resources. The term “biorefinery” is used as an analogy for oil refinery, which means that green products and energy are produced from wood (Alén, 2011). Together with the development of the biorefinery concept, research and development has also been focusing on how to improve the efficiency of the processes to save energy. Here, it is also important to integrate the processes internally within the mill, and maybe also with other industries in the vicinity, in order to achieve an overall high efficiency (Sandén & Pettersson, 2014).

1.2 Kraft pulping and chemical recovery

There are two main types of processes for producing pulp: mechanical and chemical pulping. The predominant process used in the latter is called Kraft pulping, and is shown schematically in Figure 1.1. The first step is the wood handling, where the logs are debarked and cut into chips. These are then cooked in a water solution of sodium hydroxide and sodium sulphide called white liquor. Cooking disintegrates the wood and liberates the fibres within it. After washing, these fibres are bleached and treated further to obtain a pulp with the properties desired. Pulp that is not to be used directly on site, for example to produce paper or board, is dried and baled so that it may be transported (Gullichsen & Fogelholm, 1999).

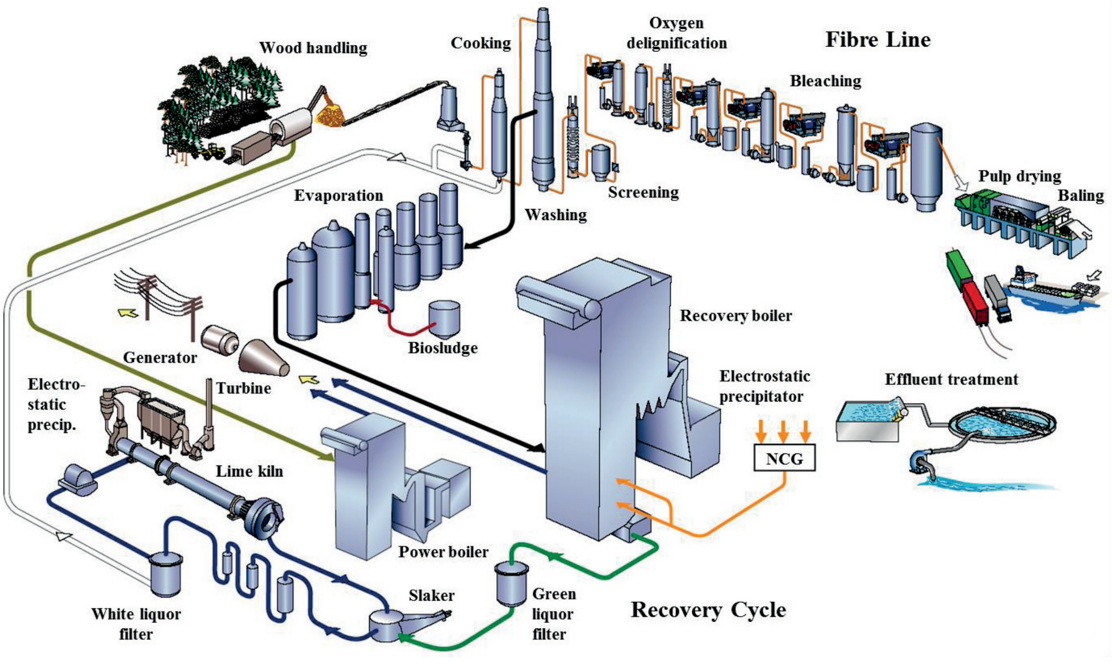

Figure 1.1 Process flow diagram of the Kraft pulping process. Courtesy of Valmet (2015).

The three main components of wood are cellulose, hemicellulose and lignin. As a rule of thumb, each contribute to one third of the wood, although this varies depending on the species and growth conditions of the tree. The principle of chemical pulping is to dissolve as much of the lignin as possible to free the fibres, doing as little damage as possible. The resulting pulp (i.e. fibres) will then consist mainly of cellulose and some hemicellulose. The part of the wood that is dissolved (i.e. mainly lignin) will remain in the spent white liquor, which is separated from the pulp in the washing step. This spent liquor is called black liquor and consists of about 85% water. It is important, for economic and environmental reasons, to recover the energy and chemicals in the black liquor. This is done in a process called the recovery cycle (Green & Hough, 1992). which comprises the following principle unit operations:

- Evaporating black liquor to make it concentrated and combustible
- Combusting black liquor in the recovery boiler to (i) recovery energy from the organic fraction and (ii) produce sodium carbonate and sodium sulphide (green liquor)
- Causticizing sodium carbonate into sodium hydroxide using lime, i.e. producing new white liquor
- Regenerating lime in the lime kiln

In the evaporation plant, the black liquor is concentrated from a dry solids content of about 15% to 75%. Thereafter it is combusted in the recovery boiler to produce steam and electricity that are used in the processes. Modern pulp mills, however, produce more electricity and heat than is required for the process (Gullichsen & Fogelholm, 1999). The evaporation plant is normally the largest consumer of process heat at the pulp mill: Axelsson, Olsson and Berntsson (2006) found that the evaporation plant and the condensate stripper used together 29% of the steam produced.

The most common type of evaporator employed in Kraft mills is the multiple stage falling film evaporator. Multiple stage means that a number of heat exchangers are connected in series, which allows evaporated steam to be reused from stage to stage, thereby reducing the primary steam demand: the whole plant becomes more energy efficient. New plants normally have 6-7 stages, where the concentration of the black liquor increases successively. Each heat exchanger (stage), normally called an effect, has a thin falling film of black liquor that evaporates on the heat transfer surface, which is heated by steam condensing on its other side (Gullichsen & Fogelholm, 1999).

1.3 Fouling in black liquor evaporators

It is important, in all heat exchangers, that the transfer of heat between the evaporating black liquor and the heating steam is sufficient if the capacity of the equipment is to be maintained. Black liquor is a complex solution of organic and inorganic compounds: it has the potential of adhering to the heat transfer surface and thus decreasing the heat transfer. If such fouling is not removed, it will eventually cause the failure of the whole evaporator plant and, ultimately, the entire mill.

The most common causes of organic fouling are lignin, soap and fibres, although they mainly cause problems when there are malfunctions in other parts of the mill. Lignin will stay in solution as long as the pH levels are not significantly decreased, whereas soap and fibre fouling is common if the upstream separation equipment fails (i.e. soap skimming and wash filters). The effects with medium concentrations (2, 3 and 4) are usually those that are fouled (Gullichsen & Fogelholm, 1999).

When the solubility limit is exceeded, the inorganic salts present in black liquor have the potential of crystallizing to form scales on the heat transfer surface. Such fouling, or scaling, is common and quite complicated to control. There are three main type of scales that form in black liquor evaporators (Gullichsen & Fogelholm, 1999):

- Calcium scales
- Aluminium or silicate scales (or other non-process elements)
- Sodium scales

Calcium is used to prepare white liquor in the causticizing plant. Efficient white liquor settling or filtering is important in achieving a low content of calcium in the black liquor. Calcium is bound to organic components in black liquor, making calcium scaling sensitive to temperature. When a temperature of 90-130°C is reached, the calcium ions become free and can potentially form calcium carbonate on the heat transfer surfaces; either acid washing or hydroblasting is often needed to remove the calcium scales thus formed (Gullichsen & Fogelholm, 1999). If the extent of calcium scaling is such that significant problems are experienced, a method can be employed whereby the liquor is heated to 110-145°C for 1-20 minutes to allow it to precipitate before being fed into the evaporator plant (Eneberg, Kaila & Kiiskila, 2002).

Aluminium silicate scales (or salts containing other non-process elements) grow very slowly due to the low concentration of these elements. On the other hand, they are very hard and glass-like, which makes them difficult to remove. Avoiding the accumulation of non-process elements means these type of scales can normally be avoided (Gullichsen & Fogelholm, 1999).

Figure 1.2. Example of scaling in a black liquor evaporator. Courtesy of Valmet (2015).

In contrast to calcium and non-process elements, the sodium content of black liquor cannot be reduced since sodium is an essential part of the Kraft process. Scaling caused by sodium is therefore very common and most mills cannot avoid it: the situation is addressed by having routines for its management. Sodium scales normally consist of double salts of sodium carbonate and sodium sulphate; it is in the part of the plant with the highest concentrations that their solubility is exceeded. Due to the high concentrations of these salts in black liquor, scaling can occur very rapidly and the evaporator can lose almost all its capacity in a matter of hours if operated incorrectly. Fortunately, sodium scales are water soluble and relatively easy to remove. There are also other sodium salts that can cause scaling, for example sodium oxalate, but they are less common (Gullichsen & Fogelholm, 1999). Throughout this thesis, the terms sodium salts and sodium scales refer to sodium carbonate and sodium sulphate salts, respectively.

1.4 Previous work

In an early study by Grace (1975), the extent of scaling in industrial evaporators was mapped. Grace (1976) was then first to measure the solubility of sodium carbonate and sodium sulphate in black liquor, and used it as a tool to understand evaporator scaling. He defined, for example, "critical solids", a term that is commonly used. The exact definition is, however, unclear as it can have two slightly different meanings: in Grace (1975) it is defined as "the solids (content) level at which it (the liquor) just becomes saturated with respect to Na_2CO_3 and Na_2SO_4", while in Grace (1976) it is referred as "the critical liquor solids content for the onset of Na_2CO_3+Na_2SO_4 precipitation". Crystallization and precipitation normally start once the concentration is supersaturated (see Section 3.1): the dry solids content will therefore be greater than if the definition used is the dry solids content when the solubility limit is exceeded. Nevertheless, the concept of critical solids clarified in which evaporator effect(s) scaling could be expected, and is in general use today. Grace also found the most common type of sodium scale that was formed to be the crystal species burkeite ($Na_2CO_3 \cdot 2Na_2SO_4$). Other early studies were made by Novak (1979), Sandquist (1983) and Söderhjelm, Virkola and Fagerström (1985), who all conducted evaporation experiments to study scaling.

The early studies mainly considered long-tube vertical (LTV) rising-film evaporators, which were common at that time, but they were, however, sensitive to scaling. The trend during the subsequent years of increasing the final concentration of the black liquor to recover more energy meant that falling film evaporators became more common, as they are less sensitive to scaling (Schmidl & Frederick, 1998).

During the 1990s and 2000s, substantial work at The Georgia Institute of Technology and Institute of Paper Science and Technology (IPST) in the USA provided new important knowledge of the mechanisms of scaling (Euhus, 2003; Shi, 2002; Smith, 2000). For a long time it was believed that burkeite and sodium carbonate were the main species of sodium scales that crystallized in the evaporators (Golike *et al.*, 2000). However, a new unknown crystal species was found, with the approximate composition $Na_2CO_3 \cdot 2Na_2SO_4$. Named dicarbonate (Shi, Frederick & Rousseau, 2003), it was reported to cause more rapid scaling than burkeite since it had a stronger tendency to adhere to the heat transfer surface (Euhus *et al.*, 2003). Also, a third crystal species, sodium sulphate carbonate, was suggested by DeMartini and Verrill (2007) but has not been investigated further. Other important findings were that dicarbonate cannot crystalize on burkeite crystals (i.e. black liquor can have a second concentration limit when primary nucleation occurs, which was called second critical solids) and that calcium ions can inhibit primary nucleation (whereas calcium carbonate scales can induce sodium scaling) (Frederick, Shi, Euhus & Rousseau, 2004).

A more complete picture of sodium salt scaling in black liquor evaporators can be provided by complementing the more fundamental understanding mentioned above with pilot studies. Only then can the true behaviour of scaling during the evaporation of black liquor be revealed and how it is influenced by operational parameters and evaporator design. Studies on both laboratory and pilot-scale have been carried out during the last 50 years, although most work pertaining to falling film evaporation, which is most common today, has been carried out in the last 20 years. Pilot investigations by Euhus (2003) showed relationships between bulk and surface crystallization, and that dicarbonate causes more rapid fouling than burkeite. In investigations made by Gourdon (2009) the large pilot plant at Chalmers University in Gothenburg, Sweden, was used (as was the case in the present study): the findings of Euhus (2003) were confirmed and new findings connected to the operation and design of the evaporator were made. For example, it was shown that scaling was most severe when passing, or operating close to, the critical solids level (causing primary nucleation), and that the scales always grew upwards from the bottom of the heat transfer surface (Gourdon, Vamling, Andersson & Olausson, 2010b). It was also shown that the scaling was faster at higher heat loads (differential temperature over the heat transfer surface) and at lower wetting rates (flow rate). These two parameters were then analysed further to show that the increase in concentration along the heat transfer surface was major driving force of fouling (Gourdon, 2011). Regarding the design of the evaporator, it was found that the residence time had no significant effect on scaling in the range investigated: supersaturation is released relatively rapidly (Gourdon, Vamling, Strömblad & Olausson, 2008).

During the years there has been a drive for increasing the final concentration of black liquor because it improves steam economy and recovery boiler operation (Nikkanen, 1993). Especially in Nordic countries it has become more and more common to have a final concentration of 80-85% dry solids content. This change has not increased the problems with scaling according to practical experiences (Kaila, Jaakkola & Veitola, 2004). Even higher final dry solids contents has been tested, up to 90%, in mill studies and was found possible (Vakkilainen, 2000).

1.4.1 Solubility models

Following on from the pioneer work undertaken by Grace, several later attempts have been made to model the solubility of the sodium carbonate–sodium sulphate system as well as the composition of their crystals. Using data from Grace (1976), Rosier (1997) developed an industrially-applicable model for critical solids in black liquor based on the operational parameters of mills. Golike *et al.* (2000) used the Pitzer method to implement their model in the commercial programme NAELS, although they only considered the crystallization of burkeite. Bialik, Theliander, Sedin, Verrill and DeMartini (2008), along with Wadsborn and Rådeström (2009), also used the Pitzer method to develop scientifically-orientated models that also include variations in the compositions of crystals. The Pitzer method was nevertheless questioned by Picot, Mortha, Rueff and Nortier (2012), who claimed their e-NRTL model to be more thermodynamically consistent. These scientifically-orientated models were only used for aqueous solutions and not extended to embrace black liquor. A group in Brazil has recently studied the solubility of sodium salts in eucalyptus black liquor but it is uncertain if their modelling attempts were successful (Leite, Andreuccetti, Leite & D'Angelo, 2014).

1.4.2 Mitigation and cleaning strategies

The main focus of many later studies has been to apply existing fundamental knowledge of scaling and provide direct advice of how to operate the evaporator to control it (DeMartini & Frederick Jr., 2008; DeMartini & Verrill, 2007; Frederick & Euhus, 2015; Gourdon, Vamling*, et al.*, 2010b; Verrill & Frederick, 2006). The general rules are (i) avoid operation close to critical solids, as this will risk primary nucleation and cause rapid scaling, and (ii) avoid a high carbonate-sulphate ratio, because it will result in the crystallization of dicarbonate and thereby cause more scaling than burkeite. These mitigation strategies have been proven to work on a full scale in a number of case studies (DeMartini & Verrill, 2005; Verrill & Giehl, 2004).

Concentrations clearly above the solubility limit imply the presence of a significant amount of bulk crystals, and is the reason for not operating close to critical solids. The supersaturation of sodium salts caused by the evaporation process would, to a larger extent, lead them to crystallize on these bulk crystals instead of on the scales. The population of bulk crystals can also be increased by recirculating black liquor of higher concentration and thereby introduce additional (seed) crystals. This is used in some mills today, and has been discussed in a number of studies (Adams, 2001; Frederick & Euhus, 2015; Verrill & DeMartini, 2006). However, there is no experimental data that investigates the influence of bulk crystal recirculation. A disadvantage of recirculating highly concentrated black liquor is that organic compounds would be also recirculated, which would increase viscosity and decrease capacity. A solution for this is suggested in a patent solution (Olausson, Andersson, Gourdon & Vamling, 2011) whereby a hydrocyclone is used to separate a crystal-rich fraction from the highly concentrated liquor before it is recirculated.

Some studies (Adams, 2001; Frederick & Euhus, 2015) argue that a large sump volume is needed to give sufficient residence times to relieve all supersaturation. The pilot studies conducted by Gourdon, Vamling*, et al.* (2010b), however, showed no need of a large sump volume.

Most mills still require regular cleaning to remove sodium scales even if the mitigation strategies mentioned above are used. Very little research has been carried out to understand how such scales may be removed most efficiently; existing studies mainly discuss cleaning on an operational level to provide guidelines. The most comprehensive work that has been carried out is by Verrill and DeMartini (2006), which combines knowledge of crystallization chemistry with mill studies. They emphasize the importance of reintroducing the wash liquor to the evaporators in such a way that rapid scaling is avoided, as they observed situations where the majority of the dissolved scales recrystallize on the heat transfer surfaces. They also suggest that the cleaned evaporator be reseeded when being returned to operation by introducing liquor of high concentration: this avoids primary nucleation, which can cause rapid scaling (also mentioned by DeMartini and Frederick Jr. (2008)). There are also suggestions of methods for optimizing the cleaning interval: for heat exchangers in general (Ishiyama, Paterson & Ian Wilson, 2011) and black liquor evaporators in particular (Bremford & Müller-Steinhagen, 1999)

1.4.3 Knowledge gaps

Summarizing previous work, knowledge gaps were found that show the importance of further investigations being made. Many mills operate at liquor concentrations above 80%

dry solids content, but there is very little data of scaling above 70% dry solids content. The whole concentration range should be investigated to obtain a complete picture of exactly where in the equipment scaling is most likely to occur.

Studying the literature, one of the most common recommendations for mitigating scaling is to ensure a stable bulk crystal population, for example by recirculating liquor of higher concentrations. This is founded on both general knowledge and experience of crystallization, and has a theoretical base. Nevertheless, there is no experimental data available of how the recirculation of bulk crystals influence scaling in black liquor evaporators: the recommendations are on a conceptual level only. Experimental data would give a solid base for recommendations which, in turn, would be more precise and adapted to different situations. Here, more fundamental knowledge is needed of how scaling is influenced by the bulk crystal population, and how they can be recirculated efficiently. If recirculation is to be used, then only a crystal-rich fraction is required, and the hydrocyclone separation technology should be evaluated and developed to ensure this.

The current fundamental understanding of scale removal is weak, and recommendations of how to deal with it are based mainly on trial and error. Understanding and modelling the fundamental mechanisms should allow more precise recommendations to be made, and maybe even new ways of cleaning to be developed.

1.5 Objectives

The main objective of this research was to increase understanding of, and thereby minimize, the disturbances and operational problems caused by sodium scales in black liquor evaporators. The work is divided in two parts:

- **The formation and mitigation of scales:** Develop the current understanding of scaling and methods for its mitigation. As essential work has already been done, the focus here was to fill the most important gaps. This gave rise to the following research questions:
    - How does the concentration of the liquor influence the scaling rate? What are the critical concentrations in terms of scaling? Being relatively unexplored, the highest concentrations (70-90% dry solids content) are of the most interest here.
    - How does the bulk crystal population influence the rate of scaling?
    - In what way can the recirculation of bulk (seed) crystals mitigate fouling under industrial-like conditions?
    - How can hydrocyclone technology be used to produce a crystal-rich stream that can be recirculated?
- **The dissolution of scales and cleaning evaporators:** Develop the current understanding of scaling and methods for improving the removal of scales. In terms of research, this is an unexplored field: both fundamental and applied knowledge are needed. The following research questions that arise are:

- How can the dissolution and removal of scales be studied under controlled conditions?
- What are the fundamental mechanisms involved when scales are removed during cleaning?
- How can the cleaning methods used today be improved by the knowledge gained and the models developed?

1.6 Outline of the thesis

Chapter 1 provides a general introduction to the field and previous work is summarised to set this work in context. In Chapter 2 the evaporation of black liquor is described, with the focus placed on the parts that are most relevant here: the formation of scales and the cleaning of evaporators. The most important theory related to this work is explained in Chapter 3, which includes the fundamentals of crystallization, formation of scales and dissolution, along with heat and mass transfer.

The experimental equipment and procedures are explained in Chapter 4 together with methods for evaluating raw data. The dissolution and cleaning models that are developed are described in Chapter 5.

Chapter 6 starts with a summary of the results and the conclusions drawn from the six papers. Then, some of the data from the papers is analysed further and compared with work by others: results from related work conducted by our research group but not included in the papers are also presented. The conclusions are presented in Chapter 7 and Chapter 8 offers suggestions for future work.

2

Evaporation of Black Liquor

2.1 Black liquor

The composition and properties of black liquor depend on the raw material (wood species and growth conditions) and pulping process used. When it enters the evaporation plant, black liquor consists mainly of water (about 85%) and is a complex mixture of dissolved inorganic and organic compounds; the very small amount of suspended material present is mostly in the form of fibres. Bulk crystals are also present, however, because the liquor is concentrated and the solubility of various salts is therefore exceeded. Black liquor also contains small amounts of soap that is often separated at about 30% dry solids content. The inorganic part is comprised mainly of sodium salts originating from the white liquor, whilst the organic part is mainly lignin and polysaccharides (about two-thirds of the dry solids mass) (Adams, 2001). Schmidl and Frederick (1998) analysed samples of black liquor from mills in North America, the results of which are presented in Table 2.1. As can be seen, the concentration of sodium is high, explaining why sodium scales foul the heat transfer surface rapidly.

Table 2.1 Typical composition of black liquor taken from mills in N. America and analysed by Schmidl and Frederick (1998).

Analyte	Mean	Standard Deviation	Range
Na_2CO_3, wt. %	10.0	2.6	4.77 - 14.5
Na_2SO_4, wt. %	6.03	4.18	1.94 - 16.1
Na_2CO_3/Na_2SO_4, mol/mol	2.49	1.67	1.94 - 16.1
Na_2S, wt. %	0.79	0.92	0.06 - 2.97
Residual active alkali, wt %	5.69	0.92	2.81 - 7.66
Sodium, wt. %	18.4	1.65	14.0 - 20.3
Potassium, wt. %	2.02	1.19	0.82 - 5.05
Residual soap, wt. %	0.85	0.48	0.32 - 2.02
Fibre [a], wt. %	0.23	0.24	0.04 - 1.08
Critical solids, wt %	52.2	2.8	49.0 - 60.3
Inorganic carbon, wt. %	1.14	0.30	0.54 - 1.64
Organic carbon, wt. %	33.5	2.50	30.2 - 39.7
Sulphate, wt. %	4.08	2.83	1.31 - 10.9
Thiosulphate, wt. %	3.98	1.25	2.40 - 6.49
Chloride, mg/kg	4 810	3 170	1 570 - 12 700
Oxalate, mg/kg	5 250	3 350	2 000 - 13 400
Calcium, mg/kg	409	278	118 - 1 050
Silicon, mg/kg	676	345	367 - 2 080

[a] Fibre measurements from different researchers varied, depending on the pore size of the filters used.

The physical properties most important for the evaporation of black liquor are viscosity, density and boiling point rise. At 15% dry solids content, the viscosity of black liquor is two or three times that of water and, as the liquor becomes concentrated, it increases exponentially: at 80% dry solids content, the viscosity is about one million times that of water (Adams *et al.*, 1997). The evaporator operation is enabled by increasing the temperature of the liquor as its concentration increases, which keeps its viscosity down. The viscosity is controlled mainly by the organic compounds: their molecular weight and colloidal state is important in determining the viscosity of any particular liquor. There are therefore large variations in the viscosity of liquors, and a tenfold difference is not uncommon (at the same temperature and concentration). Some authors, for example Adams (2001), argue that black liquor at about 50% dry solids content is transformed from a polymer solution (i.e. macromolecules dissolved in water) into a polymer blend (i.e. polymers constitute the continuous phase) with water acting as a plasticizer. The source of this behaviour is work by Masse, Kiran and Fricke (1986), whose experiments found that black liquor changed from freezing to glass transition when it had a dry solids content of about 50%. The transition was however observed at around -80°C, a temperature not relevant to black liquor evaporation. Presupposing that this transition will take place at the same concentration during evaporation at around 100°C seems risky, since physico-chemical properties are strongly dependent on temperature.

Both the density and the boiling point rise of black liquor are influenced mainly by its inorganic components. Density has a close to linear dependency on concentration up to 65%: above this, the change to the polymer-continuous phase changes its behaviour. Boiling point rise is strongly dependent on concentration (exponential behaviour): at 80% dry solids content, it is about 30°C. Density has a strong dependency on temperature whilst that of boiling point rise is relatively weak (Adams *et al.*, 1997).

2.2 Evaporators

Evaporation is a widely-used unit operation and a simple way of concentrating a solution by evaporating the solvent. It can be used to separate volatile components from other components that are essentially non-volatile and has numerous applications, such as in the food (e.g. to evaporate milk, juice and sugar) and chemical industries (e.g. to crystallize salts or other products) as well as for desalting seawater. The aim of evaporating black liquor is (with minimal losses) to produce a concentrated mixture that can be combusted in the recovery boiler and thereby recover both energy and chemicals. In addition to water, however, the condensate contains other components that are e.g. poisonous, odorous and flammable and requires treatment. A condensate striping column is therefore normally included in the evaporator train to segregate the clean and foul fractions of condensate. Methanol and turpentine are examples of substances that can be extracted and purified further; soap is another substance that needs to be separated (by skimming) and can be refined to give tall oil (Gullichsen & Fogelholm, 1999).

2.2.1 The evaporator train

A high thermal efficiency is often attained in the evaporation process by the use of multiple effect evaporation. Multiple steps allow evaporated vapour from one effect to heat the subsequent effect, which is possible because the pressure is decreased and thus lowers the boiling point of the liquor in the following effect. The effects are numbered according to the steam flow: the first effect is where primary steam is introduced, and the steam from the last effect is condensed on a surface condenser. The liquor flow can then be coupled in different ways, with pure counter-flow or a combination of counter and parallel-flow being the most common (Gullichsen & Fogelholm, 1999). Today, seven effects are common in new plants, an example of which can be seen in Figure 2.1. Low pressure steam (about 145°C) is introduced into Effect 1, which also has the highest concentration. Effects 1-4 have counter-flow while Effects 5-7 have parallel-flow. To complicate the flows, some steam from Effect 1 is used to heat the condensate stripper, and liquor streams are preheated in its condensers. Weak liquor enters the system at about 15% dry solids content and is concentrated to about 75% when it exits Effect 1. Some mills also have an additional concentrator to increase the final concentration to 80-85% dry solids content: medium pressure steam is used here to enable the high temperature needed in this effect to prevent too high a viscosity and to overcome boiling point rise. Real evaporators are more complicated and often adapted to the situations at the mill in question; they can also be integrated with the rest of the mill to varying extents (Olsson, 2009).

Different types of residual streams from other parts of the mill are often introduced into the evaporator train either for treatment or to recover chemicals. Although these streams are often relatively small, they can sometimes influence the behaviour of scaling. The most important stream for sodium scaling is electrostatic precipitator (ESP) ash from the recovery boiler, which contains significant amounts of sodium sulphate. It is often introduced before Effect 1 (Figure 2.1) or in the weak liquor mixing tank. Different types of spent acids, for example from the preparation of bleaching chemicals or tall oil, also contain sulphate (Gullichsen & Fogelholm, 1999).

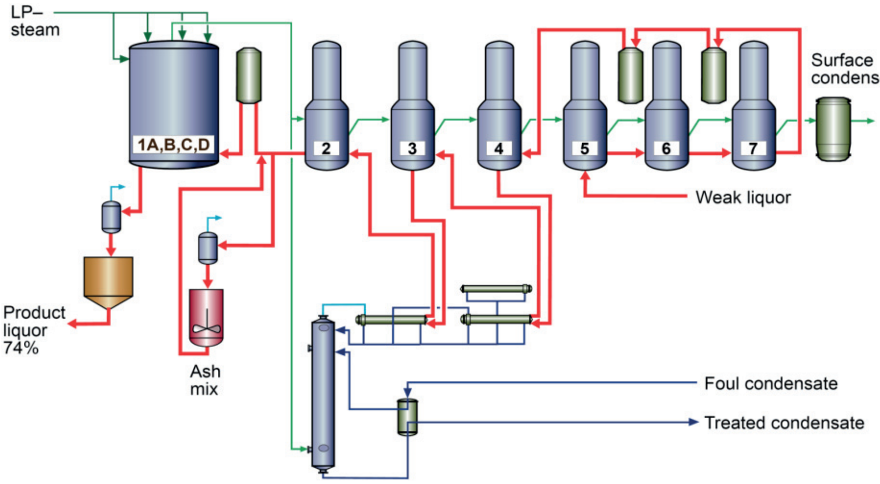

Figure 2.1. Simplified process flow diagram of a modern black liquor evaporator train, including a condensate stripper and an additional concentrator. Courtesy of Valmet (2015).

Effect 1 is often called the concentrator and is different from the other effects. The concentration of the liquor in it is high (above 50% dry solids content) and it therefore should be designed to handle both high viscosity and the crystallization of sodium salts. It needs to be overdesigned to allow for some fouling and be equipped to simplify cleaning. It is also normally divided into two, three or four chambers (Units A, B, C and D) supplied with low pressure steam, in which the liquor flow is in series (i.e. concentration increases gradually in each step) but the steam flow is parallel. This configuration provides for some back-up since one unit can often be bypassed if it is too fouled and the flow sequence can often be switched to level out fouling. Moreover, it is often possible to clean one unit at a time, which allows other units to continue operating (Gullichsen & Fogelholm, 1999).

2.2.2 Falling film evaporation

Some decades ago, as mentioned previously, long-tube vertical (LTV) rising-film evaporators were gradually replaced by falling film evaporators due to their superior resistance to fouling. Falling film evaporators are also characterized by a short contact time between the black liquor and the heat transfer surface, and their high heat transfer coefficients. They have a fixed (sump) level at the bottom and use a pump to recirculate the liquor up to the top. The heating elements can be of two types: plate (lamella) or tube. In the case of tubes, the liquor can be on either inside or outside of the tubes, where the latter is shown in Figure 2.2. The configuration with liquor inside the tubes is used for Effects 2-7 as it is less costly; the liquor in Effect 1 should be on the outside, as this is more robust in terms of scaling issues (complete plugging can result from scaling inside tubes) (Gullichsen & Fogelholm, 1999).

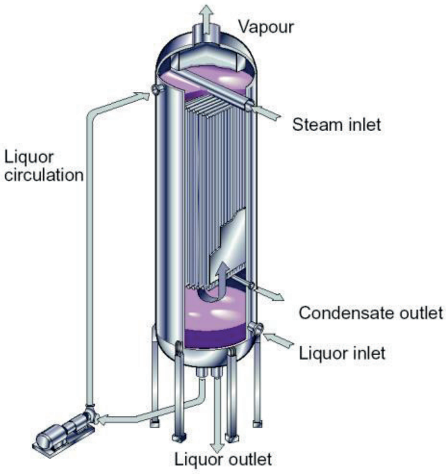

Figure 2.2. Typical falling film evaporator of the tube type, with the liquor on the outside of the tube. Courtesy of Valmet (2015).

In all types of falling film evaporators, the liquor is pumped to the top and distributed over the heat transfer surface. Gravity then causes it to fall fast, in a thin film along the heat transfer surface, giving it a short contact time and a high heat transfer coefficient. As the liquor falls, it is heated and partly evaporated. It is important to have good wetting of the heat transfer surface to prevent it from drying out and to mitigate fouling; an efficient distribution system at the top and sufficient recirculation flow are needed (Gullichsen & Fogelholm, 1999).

A third type of evaporator, called a forced circulation evaporator or crystallizer, is sometimes used as the concentrator. These are even less sensitive to fouling than falling film evaporators because heating and evaporation are (partially) separated, but they have a higher power consumption (Gullichsen & Fogelholm, 1999).

2.3 Sodium salt scaling

Scales of sodium carbonate-sodium sulphate crystals are one of the most common types of fouling in black liquor evaporators. This is simply because black liquor contains high concentrations of these salts and the final concentration of the liquor is far above their solubility; crystallization is inevitable and it is therefore likely that crystals will form on the heat transfer surface. The term critical solids is defined as the liquor concentration at which solubility is exceeded or when precipitation begins (see Section 3.1), and evaporator effects operating above this limit have to be adapted to crystallization. As mentioned above, a modern evaporator train is constructed so that all crystallization occurs in the concentrator, i.e. Effect 2 operates clearly below the critical solids level and the concentrator clearly above. The current state of knowledge on how to handle scales was mentioned briefly in Section 1.4. In the following two sections, the mitigation strategies and methods for cleaning concentrators used today are explained in more detail.

2.3.1 Mitigation strategies

All mills are unique, with respect to both the evaporation plant and the other parts of the mill that affect it and troubleshooting and problems therefore must often be treated case by case. However, there are some general strategies that can be employed to mitigate scaling:

- Design the concentrator to ensure sufficient wetting and prevent the heat transfer surfaces from having too high a temperature. Overdesign allows for some scaling to occur but still have sufficient evaporation capacity.

- Avoid operation close to the critical solids because it can mean a high level of supersaturation with few or no bulk crystals, making crystallization on the heat transfer surface more likely.

- Avoid fluctuations in both operation and liquor properties as much as possible (especially the parameters mentioned here). These can shift the operation into an unstable state and result in severe scaling.

- Favour the crystallization of burkeite over dicarbonate (which gives more scaling, see Section 3.1.1) by increasing the concentration of sulphate in relation to carbonate.

- Increase the amount of bulk crystals in the concentrator by recirculating product liquor.

- Reseed the concentrator when starting up after cleaning or shut-down by filling it with liquor containing bulk crystals. This will avoid passing the critical solids level during evaporation, which often causes scaling.

The ratio between carbonate and sulphate in black liquor is influenced by the sodium and sulphur balance of the whole mill and can therefore be difficult to change. One possible measure is to improve the causticizing efficiency since this will reduce the amount of carbonate (sodium carbonate is converted into sodium hydroxide). However, the causticizing reaction is an equilibrium reaction, where the equilibrium composition is determined by the total strength of the liquor (alkalinity of the white liquor). This means that all of the carbonate cannot be removed even if the equipment works perfectly. Another measure that may be taken is to add sulphate by introducing sulphate-rich streams. Streams of spent acids from other parts of the mill are normally introduced into the black liquor and, whilst they are sulphate-rich, they are often relatively small. Electrostatic precipitator (ESP) ash from the recovery boiler is normally added before the concentrator, as mentioned above, and normally contains enough sodium sulphate to give a significant change in the carbonate to sulphate ratio (if it is dissolved). It has been suggested that the crystals of sodium sulphate in the ash will function as seed crystals and thereby decrease scaling (if it is not dissolved). However, this can be questioned since it has been shown that burkeite and dicarbonate only crystalize on their own crystal species. It has also been shown that sodium sulphate dissolves as it is mixed into concentrated liquor (DeMartini & Frederick Jr., 2008).

Recirculation of highly concentrated liquor is commonly suggested in the literature and is also used in industry: one example is removing a part of the stream exiting 1A and mixing it into the stream entering 1D, according to Figure 2.1. Concentrators have different designs and therefore also different ways of recirculating liquor, but the principle is the same, i.e. to mix a crystal-rich stream into the feed to the first unit (or the one most affected by scaling). A drawback of this concept is that organic compounds that are also being recirculated increase the viscosity of the stream and thereby affect the capacity of the concentrator. A possible solution would be to separate the crystals from the black liquor and only recirculate this crystal-enriched stream, as shown in Figure 2.3. Olausson *et al.* (2011) proposed the use of a hydrocyclone for this separation: it is well-tested technology, already used in other applications involving crystallization, and the equipment has a low investment cost. In any case, tests are necessary to verify that crystals can be separated efficiently from high viscous liquor and that the recirculation of these crystals has a significant effect on scaling.

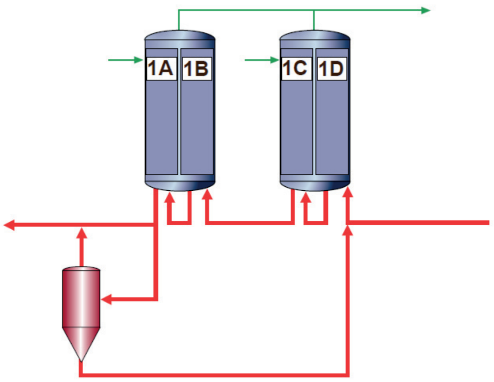

Figure 2.3. The principle for recirculating seed crystals proposed by Olausson et al. (2011). A crystal-rich stream is separated from the product liquor and introduced into the feed via the concentrator.

Process disturbances and changes in operation (both in the evaporator and other parts of the mill) can initiate scaling, for example by affecting the carbonate to sulphate ratio or the bulk crystal population. Start-up after cleaning or a stop can also lead to situations whereby operation is above the critical solids without there being bulk crystals present, leading to primary nucleation and severe scaling. Reseeding after cleaning has been suggested in the literature, for example by Verrill and DeMartini (2006) but, to the author's knowledge, it is not currently used in industry.

2.3.2 Cleaning concentrators

As mentioned in Section 2.2.1, concentrators are normally divided into 2-4 individual chambers or units (Effect 1A, 1B, etc.) operating in series on the liquor side while they are all heated (in parallel) by primary steam. The units are normally cleaned one or two at a time, while the remaining units continue producing firing liquor. When shifting to cleaning mode, the liquor stream is bypassed and the wash liquid is fed into the unit while the outflow is now returned to the mix liquor tank or collected in a separate wash liquor tank. It is desirable that the vapour flows are maintained in the evaporator train and that only the streams on the liquor side are changed, so that disturbances during the cleaning procedure are minimized. Primary steam is therefore still supplied to all units but it is often redistributed with a higher feed to the units that are under normal operation, because they now have a higher load, and a lower feed to the unit under cleaning. The vapour produced can then still support Effect 2 with heat and thereby keep the whole train in operation.

An example of a concentrator with 4 units is shown in Figure 2.4. The black liquor is fed to unit 1B, giving the liquor flow sequence B-A-D-C, but it is possible to shift the sequence to D-C-B-A. The valves can be shifted to allow cleaning (by the wash liquid, yellow in the figure) of two units in series, while the other two units can continue to produce heavy black liquor.

It is not uncommon that Effect 2 also experiences fouling: it is therefore common, in a modern evaporation plant, to divide Effect 2 into two units, (2A and 2B) to simplify cleaning. Then, following the flow of black liquor, the default order of the evaporators might be: 3 → 2B →2A → 1D →1C →1B →1A. However, in some cases, the flows are shifted between the units in each effect (e.g. 3 → 2A →2B → 1A →1B →1C →1D) on a regular basis to even out scaling.

Either black liquor or condensate (water) can be used as wash liquid. The spent wash liquid needs to be treated, which is usually done by feeding it back to the evaporation plant. The benefit of using black liquor as wash liquid is that no additional evaporation load is created, which would be the case if condensate is used because it would introduce additional water. Condensate, on the other hand, has a higher cleaning potential than black liquor since the driving force for dissolution is higher. However, condensate has a significant disadvantage, particularly where softwood black liquors are concerned: when the dry solids content in the evaporator drops below 20%, severe foaming can cause operational problems.

There are two types of cleaning used in industry today: standard and boil out. In the former, the sump volume is either similar to that used in normal operation or slightly below. The latter involves the evaporator being filled with wash liquid to submerge the whole heat transfer surface, and is known as boil out (a term that is sometimes also used for cleaning in general which can be confusing). Although it is easier to dissolve large chunks of scales when the whole evaporator is filled, the procedure is more complicated and has a larger impact on the evaporator operation.

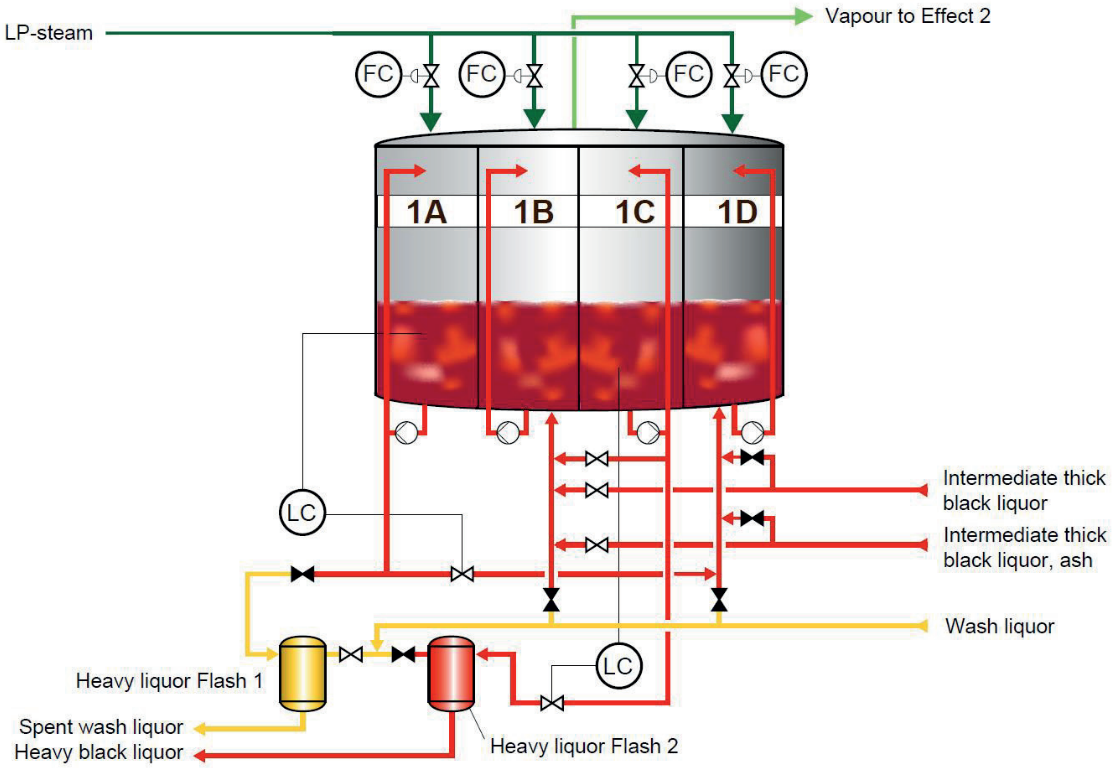

Figure 2.4. Example of a concentrator with 4 units in normal operation. White valves: open pipes. Black valves: closed pipes. Courtesy of Valmet (2015).

3

Theory

3.1 Crystallization

Crystallization is the process whereby crystals are formed, usually when a liquid is transformed into a solid state. Within each crystal the atoms, ions or molecules are highly organised into some fixed and rigid pattern known as a lattice. The properties and structure of the crystal depends on the components that compose it and, depending on the physical and chemical environment, the same components can also build different crystal species. Temperature, for example, might shift the thermodynamics of the solid states, affecting which crystal species is actually formed (Mullin, 2001).

Evaporative crystallization, which is studied in this thesis, is driven by the supersaturation caused as the solvent is evaporated. Crystallization will, however, only occur on surfaces of the same crystal species: if none are available, then crystallization will not occur despite reaching supersaturation. Nuclei, or seeds, need to be formed before crystallization can begin. This process is called nucleation, and is where the dissolved ions (in the case at hand) start to gather into clusters. The clusters need to reach a certain size to become thermodynamically stable, the probability of which increases as the degree of supersaturation increases. In practice, it is first when supersaturation reaches a critical limit, called the metastable limit, that nucleation starts spontaneously. The term primary nucleation is used for this event to distinguish it from secondary nucleation, in which new nuclei are formed by fragments breaking loose from existing crystals. Primary nucleation can be either homogeneous or heterogeneous, where the former implies conditions where no other particles or surfaces influence the nucleation process. In reality, and especially during the evaporation of black liquor, many foreign particles and surfaces are available for catalysing nucleation, which decreases the metastable limit (Mullin, 2001).

It is important to be careful when using the concept of critical solids (introduced in Section 1.4) as it is not fully defined: it can relate to both the solubility limit and the metastable limit. Moreover, the latter can also vary, depending on the operational conditions and the availability of surfaces that can catalyse nucleation.

Once nuclei are available, they can continue to grow by direct crystallization as long as the solution is supersaturated. Small crystals (<50 μm) have a tendency to agglomerate (or aggregate) and, in many systems, this also an important mechanism for growth. Simultaneously, attrition can break apart crystals, for example due to mixing or pumping, and affect the population balance in the opposite direction.

3.1.1 The sodium carbonate-sodium sulphate system

The composition of the crystals formed depends on the molar ratio of sodium carbonate and sodium sulphate in the solution, which is defined as:

$$\phi \equiv \frac{\mathrm{Na_2CO_3}}{\mathrm{Na_2CO_3} + \mathrm{Na_2SO_4}}. \tag{3.1}$$

The two most important crystals in terms of the formation of scale in black liquor evaporators are burkeite, with an approximate composition of $2Na_2SO_4 \cdot Na_2CO_3$, and sodium sulphate dicarbonate (referred to as dicarbonate hereafter), with an approximate composition of $Na_2SO_4 \cdot 2Na_2CO_3$, where the latter is reported as having a significantly higher tendency to form scales at the heat transfer surface (DeMartini & Frederick Jr., 2008; Gourdon, Vamling, Andersson & Olausson, 2010a). Burkeite will typically form in the region of $0.2 < \phi < 0.833$ and dicarbonate in $0.833 < \phi < 0.9$. These salts, which are formed above about 30°C, have inverse solubility: their solubility decreases as the temperature increases. Sodium carbonate is formed when $\phi > 0.9$ and has also inverse solubility, but temperatures above 109°C are needed to crystallize anhydrous sodium carbonate (Shi, 2002).

The inversed solubility of burkeite and dicarbonate is shown in Figure 3.1. This behaviour means that supersaturation can actually be generated by two mechanisms, namely:

- Increased concentration caused by evaporation of the solvent, which takes place on the fluid-vapour interfaces for the low heating rates used during black liquor evaporation.

- Increased temperature caused by heating of the solution, generated on heat-transfer surfaces.

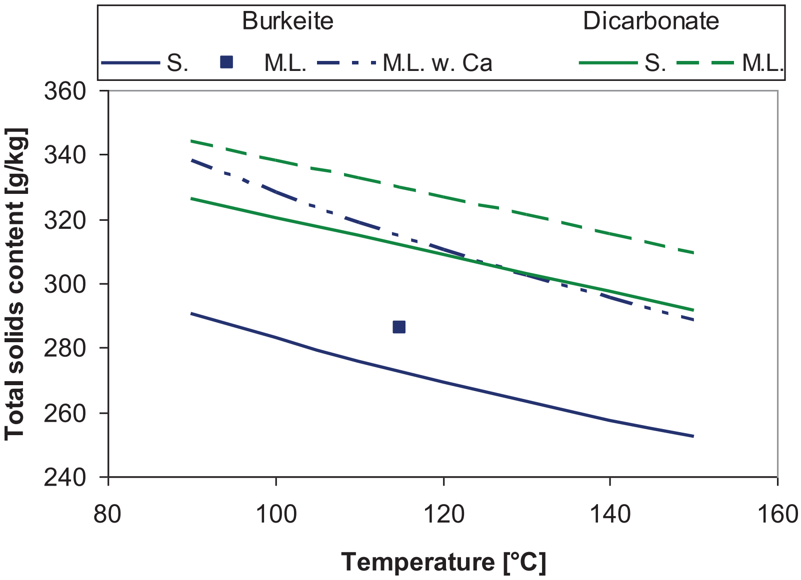

Figure 3.1. The temperature dependency of the solubility (S.) and metastable limit (M.L.) of dicarbonate and burkeite with or without the effect of Ca. Correlations obtained from Shi (2002) and Bialik et al. (2008). Adapted from Gourdon (2009).

The inversed solubility is sometimes claimed to be the driving force for the formation of scales, as the heat transfer surface has a higher temperature than the falling film during the evaporation of black liquor. It was, however, shown by Gourdon (2009) that this is only a minor effect: the increase in concentration along the heat transfer surface is the main mechanism causing scaling.

3.2 Formation of scales

3.2.1 Factors affecting scaling

There are many factors that affect scaling behaviour, as the crystallization of sodium salts on the heat transfer surface is a complex process controlled by conditions on both the macroscopic and microscopic levels. These factors can be placed in three categories, namely composition of the liquor, operational conditions and surface properties, to clarify the system and are illustrated in Figure 3.2 (Zhao & Chen, 2011). The first category includes factors such as the concentrations of the sodium carbonate, sodium sulphate and surplus sodium, as well as other components that affect scaling. Factors such as the heating rate (the differential temperature between the liquor and steam) and the flow rate relate to operational conditions. As mentioned in the review of previous work (Section 1.4), factors related to the liquor composition and operational conditions have been studied; the new knowledge gained has led to improvements being made. There are, however, relatively few studies related to the surface chemistry for application in the evaporation of black liquor, although the use of non-stick coatings is relatively common in other applications. Many experiments have shown, for example, that whilst the formation of scales was delayed for coated surfaces, it could not be avoided completely. Moreover, the long term stability of coating is insufficient (Mersmann, 2001).

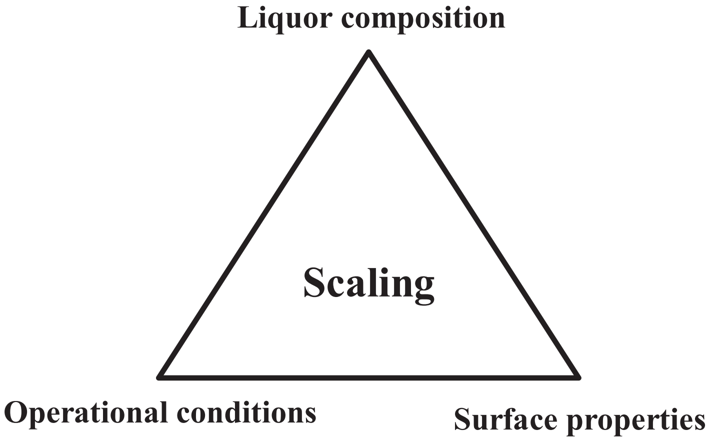

Figure 3.2. The three main factors affecting scaling.

3.2.2 Scaling mechanisms

Supersaturation is created due to the heating of, and evaporation from, the falling film of black liquor, and crystallization occurs on the heat transfer surface (as scaling) or on free bulk crystals, shown schematically in Figure 3.3. There will be competition between these two locations (as previously discussed), which is controlled by both the surface available and mass transfer phenomena: if, for example, the bulk crystals constitute the majority of the crystal surfaces available and the hydrodynamic conditions are favour a low mass transfer resistance, scaling will not be promoted.

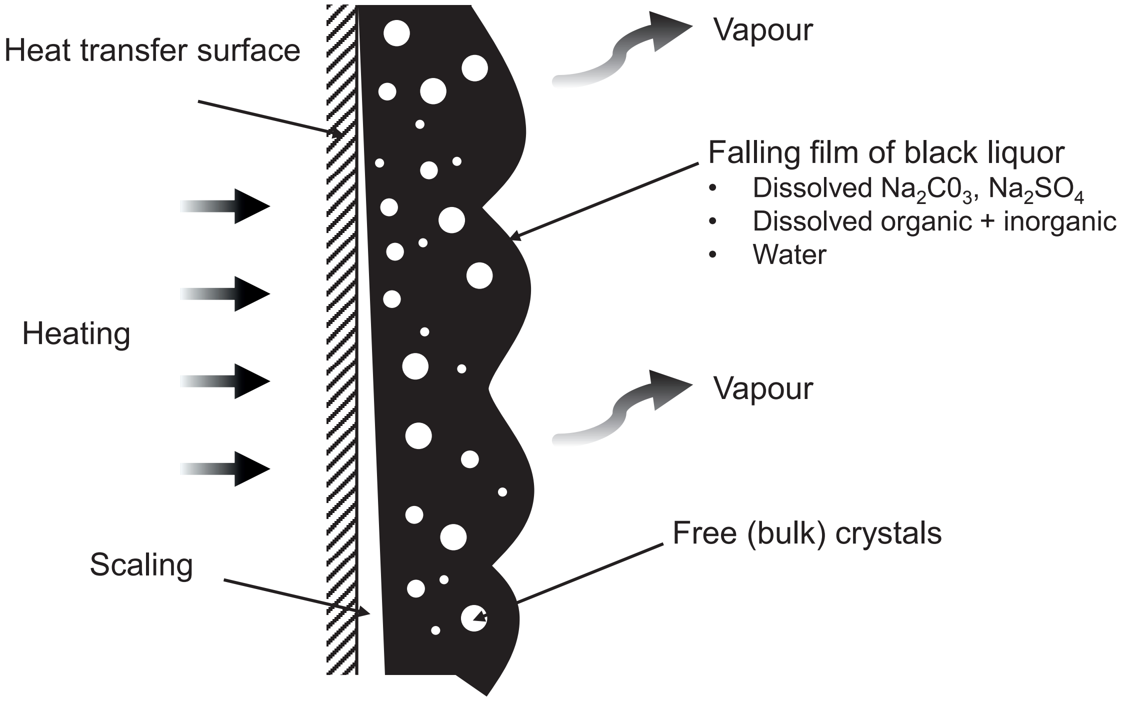

Figure 3.3. Schematic diagram of crystallization in an evaporating falling film of black liquor.

The formation of scales can be divided in two steps (Bott, 1997):

1. Initiation: the first crystals are formed on the heat transfer surface, often after a certain time known as the induction or initiation period.
2. Growth: scales grow on the surfaces available.

The first step is probably the most crucial as, once formed, scales will grow also at lower levels of supersaturation. There are two possible mechanisms for the formation of scales:

1. Crystallization of the dissolved salts.
2. Deposition of existing crystals.

In the case of initiation, the first mechanism gives nucleation on the surface, which is dependent on the surface properties: cavities in the material can, for example, catalyse nucleation (Mullin, 2001). Experiments have shown that the rate of surface nucleation can be reduced considerably by making the surface very smooth and having a low affinity for the crystallizing salts (Mersmann, 2001). The deposition of existing (bulk) crystals can potentially give very high rates of scale formation, as it is not limited by the crystallization rate, but is more likely for small crystals (<50 μm) as they have a stronger tendency to agglomerate (Mullin, 2001).

In addition to the mechanisms for the formation of scales, there are also mechanisms for their removal. High shear forces can tear off parts of the scales and cause erosion; thermal stress or vibrations can cause cracking and cause a part of the scales to fall off. In some situations, the formation process is predominant, causing a continuous growth of the scales, whilst in others, the rates of formation and removal become equal as the scales becomes thicker, giving an asymptotic growth behaviour (Mersmann, 2001).

3.3 Heat and mass transfer

In this section, the fundamental theory for heat and mass transfer relevant to the work performed in this thesis is presented. The wetting rate is normally use to define a specific mass flow rate of the falling film thus:

$$\Gamma \equiv \frac{mass\ flow\ rate}{unit\ with} = \frac{mass\ flow\ rate\ to\ the\ evaporator\ tube}{circumferance\ of\ the\ evaporator\ tube}. \tag{3.2}$$

3.3.1 Heat transfer during falling film evaporation

Dimensionless numbers are often used for the modelling and general characterization of heat transfer, where the heat transfer coefficient, h, is described by the Nusselt number. For falling film free surface evaporation, the standard definition of the Nusselt number is (Schnabel & Schlünder, 1980):

$$\mathrm{Nu} \equiv \frac{h}{\kappa}\left(\frac{v^2}{g}\right)^{1/3} \tag{3.3}$$

where κ is the thermal conductivity, v the kinematic viscosity and g the gravitational acceleration.

A correlation is normally used to model the heat transfer in which the Nusselt number is a function of Prandtl, Reynolds and/or other dimensionless numbers. The general correlations available for heat transfer in falling film evaporation have primarily been developed for fluids with relatively low Prandtl numbers, the majority of which are based on experimental data for Prandtl numbers below 7. Their range of validity is, in most cases, also limited to a certain flow regime (laminar, wavy-laminar or turbulent flow), characterized by the Reynolds number. Whilst different definitions of the Reynolds number can be found in the literature, the following is used here:

$$\mathrm{Re} \equiv \frac{4\Gamma}{\mu} \tag{3.4}$$

where μ is the dynamic viscosity.

General heat transfer correlations normally have one expression for laminar flow and another for turbulent flow. The correlation used in this work is that of Schnabel and

Schlünder (1980), who based their model on a review of measurements from different authors. They proposed the following model:

$$\mathrm{Nu}_{lam} = 1.43\mathrm{Re}^{-1/3} \tag{3.5}$$

$$\mathrm{Nu}_{turb} = 0.0036\mathrm{Re}^{0.4}\mathrm{Pr}^{0.65}. \tag{3.6}$$

In the transition region between laminar and turbulent flow, they suggested a superposition by the power of two:

$$\mathrm{Nu} = (Nu_{lam}^2 + Nu_{turb}^2)^{1/2}. \tag{3.7}$$

3.3.2 Solid dissolution into a liquid falling film under turbulent conditions

Convective mass transfer can be approximated by film theory if the dissolution process is controlled by diffusion and the flow is turbulent (Welty, Wicks, Rorrer & Wilson, 2009). Here, all mass transfer resistance is assumed to exist in a thin film close to the dissolving solid surface, in which transport occurs entirely through molecular diffusion (Figure 3.4). This film is henceforth referred to as the diffusion film in order to distinguish it from the falling film. When the dissolved substance has diffused through the diffusion film, it can be regarded as being part of the bulk flow: the resistance to mass transfer in the r-direction can then be neglected in the bulk flow. The concentration at the solid-liquid interface will be equal to the saturation concentration c^* at the current temperature. The dissolution rate (or mass flux, J_r) can then be modelled as follows:

$$J_{\mathrm{r}} = D_{AB}\frac{\partial c}{\partial r} \approx D_{AB}\frac{\Delta c}{\Delta r} = \frac{D_{AB}}{\delta_{dif}}\Delta c = k(c^* - c_{bulk}). \tag{3.8}$$

where k is a mass transfer coefficient in m/s. This coefficient accounts for diffusion from the solid surface to the bulk flow and thus includes the diffusion coefficient D_{AB} and the thickness of the diffusion film δ_{dif}. At higher Reynolds numbers (Re), δ_{dif} decreases because stronger turbulence results in stronger bulk mixing: k therefore has a positive flow dependence. Both D_{AB} and δ_{dif} are temperature dependent, i.e. diffusivity increases for liquids and δ_{dif} decreases (due to decreased viscosity) at higher temperatures. So k also has a positive temperature dependence. For the film theory to be valid, the majority of the film must consist of a mixed bulk, i.e. δ_{dif} must be significantly thinner than the total thickness of the falling film δ_{tot} (Figure 3.4). The concentration of the bulk will increase significantly for long contact times: the driving force for dissolution will thereby decrease along the surface and approach zero when the bulk becomes saturated.

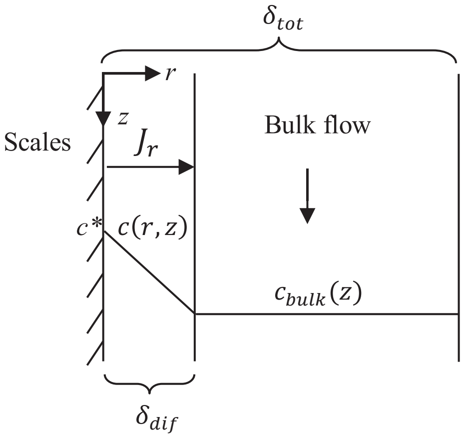

Figure 3.4. Schematic representation of the concentration profile using the film theory, where δ_{dif} is a fictive film thickness between a solid surface and the bulk flow.

The mass transfer coefficient, k, can also be described by the dimensionless Sherwood number (Sh), which is analogous to the Nusselt number used for heat transfer:

$$\mathrm{Sh} \equiv \frac{k}{D_{AB}}\left(\frac{v^2}{g}\right)^{1/3}. \tag{3.9}$$

Diffusivity is a difficult property to measure: diffusivity data is rare in the literature, particularly because the solutions used here are complex and a mixture of two salts are dissolved. Moreover, the data that can be found is normally measured at room temperature. Although the diffusion coefficient has a strong dependence on temperature, the following relation can be used to convert it to the temperature desired (Welty *et al.*, 2009):

$$\frac{D_{ABT_1}}{D_{ABT_2}} = \left(\frac{T_c - T_2}{T_c - T_1}\right)^n \tag{3.10}$$

where T_c is the critical temperature and $n = 6$ when water is used as the solvent.

3.3.3 Heat and mass transfer analogy

Heat transfer has been studied more extensively for falling films, so that knowledge is valuable for predicting mass transfer. In this work, the Chilton-Colburn analogy was used to relate heat transfer to mass transfer. Chilton and Colburn defined a *j*-factor, which is equal for both mass and heat transfer (Welty *et al.*, 2009):

$$j_d = j_h = \frac{\mathrm{Sh}}{\mathrm{ReSc}^{1/3}} = \frac{\mathrm{Nu}}{\mathrm{RePr}^{1/3}}. \tag{3.11}$$

The analogy has been proven valid for $0.6 < \mathrm{Sc} < 2{,}500$ and $0.6 < \mathrm{Pr} < 100$.

3.4 Hydrocyclone solid-liquid separation

Hydrocyclones are cost-effective and are therefore attractive separation equipment. The principle of operation is that a vortex is created, which leads to particles with a density higher than that of the liquid containing them being pressed out to the sides by centrifugal force (Mersmann, 2001). The design of the hydrocyclone creates the vortex: the inflow is fed in a direction tangential into its circular (conical) body, which creates a circular motion due to the inertia of the flow. This results in a pressure drop so separation is, in practice, driven by the additional pump power that is necessary. Larger particles are less stagnant in the flow and are therefore easier to separate.

A hydrocyclone has two outflows: one that is enriched with particles (called the coarse fraction), and one that is depleted of particles (called the fine fraction). Separation is achieved by removing the fine, or top, fraction from the middle of the vortex, where there are fewer and/or smaller particles. The flow in the outer parts of the vortex, which is enriched with (large) particles, comprises the coarse, or bottom, fraction.

3.4.1 Grade efficiency curve

The separation performance of a hydrocyclone is often characterized by a grade efficiency curve, an example of which is given in Figure 3.5. The grade efficiency is defined as the mass fraction of solids (or particles) leaving in the coarse fraction, and is a function of particle size. As the figure shows, large particles (in this case >30 µm) are easier to separate and they are all found in the coarse fraction. Very small particles (<5 µm) are stagnant in the flow and, as liquids are leaving in both the fine and coarse fractions, these cannot be completely separated. The grade efficiency curve depends on the operational conditions (inflow velocity and stream splitting between fine and coarse fractions), the design of the hydrocyclone (diameter, length, etc.), the properties of the fluid (viscosity and density) and the density of the particles (Svarovsky & Thew, 1992).

The grade efficiency curve can be described mathematically by the following expression, based in the Rosin-Rammler distribution (Silva *et al.*, 2009):

$$G(d) = 1 - (1 - L)\exp[-\ln(2)\left(\frac{d}{d_{50}}\right)^{n}], \tag{3.12}$$

where G is the grade efficiency, L is the volumetric bottom-flow-to-throughput-ratio (flow from the bottom fraction divided by the total inflow) and d is the particle diameter. Parameter d_{50} is the cut size, which represents the particle size for when 50% is separated by centrifugal force and n is the dispersion or sharpness of the separation. The separation can then be modelled by correlating d_{50} and n to dependent parameters: this was first done by Plitt and developed further by others (Svarovsky & Thew, 1992).

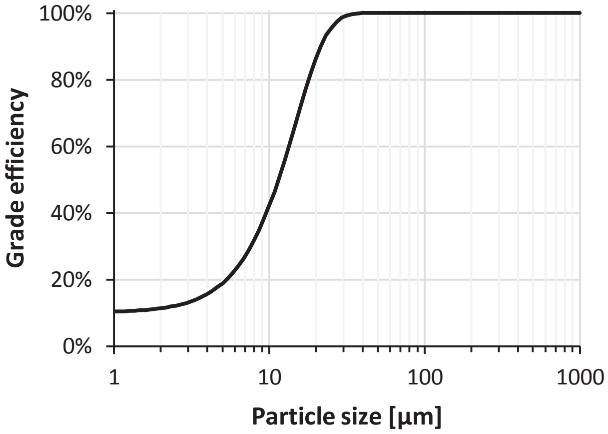

Figure 3.5. Example of a grade efficiency curve showing the separation characteristics of a hydrocyclone.

4

Experimental

The evaporation of black liquor has been studied in a number of experiments in this work. Black liquor is a very complex mixture and model solutions can be used to simplify the system to provide better control over the experiments. The experience of our group is that water solutions of sodium carbonate exhibit similar scaling behaviours to dicarbonate and, as it consists of only one salt, solutions of sodium carbonate were therefore also studied.

4.1 The pilot evaporator

The flowsheet in Figure 4.1 shows the most important equipment and sensors in the pilot evaporator, including the temperature-controlled vessel used to heat the wash liquid in the experiments of scale dissolution. The evaporator itself was of the falling film type, with the liquor on the outside of a vertical tube. It was designed to be large enough to produce results relevant to industrial conditions whilst simultaneously being sufficiently flexible to be able to simulate a high variety of operational conditions. The evaporator tube was 4.5 m long, with an outer diameter of 60 mm, giving it an active outer heat transfer area of 0.85 m^2. The tube was heated on the inside with condensing saturated steam.

The salt solution or black liquor was fed into the top of the evaporator using a circulation pump (displacement pump): an overflow distributor integrated into the top of the tube ensured that the distribution of the liquid was circumferentially uniform for a variety of flow rates. The vapour and the concentrated liquid flowed from the evaporator tube into a tank serving both as a buffer volume (about 50 l) and vapour-liquid separator (buffer tank in Figure 4.1). The bottom of the tank was then connected to the circulation pump; the vapour flowed into a condenser controlling the pressure in the system.

A hydrocyclone was used in Papers V and VI in order to test the separation of the crystals and to change the crystal composition of the bulk. It was installed together with a number of valves that enabled two operational modes, where either the fine (top) or coarse (bottom) fraction was fed into the evaporator (Figure 4.1). The remaining fraction was recirculated back to the buffer tank. The valves also enabled measurements to be made of the chord length distribution (CLD) of the bulk crystals in both the fine and coarse fractions, but only one at a time. The sensor used was focused beam reflectance measurement (Mettler Toledo Lasentec FBRM D600L) and is described further in (Gourdon *et al.*, 2008); the design and installation of the hydrocyclone is described in more detail in Paper V.

The pilot evaporator was equipped with sensors to monitor the operation and acquire data: the most important sensors are shown in Figure 4.1. The flow rate and density were measured using Endress and Hauser Promass Coriolis meters, with a stated accuracy of 0.15% for flow rate and 0.5 kg/m^3 for density. PT100 meters were used to measure temperature, with a stated accuracy of 0.1 K, and Yokogawa EJA meters were used to measure pressure, with a stated accuracy of 0.20%. The refractive index was measured at 589 nm using K-Patent PR-23-SD, with a stated accuracy of 0.0002.

The evaporator tube could be inspected visually via three sight glasses at different vertical positions: 0.15, 1.9, and 3.9 m from the inlet. A device was constructed and installed at two different positions (1.8 and 3.8 m from the inlet) so that the thickness of the scale could be measured online. This device consisted of a small flat disc that was fixed to the end of a metal rod and pushed inward until it reached the surface of the scales. The thickness of the scales was then measured from the outside of the evaporator using Vernier callipers; the accuracy of the measurements was estimated as being ±0.2 mm.

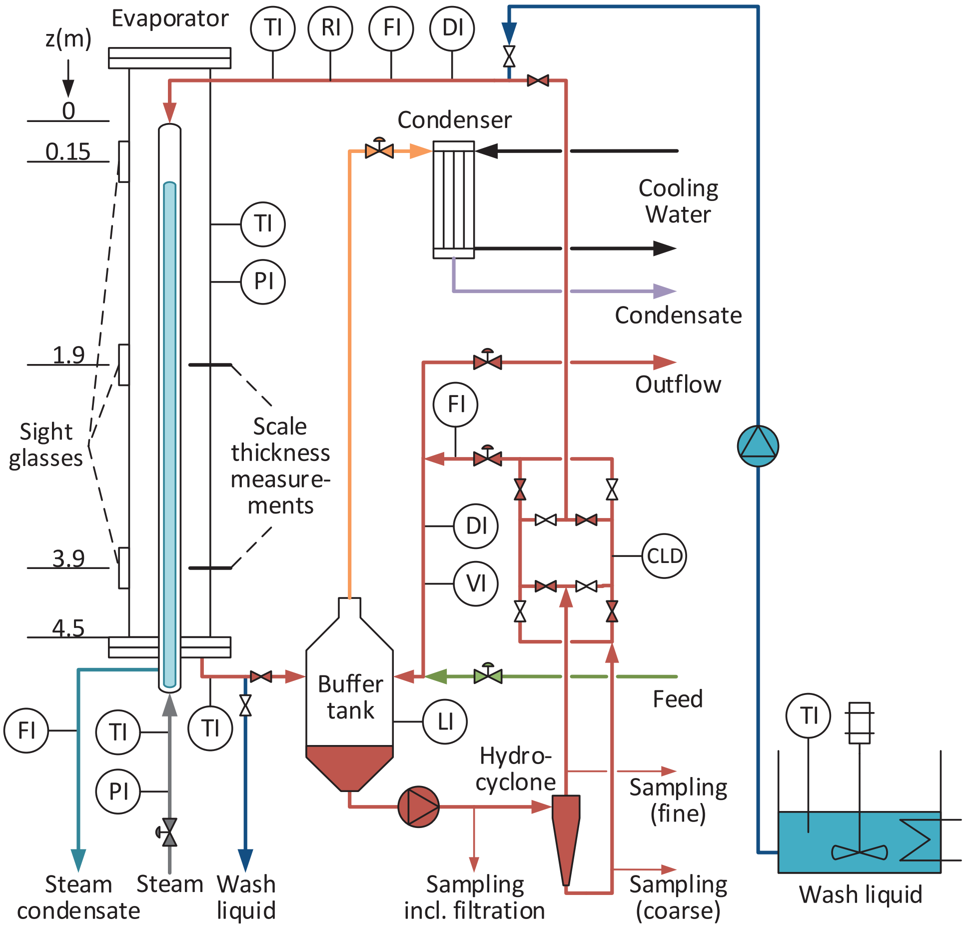

Figure 4.1. Simplified flowsheet of the pilot falling film evaporator plant. The valves are set to indicate normal operation with the coarse fraction from the hydrocyclone being sent to the evaporator (white valve = closed). CLD = chord length distribution, D = density, F = flow rate, L = level, P = pressure, R = refractive index, T = temperature and V = viscosity.

4.1.1 Installation and operation of the hydrocyclone

The hydrocyclone was purchased from Fenra AB in Sollentuna, Sweden. It is designed to separate particles larger than 50 μm at a viscosity of 50 mPa·s and an inflow of 900 l/h.

The hydrocyclone, the dimensions of which are shown in Figure 4.2, was installed according to Figure 4.1. While in operation the feed is split in two fractions: top (fine) and bottom (coarse), (see Section 3.4).

The hydrocyclone inlet was connected to the recirculation pump. One of the fractions (fine or coarse) was then fed into the evaporator while the other was recirculated back to the buffer tank. An arrangement of valves was installed according to Figure 4.1 to enable the fractions to be shifted, which also made it possible to switch the measurement of the chord length distribution (CLD) between the fine and coarse fractions. The flow rate of the fraction to the evaporator was controlled by the pump speed, and the flow rate of the fraction to the buffer tank was controlled by a control valve.

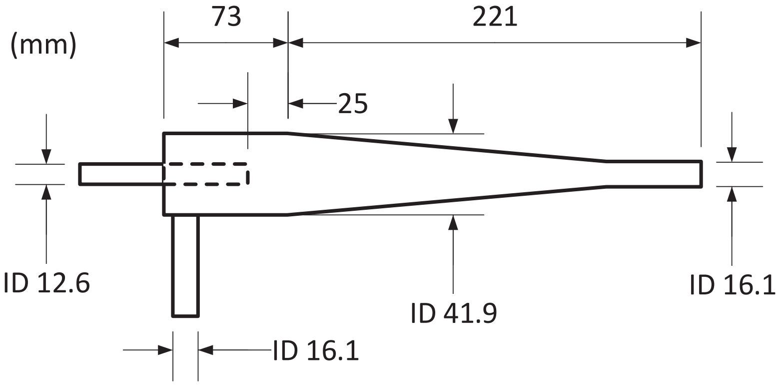

Figure 4.2. Diagram of the hydrocyclone installed in the pilot evaporator plant, where ID denotes the inner diameter. The inlet is below, the top fraction is on the left and the bottom fraction is on the right.

4.2 Experimental procedure

This section comprises two parts because the experimental procedures in the evaporation and dissolution experiments were fundamentally different. The evaporation experiments were reported in Papers I, V and VI, and the dissolution experiments in Papers II and III.

4.2.1 Evaporation experiments

The experiments were prepared by first filling the system with the salt solution or black liquor, and then heating and evaporating it to the desired conditions. Depending on the type of scaling experiment, i.e. nucleation or continuous crystallization, slightly different procedures were employed.

Nucleation (N) experiments: These experiments are called semi-batch in Paper 1. The salt solution or liquor was concentrated from below solubility to supersaturation; at a certain point the concentration became high enough (the metastable limit) to trigger primary nucleation and initiate scaling. Measurements continued until the scaling rate decreased significantly or the evaporation process stalled due to severe scaling; the running time was between 0.5 and 1 hour.

Continuous crystallization (C) experiments: In the steady-state mode, vapour was removed as in the nucleation experiments, but with fresh salt solution (below solubility) or liquor (below critical solids) being fed so that the density of the stream into the evaporator tube was kept constant. Concentrated solution or liquor was ejected to maintain a constant level in the buffer tank. This procedure gave conditions close to an industrial evaporator under steady-state operation.

A substantial amount of scales was often formed during the initial preparation to reach the desired conditions: the tube was therefore cleaned to ensure that the measurements of fouling resistance began with no scales being present. This was done by closing the valves into and out from the evaporator, recirculating the salt solution or liquor to the buffer tank to sustain mixing, and then pumping in wash liquid, see Figure 4.1. This method enabled cleaning with a minimum of disturbances; the system was back in operation after a break, on average, of 5-10 min.

In the salt solution experiments, the crystal fraction could be controlled directly by the set-point for the density in the stream into the evaporator. The feed rate was then controlled automatically to maintain a constant density: with the exception of some fluctuations at the beginning, the crystal fraction was therefore constant in the experiments. The throughflow meant that both the crystal population and the liquid solution were renewed continuously. In the black liquor experiments, a density close to the desired dry solids content was set.

Most of the steady-state salt experiments lasted for 5-22 hours: those with black liquor were more difficult and ranged between 2-6 hours. In Paper 1, however, the duration was only 1-2 hours.

Hydrocyclone operation: The crystal population entering into the evaporator unit was changed for some of the experiments. This was achieved by operating the hydrocyclone in the following three different modes:

- **Total:** the whole flow from the buffer tank was fed into the evaporator, i.e. the hydrocyclone was not in operation.
- **Coarse:** the coarse fraction (bottom fraction) was fed into the evaporator unit. The fine fraction was recirculated back to the buffer tank.
- **Fine:** the fine fraction (top fraction) was fed into the evaporator unit. The coarse fraction was recirculated back to the buffer tank.

4.2.2 Dissolution experiments

Each experiment consisted of two steps: a layer of salt (scales) was first built up on the evaporator tube and then dissolution experiments were performed by washing the tube carefully. The experiments were designed to test variation of two operational parameters: temperature and wetting rate. Three different wash liquids (solvents) were used: water (Paper 2), salt solutions (Paper 2) and black liquor (Paper 3).

Scale build-up: The build-up of scales was achieved by evaporating a salt solution of sodium carbonate and sodium sulphate, with a sodium carbonate mole fraction of approximately 0.87. The system was operated at atmospheric pressure on the solution side of the system, corresponding to 105−107 °C. The density of the salt solution was increased over the course of the evaporation to reach the first nucleation point, i.e. the first precipitation of crystals. Evaporation continued for 3−5 h, which typically corresponded to a scale build-up of 2−5 mm in the lower part of the evaporator.

The initial thickness of the scales was measured, and the tube was inspected visually to determine their quality and distribution, before the dissolution was sequence started.

Dissolution: The wash liquid used in the dissolution experiments was first preheated to the desired temperature in a separate vessel. After the build-up sequence ended, the evaporator was set in cleaning mode by closing the valves to the buffer tank and at the inflow, and opening the two valves for the in and outflow of wash liquor (Figure 4.1). Prior to the start of the dissolution experiment, the desired temperature was obtained by cooling the hot tube with water on the inside. When the experiment began, the wash liquid was pumped into the evaporator and distributed using the same distributor as for evaporation, thereby ensuring an even film. The flow rate was controlled to yield the desired specific mass flow rate.

Video cameras were mounted at the three sight glasses, and the entire experiment was recorded to monitor the dissolution process. The video films supplied information on how the scales were dissolved and when the tube could be considered clean. The outgoing wash liquid was sampled during the experiment in plastic containers 1-5 l in volume. The sampling time and temperature of the exiting wash liquid was recorded together with the mass and density (using a hydrometer) of each sample. The flow of wash liquid was stopped and the experiment ended when the tube was determined visually as being clean. The mass fraction of salt was measured by determining the dry solids content for a few of the samples. The density was correlated to the salt mass fraction and temperature, thus enabling the mass of salt to be calculated in all samples (see Section 5.1.2).

4.3 Monitoring bulk crystals

Two different methods were used to determine the amount of bulk crystals present in the stream entering the evaporator. In the experiments with salt solutions, density measurements were used and made as follows: during steady-state operation, with a well-developed bulk crystal population, the solution was saturated in the streams where the density was measured, i.e. the retention time in the buffer tank was sufficiently long to allow equilibrium to be reached between the bulk crystals and the solution. Values from the literature were used for the density of the crystals, which should be close to that of burkeite, i.e. 2570 kg/m^3 (Giuseppetti, Mazzi & Tadini, 1988); the total density was measured during the experiments. The density of the saturated solution was obtained from measurements of the refractive index, which is unaffected by the presence of crystals, using a correlation developed from data where a salt solution in which no bulk crystals were present was evaporated at the same operational conditions (i.e. by increasing the concentration gradually, from below solubility to metastable). The mass fraction (*cf*) of the crystals was calculated from:

$$cf = \frac{\frac{1}{\rho_{tot}} - \frac{1}{\rho_{sol}}}{\frac{1}{\rho_{cry}} - \frac{1}{\rho_{sol}}}. \tag{4.1}$$

This expression was derived using the conservation of mass and volume, and is valid for both fine and coarse fractions from the hydrocyclone.

A different method was used to calculate the crystal fraction in the black liquor: being a complex mixture, its density is not only dependent on its contents of salt and crystal. Instead, samples were taken and the dry solids content analysed. The crystal fraction could then be calculated by samples of liquor both with and without crystals (removed by filtering). The following expression was derived from a mass balance over the filter:

$$cf = \frac{DS_{unfilt} - DS_{filt}}{1 - DS_{filt}}. \tag{4.2}$$

The online sample filtration method developed by Gourdon (2009) was used. A filtration unit was connected to a stream that was recirculated over the recirculation pump (shown in Figure 4.1 after the buffer tank); a sintered filter element with 7 µm pore size was used. It was assumed that the crystals small enough to pass through the filter constituted only a negligible part of the total mass of crystals.

Sampling failed in some of the experiments with black liquor, so density measurements were used instead to estimate the crystal fraction. The accuracy of the crystal fractions determined was estimated to 0.5 percentage points for both the salt solution and the black liquor.

The chord length distribution of the bulk crystals was also monitored. However, the instrument was used mainly for experiments with salt solution: when the Lasentec FBRM (Focused Beam Reflectance Measurement) sensor was used on the black liquor, it absorbed the light from the laser and the visibility of the particles (crystals) changed with the dry solids content.

4.4 Monitoring scaling

The rate of scaling was monitored using both the total and local heat transfer. The total heat transfer coefficient, i.e. the average of the entire heat transfer surface, is based on the measurement of the steam condensate flow, which is a direct measurement of the rate of heating, Q. A condensate flow value solely related to the heating of the tube was obtained by measuring background losses separately and subtracting them. Using the rate of heating, the overall heat transfer coefficient, U, related to the outer area, A_o, was calculated as:

$$U = \frac{Q}{A_o(T_{steam} - T_{BL})}. \tag{4.3}$$

The steam temperature, T_{steam}, was determined from the pressure and the liquor temperature, T_{BL}, from a “mixing cup” in the outflow (where the difference between them is defined as the differential temperature, ΔT). From the overall heat transfer coefficient, the outer heat transfer coefficient, h_o, was calculated using the following expression:

$$\frac{1}{UA_o} = \frac{1}{h_i A_i} + \frac{\delta_w}{\varkappa_w A_m} + \frac{1}{h_o A_o} \tag{4.4}$$

where δ_w is the thickness of the evaporator tube (i.e. 5 mm), $\varkappa_w$ is the thermal conductivity of the steel and A_m is the logarithmic mean area given by:

$$A_m = \frac{A_o - A_i}{\ln\left(\frac{A_o}{A_i}\right)}. \tag{4.5}$$

The inner heat transfer coefficient, h_i, was estimated using a correlation for condensation on vertical surfaces by Numrich and Müller (2010). Since the black liquor was flowing on the outside of the tube, the outer heat transfer coefficient was the one of interest: this could be calculated using Eq. 20 since all the other variables were known.

Local heat transfer coefficients were also calculated at different vertical and circumferential positions along the evaporator tube using the temperature difference measured by pairs of thermocouples installed in the tube wall. The distance between the two thermocouples was known, as well as the thermal conductivity of the tube material, so the local heat flux could be calculated; the local outer heat transfer coefficient was then calculated in a similar procedure as above. Six local positions were studied, with distances from the top of the tube of 0.4, 2.4, 2.9, 3.4 m and two at 3.9 m (i.e. on opposite sides).

A decreasing trend in the heat transfer coefficient when all other operational parameters are kept constant, indicates the occurrence of scaling. The scaling observed was quantified by converting the heat transfer trends into fouling resistance, R, acording to the following expression:

$$R = \frac{1}{h_{fouled}} - \frac{1}{h_{clean}} = \frac{\delta_{scale}}{\varkappa_{scale}}. \tag{4.6}$$

Here, h_{fouled} is the heat transfer coefficient on the outside of the tube, including the heat transfer resistance from the growing scales, and h_{clean} is the heat transfer coefficient at clean conditions. In Paper I the fouling resistance was converted into a scale thickness, δ_{scale}, by dividing it by the thermal conductivity of the scales $\varkappa_{scale}$. The thermal conductivity of burkeite was measured by Smith (2000) as being 1.73 W/mK, which was the value used here.

The fouling resistance trend was converted into a measure of the rate of scaling in Paper VI. This was done by linearising the trend and dividing it by time (i.e. the duration of the experiment), which gave the expression $\Delta R/\Delta t$ ((m^{2}K/W)/min). Unfortunately, the rates of scaling were not always constant, tending to be higher at the beginning of the experiments. An uncertainty range was calculated for each experiment to evaluate the errors due to linearization and measurement uncertainties.

4.5 Solubility measurements

A filtration technique was used in Paper III to determine the solubility limit of the sodium salts in black liquor, wherein an excess of salt was added to the sample and allowed to equilibrate at the temperature investigated. The sample was subsequently filtered and the solubility limit determined from the dry solids content, measured using the TAPPI T 650 om-09 method: the procedure is described in detail by Gourdon (2009). The difference between the initial and saturation concentrations, i.e. the dissolution potential, can be calculated from the initial DS of the black liquor and the DS of the saturated black liquor (see Appendix 1).

4.6 Full-scale cleaning test

A full-scale cleaning test was conducted at a Swedish pulp mill in a Master's thesis project being carried out in our group (Andersson, 2015). The concentrator was newly-built and constructed as the example given in Section 2.3.2. Two units were cleaned in series, using thin liquor (25% DS) as the wash liquor. Unfortunately, it was not possible to take samples directly from the evaporator unit: samples of spent wash liquor were taken instead from a flash tank installed after the second unit. The most important data acquired during this test can be listed as being:

- Samples to measure the chemical composition and dry solids content of:
    - Feed liquor
    - Spent wash liquor
- Online sensor data (in the two evaporator units) of:
    - Overall heat transfer coefficient
        - Clean conditions measured after the cleaning procedure
        - Scaled condition measured just prior to the cleaning procedure
    - Temperature of the liquor
    - Temperature of the steam
    - Boiling point rise

The inflow and outflow of salt (sodium carbonate and sodium sulphate) were known from this data, which allowed the dissolution of the scales to be followed during the test.

5

Modelling Dissolution and Cleaning

5.1 Model for dissolution

A dissolution model was developed in Paper II and the input parameters were fitted to the experimental data. Based on film theory, it was discretised in time and space (rotational symmetry) according to Figure 5.1. The tube was discretized into several cells along the z-axis; each cell had its own local scale thickness. As the wash liquor film fell along the tube and dissolved the scales, the model tracked three quantities (using mass balances): the masses of sodium salt, water and residual dry solids. The latter originated from the black liquor and accounted for all of the organic and inorganic compounds, excluding the sodium carbonate and sodium sulphate. The amount of dissolved salt in the solution could be calculated because the natural content of the salt in black liquor is known. In the model, two different expressions of dry solid content are defined, namely:

1. DS excluding the additional dissolved salt, denoted DS_{BL} (i.e. (dry mass – dissolved salt) / (total mass – dissolved salt))
2. Total DS including the dissolved salt, denoted DS_{tot} (i.e. dry mass / total mass).

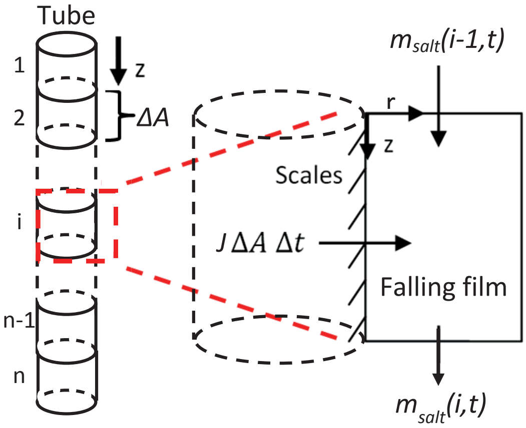

Figure 5.1. Diagram of the tube discretized into several cells along the z-axis.

In each of the cells along the z-axis, the density and solubility limit were calculated at the current temperature and salt mass fraction using the correlations developed (see below). These two parameters were then used to calculate the difference in concentration at the surface and bulk, i.e. the driving force for dissolution. Each cell had its own decreasing scale thickness, which was dependent on the dissolution rate *J* (equation 3.8). Mass fractions (*x*) were used to determine the solubility limit and salt content to simplify the calculations of mass balances. However, the concentration, *c*, was used to calculate the dissolution rate to obtain a valid mass transfer coefficient, *k*. Then, mass fractions were converted using the density correlation. MATLAB was used to perform all of the calculations.

5.1.1 Fitting parameters

In Papers II and III the mass transport coefficient, *k*, was determined using a best-fit approach to the experimental data. It was assumed to be constant for each experiment and was adjusted together with the initial distribution of scales along the tube to predict the salt concentration of the outlet and local thickness of the scales. The initial distribution of the scales was divided into 13 points that could be adjusted individually, and linear interpolation was used between the points. There were two restrictions on the scale distribution: the scale thicknesses at 0, 1.8, and 3.8 m were known from experimental measurements, and the total mass of scale was known from the total mass of dissolved salt.

5.1.2 Density of liquor with additional dissolved salt

The correlation for the density of black liquor containing different amounts of additional dissolved salt comprises two parts: one for a pure salt solution and one for a pure black liquor. The former was fitted to measurements (where *x* is the mass fraction of salt):

$$V_{factor} = 0.8341x^3 + 0.5579x^2 + 0.0267x + 1.000, \tag{5.1a}$$

$$\rho_{salt\ sol} = \frac{\rho_{water}}{V_{factor}(1-x)}. \tag{5.1b}$$

All temperature dependence is included in the density of water, ρ_{water}. The correlation is valid for a salt solution up to the solubility limit (approx. 0.33 kg_{salt}/kg_{tot}). A correlation by Adams *et al.* (1997) was used to express the density of pure black liquor (*T* in °C) thus:

$$\rho_{25} = (997 + 649 * DS_{BL}), \tag{5.2a}$$

$$\rho_{BL} = \rho_{25}(1 - 3.69 \cdot 10^{-4}(T-25) - 1.94 \cdot 10^{-6}(T-25)^2). \tag{5.2b}$$

Modelling black liquor containing additional salt, it was found that the correlation for the pure salt solution (Eq 5.1) could be extrapolated and combined with that of the pure black liquor (Eq 5.2) as follows:

$$\rho_{sol} = \rho_{salt\ sol}\{x = DS_{tot}\} - \rho_{salt\ sol}\{x = DS_{BL}\} + \rho_{BL}. \tag{5.3}$$

The performance of the correlation is shown in Figure 5.2, which presents measurements for black liquor at 20% and 41% DS doped with additional salt.

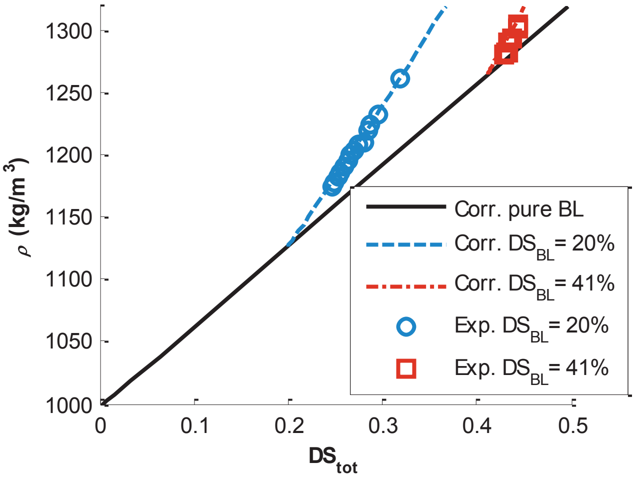

Figure 5.2. Density correlation and measurements for black liquor containing additional sodium carbonate and sodium sulphate salts.

5.1.3 Correlating the solubility limit

The solubility limit (i.e. $x*$ when defined as mass fraction; $c*$ when defined as a concentration) of the liquor investigated was measured at 20% and 41% DS at 80°C. The result was that 0.22 and 0.14 kg_{salt}/kg_{tot} could be dissolved at the two liquor concentrations (including the inherent content of sodium carbonate and sodium sulphate in the black liquor). The critical solids content (defined here as when solubility limit is passed) was measured as 56%. To develop a correlation, two additional points were also included: the solubility limit for pure water (measured by Shi and Rousseau (2001)) and zero solubility at 100% DS. A second-degree polynomial was fitted with high accuracy to the five points to develop a correlation:

$$x^* = 0.2431{DS_{BL}}^2 - 0.5711DS_{BL} + 0.3283\left[\frac{kg_{salt}}{kg_{tot}}\right], \tag{5.4}$$

where DS_{BL} is the DS of pure black liquor (from 0 to 100%), excluding any additional dissolved salt but including its natural salt content. The temperature dependence of dicarbonate crystals in pure salt solution found by Bialik *et al.* (2008) (-5.76×10^{-4} $(kg_{salt}/kg_{tot})/K$) was used to adjust the solubility limit to the current temperature.

5.2 Model for cleaning evaporators

A model was developed in Paper III to allow the cleaning of an evaporator to be simulated. It was built for tubular concentrators with the liquor flowing on the outside of the tubes; design data, such as physical dimensions, number of tubes, volume of sump and flow rates, may be chosen freely. Figure 5.3 shows the most important parts of the evaporator model, which are also described below. Further information of how the model was implemented can be found in Appendix 2.

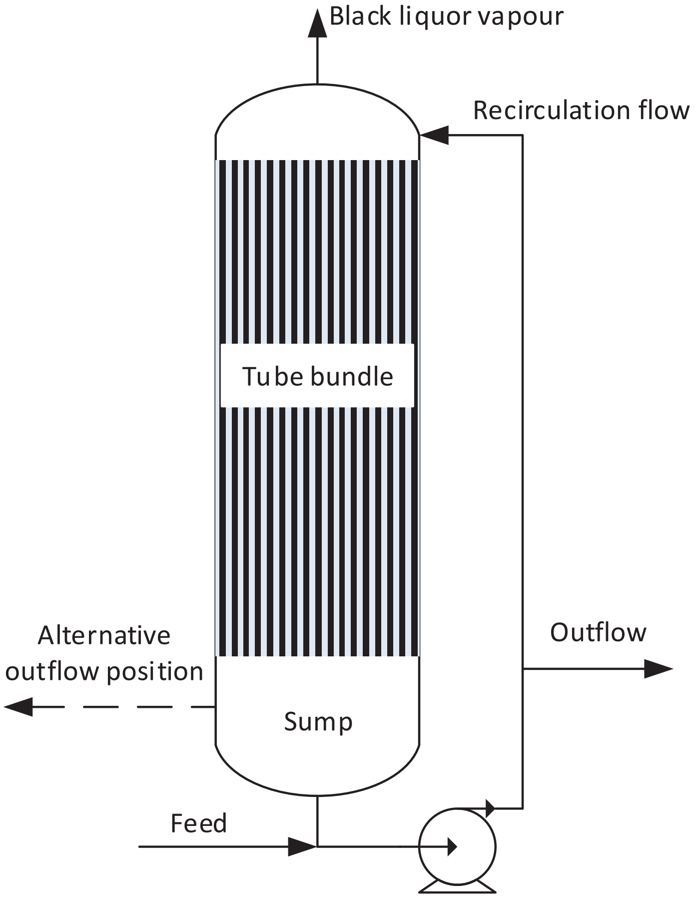

Figure 5.3. Schematic diagram of the liquor side of an evaporator effect comprised of tubes showing the most important parts of the cleaning model.

5.2.1 Evaporation

Industrial evaporators are usually heated during the cleaning process, with the result that water evaporates from the wash liquid. This process was modelled as a predefined evaporation rate, which was assumed constant both over time and along the heat transfer surface.

5.2.2 Distribution of scales

The initial thickness of the scales could be adjusted freely along the length direction to allow for different distributions of scales. All tubes were assumed to have the same distribution; circumferential variations were not considered.

5.2.3 Sump

The liquor sump may not be a perfectly mixed because there is no agitator. This non-ideality was estimated by modelling the sump as two tanks in series. The outflow from the evaporator was calculated to maintain the given volume of liquor in the sump.

5.2.4 Recirculation pipe

The recirculation pipe is important from two aspects: (i) the feed and outflow are connected to it, and (ii) it holds a considerable volume of liquor, causing delays in the system. The recirculation pipe was modelled in three steps: the sump flow was first mixed with the feed (see Figure 5.3) and then the outflow was subtracted from the flow. Finally, the flow was delayed, and the time was calculated as the total volume of the pipe divided by the flow rate. A considerable volume of liquor is located also on the heat transfer surface: this was included by adding it to the volume within the recirculation pipe.

The normal outflow position from an industrial evaporator is after the recirculation pump, but this has two disadvantages: (i) it has the lowest concentration since the feed dilutes the liquor just before the pump and (ii) the flow rate to the top of the evaporator decreases. Therefore, an alternative outflow position from the sump was also modelled, i.e. from the position with the highest concentration.

5.2.5 Dissolution of scales

The same model as described in Section 5.1 was used to calculate the dissolution of scales from the heat transfer surface. However, a model for the mass transfer coefficient was also required that addressed the full range of conditions possible, i.e. variations in the black liquor DS, flow rate and temperature. The mass transfer coefficient was estimated from the heat transfer coefficient using the Chilton-Colburn heat and mass transfer analogy described in Section 3.3.3.

The mass transfer coefficient, k, was derived by first calculating the Nu number for the current condition from the heat transfer correlation and converting it into the Sh number; k was then calculated from the definition of Sh. These steps required values of additional physical properties of the fluid, i.e. viscosity, specific heat, thermal conductivity and diffusivity. In the case of viscosity, a correlation for sodium carbonate solutions developed by Abdulagatov, Azizov and Zeinalova (2007) was found to provide nearly identical results (± 1%) to those from a correlation for black liquor by Adams *et al.* (1997) under the same DS. Therefore, it was assumed that the correlation for black liquor could be used for solutions of both black liquor and dissolved salt if the total DS, DS_{tot}, was used to define the mixture. The specific heat and thermal conductivity were also modelled by using the correlation for black liquor by Adams *et al.* (1997), i.e. neglecting the additional dissolved salt, which resulted in an error of k estimated at a maximum of 3%. Finally, diffusivity is an important parameter that, unfortunately, has been rarely studied for the salt used in this work. Nevertheless, using data by Vinograd and McBain (1941) and Zeebe (2011), the diffusivity was estimated here to be 10^{-9} m^2/s at 25°C. It was then converted to the right temperature as described in Section 3.3.2.

5.2.6 Adaption to a full-scale cleaning test

The model was extended to also calculate the boiling point rise and overall heat transfer coefficient to enable the simulation data to be compared with data acquired during the full-scale test (see Section 4.6). The boiling point rise is a measure of the salt content: its trend shows how it changes during the cleaning. As the overall heat transfer coefficient was known for the clean condition, the value for scaled conditions could be calculated from the assumed distribution of scales and compared with the value measured. It was found that these modification and measurements sufficed to perform a validation. As the total mass and distribution of scales were unknown, these were the parameters that were adapted to fit the simulation. Further details can be found in Andersson (2015).

6

Results and Discussion

6.1 Important results and questions from the papers

A summary of the work reported in the appended papers is given in Table 6.1, where the most important results are given together with questions and comments that are important to discuss.

In **Paper I**, a new experimental method was developed that enabled cleaning of the evaporator tube to be executed with minimum cooling and dilution of the circulation solution or liquor. It was important to provide precise measurements of the fouling rate by starting from clean conditions: this method was also used in the subsequent papers. An important result obtained in Paper I is that, as has been shown by others, rapid scaling only occurred during primary nucleation. It was also confirmed that black liquor can have two regions in which primary nucleation occurs (at around 50% and 65% DS, sometimes called first and second critical solids), but that the lowest concentration has the highest scaling rate. A more unique result was that operation up to 90% DS was found possible without any rapid scaling being observed (further discussed in Section 6.2).

The results in Paper I showed low repeatability of measurements of the scaling rate, which was explained by the complexity of the crystallization process. The experiments were, however, conducted at different temperatures: this was not considered in the paper and might be an alternative explanation for the large variations. It was also found that accuracy improved when the duration of the measurements was longer, as in Paper VI. In Section 6.3 the scaling rate measurements are discussed further and compared with data obtained by others.

In **Paper II**, a model for the dissolution of scales was developed for salt solutions and fitted to experimental data. Dissolution was found to be controlled by diffusion and that film theory could be used to describe the process. It was also found that the mass transfer coefficient could be estimated from a standard heat transfer correlation by using the Chilton-Colburn heat and mass transfer analogy. These findings then formed the base of the model developed in **Paper III,** where the cleaning of a typical industrial concentrator unit was modelled. The dissolution model was also extended to allow black liquor to be used as the wash liquor by developing a solubility model and a density correlation. The cleaning model allowed the fundamental results of dissolution to be converted into new practical understanding of cleaning industrial evaporators: a field that has been more or less unexplored in terms of research.

The main results obtained from the cleaning simulations in **Papers III** and **IV** were that the dissolution of scales was fast, leading to saturation of the wash liquor, and that the throughflow (feed rate) is the limiting step for cleaning. It was also shown that a high evaporation rate increased the cleaning time because this increased the dry solids content in the wash liquid. The cleaning time had an almost linear relationship with the mass of scales. The high rate of dissolution meant that the simulation results were insensitive to the distribution of the scales and the dissolution parameters. This makes the model robust and less sensitive to the fact that the exact conditions (especially the distribution of scales) in an industrial evaporator are unknown. The results are based on the assumption that there is sufficient wetting (good contact between the scales and wash liquid) and that the distribution is similar to that observed on the pilot scale. The significance to industry is discussed further in Section 6.7.

Table 6.1. Summary of the results obtained in the papers and the questions that remain.

	Method development	**Important results**	**Questions and comments**
PI	Online cleaning of the evaporator tube	-Rapid scaling only during primary nucleation -Possible to operate at DS up to 90%	-Low repeatability of scaling rates -Highest scaling rate at the highest temperature -Short duration of measurements
PII	Scale dissolution model for salt solutions	-Dissolution diffusion-controlled -Film theory applicable -Heat and mass transfer analogy valid and useful	-Measurements at low flow rates -Assumes uniform wetting and distribution of scales
PIII	Cleaning model, solubility model and density correlation for black liquor	-High dissolution rate → wash liquor saturated -Dissolution model also valid in black liquor -Insensitive to scale distribution and dissolution parameters	-Cleaning time close to linear for the mass of scales -Can the results be validated?
PIV	Simulation of cleaning in industrial cases	-Feed and evaporation rate determine cleaning time -Sump volume and recirculation rate unimportant	-Are the assumptions valid under industrial conditions?
PV	Hydrocyclone separation of bulk crystals	-Crystal separation from black liquor proven -Viscosity and flow rate most important for separation -Possible industrial implementation suggested	-Can recirculation of bulk crystal mitigate scaling? -Is the separation equipment worth the investment?
PVI	Long-time experiments with varied populations of bulk crystal	-Bulk crystals important in reducing scaling during primary nucleation -Bulk crystals of less importance during continuous operation -Large crystals most important	-Complex relation between bulk crystals and scaling -How are scales initiated? -What is the role of agglomeration?

Papers V and **VI** return focus to the formation of scales using the method developed in Paper I. The importance of bulk crystals in avoiding (rapid) scaling has been discussed for a long time and, in these papers, new knowledge is gained from the experimental results. This was enabled by the development of an experimental method where the bulk crystal population was changed by a hydrocyclone. The separation of bulk crystals from black liquor was examined in **Paper V**, where the two most important parameters for separation efficiency proved to be viscosity and the flow rate to the hydrocyclone. A concrete example was also given of how bulk crystal, after being separated and recirculated in the concentrator, has the potential of mitigating scaling. However, the degree of improvement the recirculation of bulk crystal can result in is still unknown, and whether the separation equipment is worth the investment; this is discussed further in Section 6.5.

In **Paper VI,** the relation between bulk crystals and scaling rate was evaluated for both sodium carbonate solution and black liquor. During conditions where primary nucleation was triggered it was found that bulk crystals were needed to leave the state of high scaling rate. During continuous crystallization under steady-state conditions the crystal fraction showed no influence on scaling rate, but there were indications that large crystals are needed to avoid rapid scaling. These results are to some extent contradictory and there are unfortunately not enough information to fully understand the behaviours. More research is needed to fully understand the scaling mechanisms, especially on how scales are initiated and grow (by direct crystallization or agglomeration). This is further discussed in section 6.4.

6.2 Operation with a dry solids content close to 90%

The idea that a higher content of dry solids means more scaling might be appealing, and can sound reasonable if addressing fouling in general: a high concentration can mean precipitation of different compounds, a high viscosity means increased stickiness and decreased wetting an increased risk of drying out. No reports have, however, been found showing increased problems with fouling when the final dry solids content increases to above 70%. There was no increase in the rate of sodium salt scaling detected at these high dry solids contents in the study undertaken in Paper I.

Table 6.2 shows some previously unreported data for operation close to 90% dry solids content connected to the experiments in Paper I. The main challenge when operating at 90% dry solids content was found to be the high level of viscosity: the falling film needs to have good contact with the heat transfer surface to ensure adequate heat transfer. A viscosity of around 500 mPa·s was found to be the limit; this is discussed further in the related work by Karlsson, Gourdon, Olausson and Vamling (2013).

The normal way of decreasing viscosity, and thereby improving the heat transfer properties of black liquor, is to increase the operational temperature, although this can have undesired effects on the organic compounds because their reactivity will also increase. Temperatures in the range of 160-190°C were tested in the experiments connected to Paper I. The release of malodorous (sulphuric) gases increased significantly compared to lower temperatures and, after exposure to these high temperatures for about 10 h, the visual appearance of the liquor changed: after dilution and cooling it was less homogeneous and solid black particles could be detected. It was also found that the molecular weight increased during the treatment, which was likely due to the polymerization of organic compounds. This applied especially to the experimental series SB2, which had a significant lower residual alkali. As the highest final concentration was reached in the experiment with the lowest temperature (SB1), it is probably not viable to increase the temperature even further.

An unexpected issue encountered in the experiments was the difficulty in measuring the true dry solids content. Great caution was exercised during sampling to avoid flashing and evaporation from the samples. It was found that the best way of minimising errors during dilution was to dilute the whole sample: the spread was significantly higher when just a part of the sample was diluted. The dry solids content was analysed in-house using the TAPPI T om-09 method and also sent to an external lab (MoRe Research in Sweden), which used the SCAN-N 22 method. The latter method showed significantly higher values, as shown in Table 6.2. The methods differ in that the TAPPI method uses larger samples (5-10 g instead of 1-2 g) that are dried for longer times (6 h instead of 30 min): it may be suspected that the SCAN samples were not completely dry, which is a possible explanation for the deviation.

Table 6.2. Data for operation at DS close to 90% for the three series of experiments in Paper 1.

Exp. series	**Final DS SCAN/TAPPI**[a]	**Temp.**	**Mw start**[a]	**Mw final**[b]	**Mw increase**	**Viscosity (mPas)**	**Residual alkali**[c]
SB1	91%/85%	172°C	790	980	24%	610	22.9
SB2	86%/82%	180°C	960	1350	41%	380	10.8
C1	89%/85%	175°C	920	1140	24%	570	19.2

[a] Result of the two methods SCAN-N 22 and TAPPI T 650 om-09.

[b] Arithmetic mean value of the molecular weight at the start and end of the experiment.

[c] gNaOH/l according to method SCAN-N 33:94, measured at the end of the experiment.

6.3 Scale formation in salt solutions and black liquor

6.3.1 Rates of scaling in sodium carbonate solutions

The nucleation experiments with sodium carbonate solution conducted by Gourdon (2009) are compared with the results from Paper VI in Figure 6.1. Both of these works measured similar scaling rates, although the operational conditions were slightly different. The scaling rate was a little lower in Gourdon's experiment with a 6°C differential temperature (*ΔT*), as expected. The wetting rates were considered to be close enough (1 and 1.3 kg/(m·s), respectively) to make the results comparable: there was no deviation between the works at a differential temperature of 10°C . As concluded in Paper VI, the crystal fraction showed no proportionality with the scaling rate: the crystal fraction is, of course, zero at the start so the value reported here is after a stabile bulk crystal population has been formed.

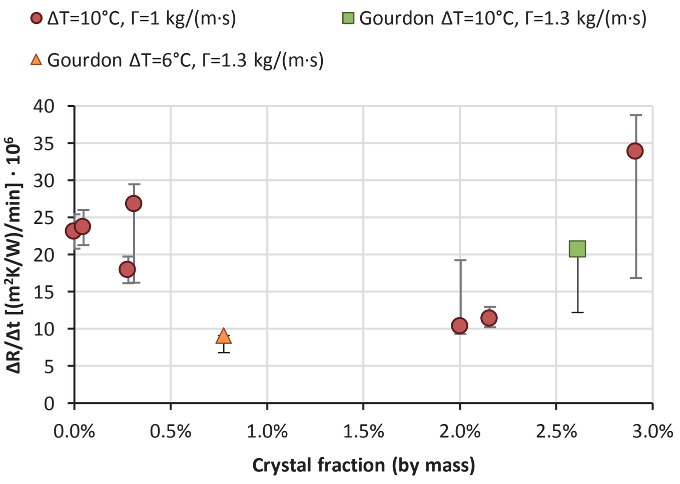

Figure 6.1. Rates of scaling in the nucleation experiments using sodium carbonate solution as a function of the crystal fraction. Data from Paper VI and Gourdon (2009).

6.3.2 Rates of scaling in black liquor

Gourdon (2011) concluded that the majority of the variation in the rate of scaling caused by the wetting rate and the differential temperature could be described by the concentration profile along the heat transfer surface. This was calculated as the initial increase of dry solids content from the top to the bottom (Δx_0), with initial referring to the reference state when measurements began: the increase in dry solids content decreases as scales are formed and decreases the heat transfer. This parameter was used in the figures below, as it allows a comparison of experiments at different wetting rates and differential temperatures to be made.

Figure 6.2 and Figure 6.3 show results from experiments with black liquor from Papers I and VI together with data from Gourdon (2011). Gourdon's measurements include both the nucleation phase and a subsequent continuous crystallization phase, so the results of the rate of scaling are not completely comparable: the values should be somewhere in between the nucleation and continuous crystallization results obtained by the author. This is also the case: the scaling rates in the nucleation experiments in Papers I and VI were indeed higher than those found by Gourdon (Figure 6.2), while those in the continuous crystallization experiment were generally lower (Figure 6.3). It should be noted that there are also other parameters that can cause differences in the comparison, for example crystal species (Gourdon was crystallizing dicarbonate whereas this work was crystallizing burkeite), liquor composition and temperature, but these were not considered here.

The nucleation experiments in Paper VI show the same positive trend as Gourdon (2011) between the rate of scaling and Δx_0, but this is only based on three measurements (Figure 6.2). The results of the primary nucleation in Paper I show no trend, with one point showing a significantly higher rate of scaling than the others.

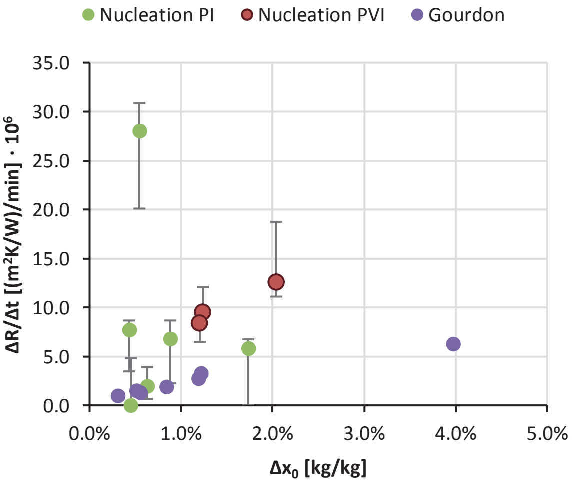

Figure 6.2. Rates of scaling in the nucleation experiments in Papers I and VI using black liquor. Data from Gourdon (2011) is included for comparison purposes.

The results from the continuous crystallization experiments show similar behaviour (Figure 6.3): the results in Paper I show no trend with Δx_0 while the results in Paper VI do. Due to the low accuracy of the measurements in Paper I, the only comment that can be made is that they are in the same range as the results in Paper VI. The results in Paper VI do not have the clear relationship shown by Gourdon, and variations in other parameters need to be considered. One such parameter is the bulk crystal population, which was varied in the experiments in Paper VI and is discussed in Section 6.4.

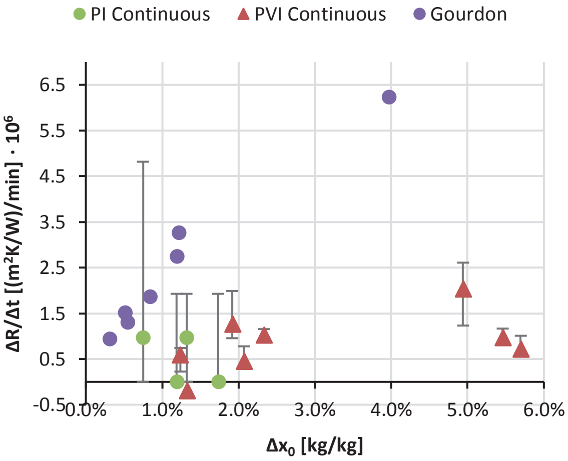

Figure 6.3. Rates of scaling in the continuous crystallization experiments in Papers I and VI using black liquor. Data from Gourdon (2011) is included for comparison purposes.

6.3.3 The influence of operational temperature

Differences in the operational temperature might explain the large deviations found in the nucleation experiments in Paper 1. The results of these are plotted together with the corresponding operational temperature in Figure 6.4. Liquor 1 showed both the highest and lowest rates of scaling when the first critical solids was passed: the only obvious difference was the operational temperature (167°C versus 91°C). The corresponding experiments for Liquor 2 showed similar rates of scaling: both experiments were conducted at the same temperature (110°C) despite the fact that Δx_0 differed significantly. The results for the second critical solids show similar trends, as the highest temperature (Liquor 1) had the highest scaling rate. Interpretation should, however, be made very carefully when two different liquors are compared.

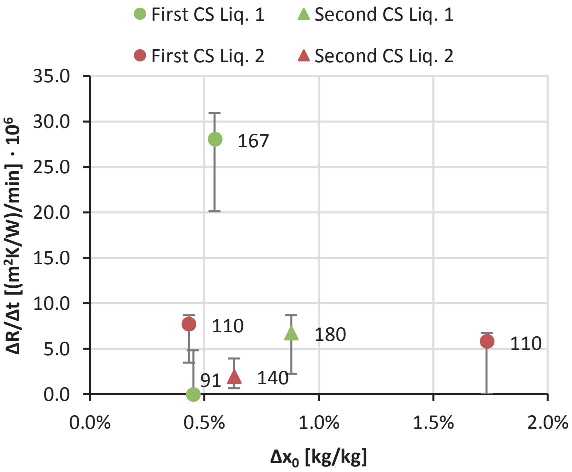

Figure 6.4. Rates of scaling in the nucleation experiments in Paper I using black liquor. Data for passing the metastable limit is shown for both the first and second critical solids (CS). The figures indicate the operational temperature in °C.

There is no obvious explanation as to why the scaling rate increases at higher temperatures. An increase in temperature gives an increase in diffusivity and a decrease in viscosity, which influences the mass transfer during crystallization. Properties related to the surface chemistry are also affected and could change the affinity for scaling on the heat transfer surface. No reports have been made that the crystal species changes at elevated temperatures, but this cannot be dismissed completely. These are the most likely explanations but the phenomenon needs further investigation.

6.3.4 The influence of crystal species

Differences between the crystal species (burkeite and dicarbonate) have not been the focus of the present work. They are nevertheless important, and some interesting observations may be made. It was concluded in Paper I that burkeite crystallized when the first critical solid was passed in Liquor 2 (Figure 6.4). As the molar ratio of carbonate was lower in Liquor 1 than in 2 (ϕ=0.77±0.02 versus ϕ=0.82), burkeite was probably also crystallizing here at the first critical solids. This, in turn, means that dicarbonate was crystallizing at the second critical solids for both liquors. Dicarbonate has been reported as giving high scaling rates but not burkeite (Frederick *et al.*, 2004; Gourdon, 2009): here it is shown that burkeite can give very high scaling rates as well (although this might be a consequence of high temperature, as shown above). It can also be concluded that dicarbonate, when crystallizing at the second critical solids, does not give significantly higher rates of scaling than burkeite crystallizing at the first critical solids.

6.3.5 Growth behaviour

In Paper VI it was found that the high scaling rates during primary nucleation are mainly caused by the high rate of scale initiation at the heat transfer surface: the thin layer that is created on a large part of the heat transfer surface in a short time has a much greater impact on the heat transfer than the same amount of salt would have on a small part of the surface. Hence, it is not the high rate of crystallization as such that causes the high scaling rates. A certain level of supersaturation is required to initiate scaling: if the black liquor is saturated when it enters the top of the evaporator, which is the case during continuous crystallization, scaling will only occur after the film has fallen far enough to acquire this level of supersaturation. This explains why scales grew only up to a certain height from the bottom during the continuous crystallization experiments in Paper VI. The height was repeatable and dependent on the operational conditions (wetting rate and differential temperature). This is in line with Gourdon *et al.* (2008), who found that scaling starts in the lower parts of the evaporator but, since the measurements in that study were made during primary nucleation, a maximum height was not detected for the scales.

The work in Paper VI also found that sufficient wetting of the heat transfer surface is important in avoiding the initiation of scaling. This can be exemplified by the following, when one of the most severe scaling situations measured in this work was produced in the pilot evaporator: a supersaturated salt solution was being evaporated when the recirculation pump stopped and all wetting was lost. Although it was back in operation after some minutes, severe scaling had been initiated. Subsequently, the steam pressure (differential temperature) was increased to compensate for the decreased heat transfer which, however, resulted in even more scaling. The overall result was that 98% of the heat transfer surface was covered with scales in a period of just 30 minutes or so.

6.4 The relation between scaling and bulk crystals

6.4.1 Experimental results

The influence of the bulk crystal population on scaling rate was analysed in Paper VI but, in the case of black liquor, no clear conclusions could be drawn because the experiments was conducted under different wetting rates and differential temperatures. Variations in these two parameters can, however, be taken into account by plotting the results as a function of the initial increase in the dry solids content from top to bottom (Δx_0), as shown in Figure 6.5. A positive relationship between the scaling rate and Δx_0 can be observed, as already presented and discussed in Section 6.3. In addition, both the crystal fraction and the operational mode of the hydrocyclone differed in the experiments; the influence of these two parameters become clearer when the data was plotted in Figure 6.5.

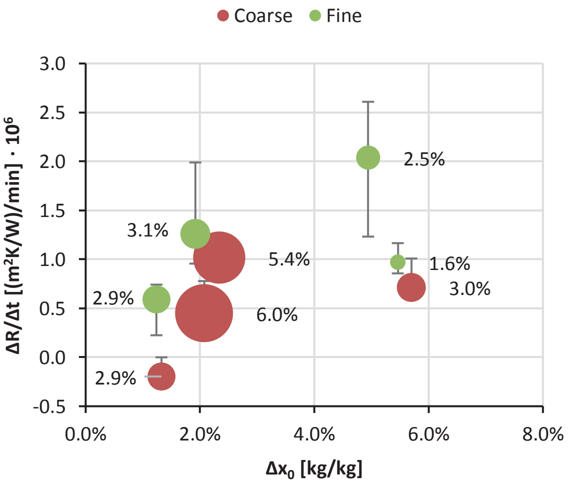

Figure 6.5. Rates of scaling in continuous crystallization experiments from Paper VI using black liquor. Coarse and fine refer to the operational mode of the hydrocyclone. The size of the circle refer to the crystal fraction, with a label giving the corresponding value.

The crystal fraction is shown in Figure 6.5 by the size of the circle, in combination with a label of the value. No correlation between rate of scaling and fraction of crystals can be observed: the two highest points (5.4% and 6.0%) do not show a lower rate of scaling. This agrees with the results obtained for salt solution in Paper VI and strengthens the conclusion that increasing the crystal fraction does not decrease the scaling rate during continuous crystallization. The figure also clarifies how the operational mode of the hydrocyclone influences the scaling rate: all points in the fine mode hade a higher rate of scaling then those in the coarse mode when comparing at the same value of Δx_0, albeit the differences are sometimes small. Large crystals seem to be important in reducing the occurrence of scaling, as was concluded in Paper VI.

The analysis made in this section consequently strengthens the conclusions drawn in Paper VI, although the results still show that the relationship between bulk crystals and scaling is complex. On one hand, bulk crystals are important in slowing down the high scaling rate that occurs during the primary nucleation but, on the other hand, no correlation between the scaling rate and the crystal fraction is apparent for salt solution in Figure 6.1. This is analysed further in Figure 6.6, where the heat transfer coefficient and chord counts are plotted for two of the nucleation experiments shown in Figure 6.1: one where bulk crystals were formed after nucleation and one where no (or few) crystals were formed. The chord count is a measure of the number of particles in the system and shows clearly how bulk crystals are formed in one of the experiments. The decrease in the heat transfer coefficient is similar in the first part of the experiments, which implies similar scaling rates: in the later part, however, the experiment with crystals stabilises at a higher value. After 37 min the evaporation stalled completely in the experiments without crystals (the operation of the condenser had to be halted to maintain the temperature of the salt solution), while operation could be continued (at a low rate) when crystals were available.

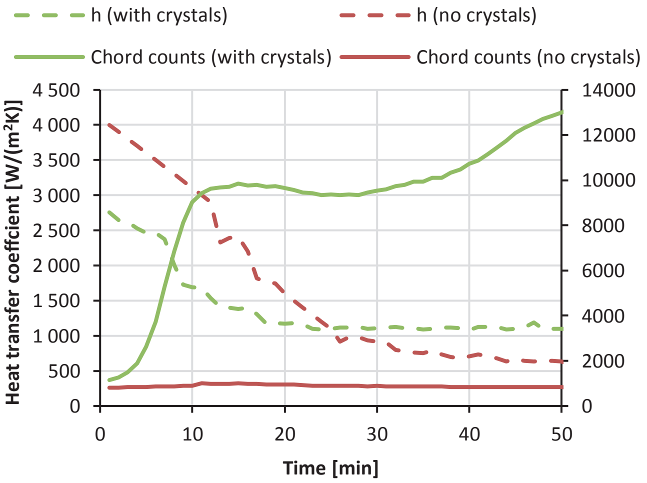

Figure 6.6. Rates of scaling in two nucleation experiments performed in Paper VI using sodium carbonate solution, one when bulk crystals were formed and one when not.

No correlation between the rate of scaling and the fraction of crystals was found in the continuous crystallization experiments but, yet, the rate of scaling increased when the larger-sized crystals were removed. A minimum amount of large crystals is probably needed to suppress scaling, whilst the system is insensitive above this limit. This can explain why no correlation with the crystal fraction was observed: the amount present in the experiments with low fractions of crystals was sufficiently high to supress scaling. No other explanations could be found, for example supersaturation (none was detected in the fine mode, as it was measured from refractive index for the salt solution), although there was slightly more fluctuation in the system, caused by experimental limitations when operating in fine mode. It appears that the minimum amount of (large) crystals required is higher during primary nucleation compared to continuous crystallization, which can be explained by the high supersaturation that causes high rates of crystallization during nucleation.

The most relevant studies by other researchers that were found have partly contradictory results. The relationship between the chord counts in bulk crystal from FBRM measurements and the scaling rate was investigated for three experiments in connection with studies of internal residence time by Gourdon (2009): no correlation was found. In three adjacent experiments, Gourdon also studied the relationship between the dry solids content and the scaling rate: the highest rate of scaling was observed close to the critical solids. This was explained by the low content of bulk crystals when operating close to solubility, and thus the dependency of the crystal fraction observed in this case.

6.4.2 Discussion of crystal surfaces

In theory, a greater amount of bulk crystals should give less scaling: more crystal surfaces are available in the bulk and therefore stimulate crystallization. In Table 6.3, the ratio between the surface of the bulk crystal and the surface of the scales is estimated for a typical experiment in the pilot evaporator using 3% bulk crystals, and the same mass of scales covering half of the evaporator tube with a layer 0.8 mm thick (if evenly distributed). The crystals are assumed to be spherical and the total mass of crystals or scales is 0.9 kg. A single particle distribution of 100 µm would mean that the surface area is 25 times higher in the bulk than on the scales. A log-normal distribution was fitted to a typical CLD (in the case of spheres, the particle size and chord length distributions are similar) giving a more reasonable crystal population: the surface of the bulk crystals is about 10 times that of scales.

Table 6.3. Example of a calculation of crystal surfaces in the pilot evaporator.

Size distribution of bulk crystals	**Log-norm.**	**Single**	**Single**	**Single**	
Mean crystal diameter	$1.0\cdot10^{-4}$	$1.0\cdot10^{-6}$	$1.0\cdot10^{-5}$	$1.0\cdot10^{-4}$	m
Number of crystals	$2.2\cdot10^{9}$	$6.7\cdot10^{14}$	$6.7\cdot10^{11}$	$6.7\cdot10^{8}$	
Total area of bulk crystals	8.1	$2.1\cdot10^{3}$	$2.1\cdot10^{2}$	$2.1\cdot10^{1}$	m^2
Bulk crystal/scales surface ratio	**9.6**	**$2.5\cdot10^{3}$**	**$2.\ 5\cdot10^{2}$**	**$2.55\cdot10^{1}$**	
Scales					
Area tube	0.848	m^2			
Area scales	0.430	m^2			
Scale thickness	$8.1\cdot10^{-4}$	m			
Assumptions					
Density of burkeite	2571	kg/m^3			
Total mass in system	30	kg			
Crystal fraction	3%				
Total mass of crystal or scales	0.9	kg			
Total volume of crystal or scales	$3.5\cdot10^{-4}$	m^3			

As the total surface of bulk crystals increases when the size of the crystal decreases for a fixed mass of crystals, it can be argued that smaller crystals should be preferred. However, the results show the opposite: operation in fine mode gave the higher rates of scaling shown in Figure 6.5. Small crystals, especially from dicarbonate, have been reported as agglomerating on the heat transfer surface (Frederick *et al.*, 2004) and might therefore be unsuitable for the prevention of scales. Small crystals are also (more) stagnant in the flow due to their low mass and are therefore less available for crystallization: mass transport is limited to diffusion only, while there is also convective mass transfer to the larger particles.

Frederick and Euhus (2015) discuss the importance of bulk crystals in providing sufficient growth area for crystallization, and have examples of calculations for estimating the retention time needed to avoid supersaturation and the primary nucleation of dicarbonate. Their estimations imply that retention times significantly longer than those currently used in industry are necessary to allow for crystallization on bulk crystals and to handle the supersaturation caused by evaporation. This, however, does not agree with the observations made in this work, where supersaturation after the buffer tank was only observed in the first part of the nucleation experiments. Not even in the experiments at very high differential temperatures (salt solution, 25°C), which showed very high scaling rates during continuous crystallization, was supersaturation detected after mixing in the buffer tank. A possible explanation for this can be the unusually low estimation of the crystal fraction: they assume that 0.0021 m^3 crystals/m^3 black liquor is formed when concentrating to 65% dry solids content. Increasing the crystal fraction by a factor of 10 would bring the value close to that expected in black liquor, and the calculated retention times required would be closer to that being used in industry today.

6.5 Recommendations for mitigating scaling

The knowledge gained from the research conducted in this study can be used to provide recommendations for how to mitigate scaling. These are, to a large extent, in line with the general recommendations of others, as summarised in Section 2.3.1. Similar to this work, Gourdon (2009) studied the relation between scaling and operational conditions. He provided a number of more specific recommendations, the following of which can be confirmed using the new methods developed for measuring scaling used in this studies:

- Keep operation as steady as possible
- Reduce the increase in dry solids content along the heat transfer surface by:
    - High wetting
    - Low differential temperature
    - Short and wide heat transfer surface (if tubes: short but more of them)

In addition, a couple of new recommendations that have arisen in the present work are offered, namely:

- If passing the critical solids is unavoidable, scaling can be reduced (potentially) if high temperatures are avoided (<110°C)
- The growth of large-sized crystals should be favoured, if this is possible.

As it is commonly recommended to favour a high content of bulk crystals in the concentrator, a new concept for scaling mitigation by recirculating the bulk crystal was presented in Paper V (similar to the patent of Olausson *et al.* (2011)). The application of this concept is, however, reduced as no decrease in the degree of scaling was found when the concentration of bulk crystal was increased in continuous crystallization (i.e. normal operation). It is still likely that the addition of seed crystals can reduce the amount of scaling during primary nucleation. The critical solids are often passed during start-up or major changes in the process (e.g. altered liquor compositions or dry solids content in Effects 1 or 2) when there are no crystals available, leading to primary nucleation. Then, when the evaporator is back in normal operation, its capacity is affected negatively by the scales that are formed. If, in this case, seeds crystals are added, scaling will probably be lesser, and the evaporation capacity higher, when it is back in normal operation. The situation is similar after the evaporator has been cleaned, which discussed further in Section 6.8.

6.6 Solubility correlation for black liquor

A new correlation for the solubility of sodium salts in black liquor was developed in Paper III. The intention was not to develop a chemical and thermodynamic model because the system is very complex, but rather to develop a practical correlation. The correlation, and the way in which it was plotted, was also found to be informative: below solubility, it shows the liquor's potential for dissolving scales (important for cleaning) and, above solubility, it shows the crystal fraction in the liquor (important when making salt balances in the evaporator), as illustrated in Figure 6.7. The intersection of the lines of solubility and salt content (the sum of sodium carbonate and sodium sulphate) indicate at which content of dry solids the solubility limit is exceeded, i.e. the critical solids. A related plot (but only showing the solubility between 50 and 65% dry solids) was made by Gourdon, Olausson and Vamling (2010) and shows similar values.

The correlation can be adjusted relatively easily to fit other black liquors: the only parameters needed are the total content of sodium carbonate and sodium sulphate and the critical solids (based on the definition related to the solubility limit). Step 1 is to draw the line for salt content, as indicated in Figure 6.7. As the end points of the solubility line are fixed (0 and 100% dry solids content), the critical solids will give a third point that determines at which dry solids content the two lines will intersect.

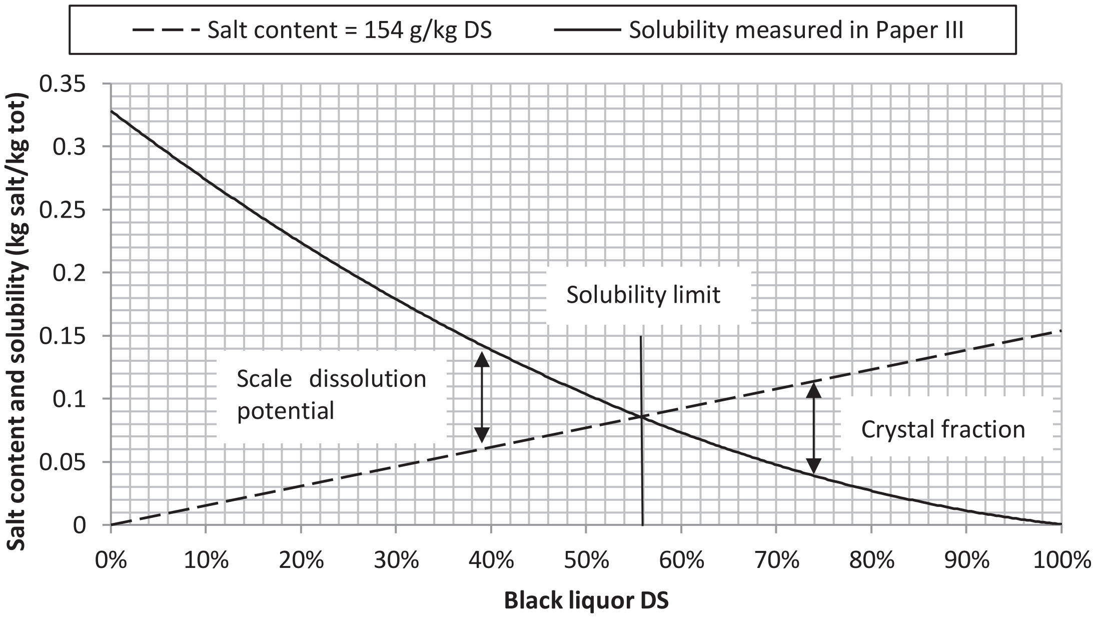

Figure 6.7. Solubility correlation in Paper III. Salt content refers to the sum of sodium carbonate and sodium sulphate in the liquor.

6.7 Simulating cleaning and significance to industry

The most important parameters affecting cleaning performance were simulated in Papers III and IV for a typical concentrator unit using the cleaning model developed. Work was also done in the Master's thesis carried out in our group to verify the model in a full scale test (Andersson, 2015); some results from this are shown in Figure 6.8. The thin liquor was feed into Unit D and its outflow was then feed into Unit C. It was possible to fit the model to give relatively good agreement with the boiling point rise, at least at the beginning of the experiment. It was not, however, possible to also have good agreement for the salt content measured in the outflow and the overall heat transfer coefficient (calculated from the fitted scale distribution (see Section 5.2.6). In the evaluation, it was found that the quality of the data collected was not high enough to fully validate the model: chemical analysis of the salt content showed large variations, and it was probable that both the boiling point rise measured and the flow rate deviated. The system whereby two units are cleaned in series was also found to be too complex and increased errors. Still, the method developed for applying the cleaning model in industry was found to be successful and can be used in other cases.

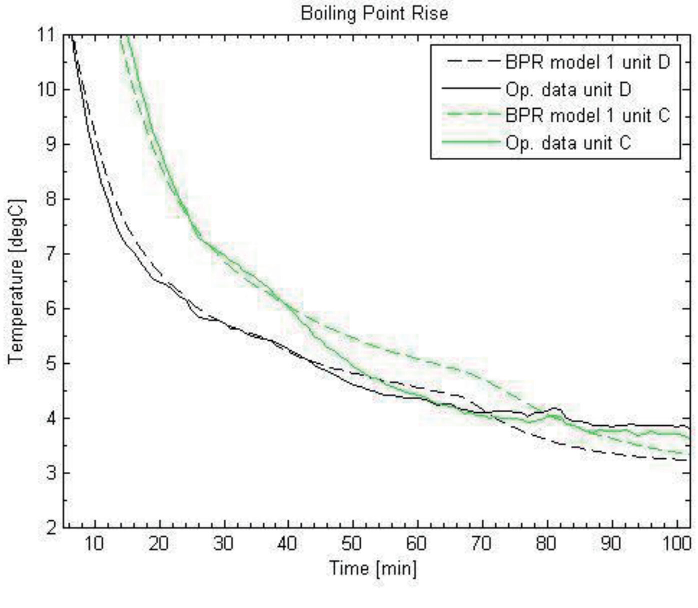

Figure 6.8. Simulation results and measurements of boiling point rise during the full-scale cleaning test. Two concentrator units were cleaned in series, where the first unit (D) was feed with thin liquor. Courtesy of Andersson (2015).

The boiling point rise was found, from evaluation of the mill data, to be a robust parameter for monitoring the cleaning process, as its trend provides information on how the salt content changes during cleaning (the absolute value not so important for just monitoring the process); this parameter is already being measured at virtually all pulp mills. The evaporator is clean when the boiling point rise has stabilised at a reasonable low level. In Paper IV, it was concluded that the salt content (and dry solids content) in the evaporator should reach a plateau after an initial dilution period and then decrease further once all the scales have been dissolved. This was not observed in the full-scale test here: in discussions with people working in the industry, however, it was established that behaviour similar to that reported in Paper IV can be observed. In the experimental work in Paper III, both behaviours were actually observed (i.e. with and without a plateau). The difference is likely related to the distribution of scales and the degree of contact between the wash liquid and the scales. Scales can, for example, be distributed differently between the tubes or clusters of scales might be formed between the tubes: such situations cannot be simulated in the current model.

6.8 Recommendations for cleaning evaporators

Inadequate cleaning can potentially lead to poor performance in the evaporator and ultimately disturbances in the process. The capacity of the evaporator can most likely be improved by avoiding unnecessary and insufficient cleaning: the main idea is to clean only when needed and ensure that all scales are removed before returning to operation. The following recommendations are offered to help achieve this in practice:

- Measure the overall heat transfer coefficient and use it to decide when cleaning is required. Some systematic work might be necessary to determine the values for clean conditions for all of the concentrator's units. The amount by which the coefficient should be allowed to drop before cleaning is triggered should be determined from case to case: 50% can be a rule of thumb, as this corresponds to duplication of the differential temperature.

- The evaporation rate should be low during cleaning, if possible: it is the water that dissolves the scales.

- The feed rate of the wash liquor will be the main parameter determining the cleaning time if the scales are distributed evenly. High feed rates can therefore be tolerated if short cleaning times are necessary.

- The boiling point rise should be monitored during the cleaning as it can supply important information. Some systematic work is required here, too, to determine the values for when cleaning is completed and to interpret variations in the trend (such as plateaux).

Once the evaporator is considered clean, the next (important) step is the return to operation. As the dry solids content is increased from below to above critical solids, this involves the primary nucleation of the sodium salts. The following procedure is recommended to avoid considerable scaling from occurring before the evaporator is back in normal operation:

- Feed the clean evaporator with thick liquor, or other crystal rich liquor, to increase the dry solids content by mixing instead of normal evaporation: the latter would give high levels of supersaturation, leading to a substantial propensity for scaling. The types of seed crystals used are important: electrostatic precipitator (ESP) ash will probably not work.

- Keep the rate of evaporation low, if possible.

- The more the concentration is increased through mixing instead of evaporation, the lower the risk of scaling.

The importance of a correct start-up is discussed by Verrill and DeMartini (2006), who also conclude that the addition of seed crystals is important. Correct start-up can be considered at least as important as correct cleaning, and should not be forgotten when troubleshooting scaling problems.

7

Conclusions

The following conclusions can be drawn from the work undertaken in this thesis:

- The rate of scaling is tenfold greater during primary nucleation than continuous crystallization. This is mainly due to the high degree of supersaturation in the former, as it causes a rapid initiation of scaling on the majority of the heat transfer surface.

- Scaling is not a substantial problem when black liquor is evaporated at very high dry solids content (values up to 90% DS were tested experimentally here).

- It was found that burkeite can give severe scaling during primary nucleation (previously reported mainly for dicarbonate). The trigger for the occurrence was probably have been a high operational temperature (167°C).

- Bulk crystals are required to stop the high scaling rate during primary nucleation. All crystallization will otherwise occur on the heat transfer surface, leading to severe operational disturbances and the need for cleaning within hours or less.

- Providing that a minimum amount of bulk crystals is available during normal operation (continuous crystallization), a further increase in the amount of bulk crystals will not decrease the rate of scaling.

- The larger crystals contribute to a lower degree of scaling and are therefore more important in the system than the smaller crystals.

- The capacity of the evaporator can be improved by avoiding unnecessary and inadequate cleaning. Cleaning can be improved by taking a systematic approach: important process data should be utilized to trigger and/or schedule cleaning.

- The overall heat transfer coefficient is a good measure for deciding when cleaning is necessary. The boiling point rise is a good measure for monitoring the performance of the cleaning operation and to decide when the evaporator is clean.

- It is important to feed the evaporator with crystals during start-up after cleaning: primary nucleation will otherwise be initiated, with a high risk of substantial scaling occurring before the evaporator is back in normal operation.

8

Future research

Many ideas for interesting studies emerged in the duration of this thesis; many interesting observations were made that could attract further investigation. Experimental work is, however, very time-consuming and it has not been possible to follow all these paths. The most interesting of these future research topics are listed below:

- The role of temperature during the primary nucleation of sodium salts. The indication was that the scaling rate is substantially higher at around 160°C than at 90°C, so this should be investigated further to discover the operational conditions that should be avoided.

- Understanding of the phenomena connected to surface chemistry could supply new tools for the controlling scaling: significant progress would be made if the surface can be modified to inhibit scaling.

- More research is required into the role of bulk crystals and how they interact with scale growth, especially during continuous crystallization. Hopefully, this will provide new understanding of the mechanisms of the initiation and growth of scale: it is important that these are understood in order to develop effective strategies for mitigating scaling. The role of agglomeration, for example, is probably important but not yet fully understood.

- Much new knowledge has been gained regarding evaporator cleaning thanks to this study, yet more research is necessary to enhance understanding of dissolution and its behaviour during full-scale cleaning. This will improve the quality of recommendations offered and help optimise cleaning.

- Avoiding scaling during start-up after cleaning is important. More research is imperative to examine the problems encountered and to unearth good strategies for avoiding primary nucleation.

- The experiments performed here employed an evaporator tube of length 4.5 m, opposed to the 10-15 m used in industry: the ways in which the length of the tube (or the heat transfer surface) affect scaling behaviour should also be investigated.

- Different types of residual streams from other parts of the mill are often introduced into the evaporator, e.g. ESP ash and spent acids, and may influence the behaviour of scaling; the optimal way of adding these therefore requires further investigation.

Acknowledgements

The financial support of **Valmet AB**, **Energimyndigheten** (Swedish Energy Agency), **Troëdssons forskningsfond**, **Bo Rydins stiftelse** and **Chalmers Energy Initiative** made this work possible and is gratefully acknowledged.

Firstly, I would like to thank you, **Mathias Gourdon,** for all the work you put into helping me: without it I would not have reached this far in my research. Now, in retrospect, I really appreciate the tough times we shared during late nights in the lab, when we struggled to get the equipment running or tried to figure out the next step when experiments failed. I am also very appreciative of you welcoming me so warmly as a new employee and to my new home town of Gothenburg.

Thank you, **Lennart Vamling,** for all the good discussions we had, and for teaching me how to become a researcher. I am indebted to you for your support during hard times and, in addition to research and achievements, for also showing care for me as a person. Thanks also go to **Lars Olausson** and **Olle Wennberg,** whose sound knowledge of black liquor evaporation supplied input and discussions that improved my research, and to **Helena Fock** for her work and discussions related to cleaning evaporators.

Special thanks are extended to the following Master students whom I supervised, and for the great contributions their thesis projects have made to my research: **Emil Lagerberg Nilsson**, **Anna Broberg**, **Anders Åkesjö**, **Karin Öhrman**, **Martin Pettersson** and **Mikaela Andersson**. Good luck to you all in the future!

Maintaining the pilot evaporator took a lot of work and I would like to thank **Erik Larsson** and the late **Bengt Erichsen** for their invaluable help.

My sincerest thanks go to my **former colleagues** at Värmeteknik och Maskinlära (Heat and Power Technology) and my **new colleagues** at Skogsindustriell Kemiteknik (Forest Products and Chemical Engineering) at Chalmers. Thank you, **Valeria Lundberg**, **Hanna Ljungstedt** and **Maria Arvidsson,** for the yoga classes we shared. **Tallal Belkheiri**: I enjoyed sharing an office with you. **Anders Åkesjö**: you became a friend and a very kind colleague and I thank you for all your support and the work we did together!

Finally, my deepest thanks go to you, **Emma Svedlund**, for all your support and patience. You make my life complete!

Nomenclature

Abbreviations

BPR	Boiling point rise
C	Continuous crystallization experiment
CLD	Chord length distribution
CS	Critical solids (content)
ESP	Electrostatic precipitator (ash)
FBRM	Focused beam reflectance measurement
LP	Low pressure (steam)
MP	Medium pressure (steam)
N	Nucleation experiment
Nu	Nusselt number
Pr	Prandtl number
Re	Reynolds number
Sc	Schmidt number
Sh	Sherwood number

Symbols

A	Area [m^2]
c	Concentration [kg/m^3]
cf	Crystal fraction [kg/kg$_{tot}$]
d	Particle diameter [µm]
d_{50}	Particle cut size diameter [µm]
D_{AB}	Diffusion coefficient [m^2/s]
DS	Dry solids content [kg/kg]
g	Gravitational acceleration [m^2/s]
G	Grade efficiency [-]

h	Heat transfer coefficient [W/(m^2·K)]
J	Mass flux or dissolution rate [kg/(m^3·s)]
j	Chilton and Colburn *j*-factor [-]
k	Mass transfer coefficient [m/s]
L	Volumetric bottom-flow-to-throughput-ration
m	Mass [kg]
n	Sharpness of separation [-]
Q	Heat load [W]
R	Fouling resistance [m^{2}K/W]
r	Radial direction (coordinate) [m]
T	Temperature [T]
t	Time [s]
U	Overall heat transfer coefficient [W/(m^2·K)]
V	Volume [m^3]
x	Mass fraction of Na_2CO_3+Na_2SO_4 in solution[kg/kg]
z	Vertical direction (coordinate) [m]
Γ	Mass flow rate per unit with [kg/(m·s)]
ΔT	Temperature difference between heating steam and evaporating liquor or salt solution (referred to as differential temperature) [K]
Δx	Mass fraction (*DS*) increase along the heat transfer surface [kg/kg]
δ	Thickness [m]
κ	Thermal conductivity [W/(m·K)]
μ	Dynamic viscosity [Pa·s]
ρ	Density [kg/m^3]
ν	Kinematic viscosity [m^2/s]
ϕ	Molar ratio Na_2CO_3/(Na_2CO_3+Na_2SO_4)

Subscripts

0	Initial conditions
bulk	Bulk (fluid)
BL	Black liquor
c	Critical
cry	Crystal
dif	Diffusion

filt	Filtered
h	Heating
i	Inner
lam	Laminar
m	Mean
o	Outer
salt sol	Salt solution
sol	Solution
tot	Total
turb	Turbulent
unfilt	Unfiltered
w	Wall

Superscripts

*	Saturated

References

Abdulagatov, I. M., Azizov, N. D., & Zeinalova, A. B. (2007). Density, apparent and partial molar volumes, and viscosity of aqueous Na_2CO_3 solutions at high temperatures and high pressures. *Zeitschrift für Physikalische Chemie, 221*(8), 963-1000.

Adams, T. N. (2001). *Black liquor properties, crystallization, and sodium salt scaling in concentrators.* Paper presented at the TAPPI Pulping Conference, Seattle, USA.

Adams, T. N., Frederick, W. J., Grace, T. M., Hupa, M., Iisa, K., Jones, A. K., & Tran, H. (1997). *Kraft Recovery Boilers*. Atlanta, USA: Tappi Press.

Alén, R. (2011). *Biorefining of Forest Resources*. Helsinki, Finland: Paperi ja Puu Oy.

Andersson, M. (2015). *Modelling of Black Liquor Evaporator Cleaning - A case study of Skärblacka pulp mill.* (Master Thesis), Chalmers University of Technology, Göteborg, Sweden.

Axelsson, E., Olsson, M. R., & Berntsson, T. (2006). Heat integration opportunities in average Scandinavian kraft pulp mills: Pinch analyses of model mills. *Nordic Pulp and Paper Research Journal, 21*(4), 466-475.

Bialik, M. A., Theliander, H., Sedin, P., Verrill, C. L., & DeMartini, N. A. (2008). Solubility and solid-phase composition in Na_2CO_3-Na_2SO_4 solutions at boiling temperature: A modeling approach. *Industrial and Engineering Chemistry Research, 47*(9), 3233-3238.

Bott, T., R. (1997). Aspects of Crystallization Fouling. *Experimental Thermal and Fluid Science, 14*, 356-360.

Bremford, D. J., & Müller-Steinhagen, H. M. (1999). Multiple-effect evaporator performance for black liquor - Part III: The effects of fouling on evaporator performance. *Appita Journal, 52*(1), 30-36.

DeMartini, N. A., & Frederick Jr., W. J. (2008). *Review of Sodium Salt Scaling in the Liquid Streams of the Chemical Recovery Cycle of Kraft Pulp Mills.* Paper presented at the TAPPI Engineering, Pulping and Environmental Conference, Portland, USA.

DeMartini, N. A., & Verrill, C. L. (2005). *Evaporator fouling mitigation - Case studies.* Paper presented at the TAPPI Engineering, Pulping, Environmental Conference, Philadelphia, USA.

DeMartini, N. A., & Verrill, C. L. (2007). *Minimizing soluble scales in black liquor evaporators: Application of metastable and solubility limit data for the Na-CO_3-SO_4 system.* Paper presented at the International Chemical Recovery Conference, Quebec City, Canada.

Diesen, M. (1998). *Economics of the Pulp and Paper Industry*. Helsinki, Finland: Fapet Oy.

Eneberg, H., Kaila, J., & Kiiskila, E. (2002). Method of inhibiting scaling in black liquor evaporators, CA2229973.

Energimyndigheten. (2013). *Energiläget 2013*. Retrieved from Energimyndigheten: www.energimyndigheten.se

Euhus, D. D. (2003). *Nucleation in bulk solutions and crystal growth on heat-transfer surfaces during evaporative crystallization of salts composed of Na_2CO_3 and Na_2SO_4.* (PhD Thesis), Georgia Institute of Technology, Atlanta, USA.

Euhus, D. D., Rousseau, R. W., Frederick Jr., W. J., Schmidl, W., Lien, S. J., Thorn, P. A., & Smith, P. K. (2003). *Eliminating sodium salt fouling in black liquor concentrators: Crystallization behavior and fouling in pilot evaporation trials.* Paper presented at the TAPPI Fall Technical Conference, Chicago, USA.

Frederick, W. J., & Euhus, D. D. (2015). A practical approach to eliminating rapid sodium carbonate - Sodium sulfate scaling in black liquor concentrators. *TAPPI Journal, 14*(7), 431-437.

Frederick, W. J., Shi, B., Euhus, D. D., & Rousseau, R. W. (2004). Crystallization and control of sodium salt scales in black liquor concentrators. *TAPPI Journal, 3*(6), 7-13.

Giuseppetti, G., Mazzi, F., & Tadini, C. (1988). The crystal structure of synthetic burkeite. $Na_4SO_4(CO_3)_t(SO_4)_{1-t}$. *Neues Jahrbuch für Mineralogie Monatshefte, 5*, 203-221.

Golike, G. P., Pu, Q., Holman, K. L., Carlson, K. R., Wollwage, P. C., Folster, H. G., & Rankin, S. C. (2000). New method for calculating equilibrium solubility of burkeite and sodium carbonate in black liquor. *TAPPI Journal, 83*(7), 68.

Gourdon, M. (2009). *Sodium Salt Scaling in Black Liquor Evaporators.* (PhD Thesis), Chalmers University of Technology, Göteborg, Sweden.

Gourdon, M. (2011). *The Effects of Flow Velocity on Crystallization Fouling in Falling Film Black Liquor Evaporators.* Paper presented at the Heat Exchanger Fouling and Cleaning Conference, Crete Island, Greece.

Gourdon, M., Olausson, L., & Vamling, L. (2010). Crystallization in a pilot evaporator - Comparison between black liquor and black liquor model substances. *Nordic Pulp and Paper Research Journal, 25*(1), 21-30.

Gourdon, M., Vamling, L., Andersson, U., & Olausson, L. (2010a). Crystallization in a pilot evaporator: Aqueous solutions of Na_2CO_3 and Na_2SO_4. *Industrial and Engineering Chemistry Research, 49*(5), 2401-2409.

Gourdon, M., Vamling, L., Andersson, U., & Olausson, L. (2010b). Sodium salt scaling in black liquor evaporators - Pilot plant results and industrial significance. *Journal of Pulp and Paper Science, 36*(3-4), 98-106.

Gourdon, M., Vamling, L., Strömblad, D., & Olausson, L. (2008). Scale formation and growth when evaporating black liquor with high carbonate to sulphate ratio. *Nordic Pulp and Paper Research Journal, 23*(2), 231-239.

Grace, T. M. (1975). *A survey of evaporator scaling in the alkaline pulp industry*. Retrieved from Georgia Institute of Technology: http://hdl.handle.net/1853/523

Grace, T. M. (1976). Solubility limits in black liquors. *AIChE Symposium Series, 72*(157), 73-82.

Green, R., & Hough, G. (1992). *Chemical recovery in the alkaline pulping processes, Third edition*. Atlanta, USA: TAPPI Press.

Gullichsen, J., & Fogelholm, C.-J. (1999). *Chemical pulping*. Helsinki, Finland: Fapet Oy.

IEA. (2008). *Worldwide Trends in Energy Use and Efficiency: Key Insights from IEA Indicators Analysis*. Paris, France: International Energy Agency.

Ishiyama, E. M., Paterson, W. R., & Ian Wilson, D. (2011). Optimum cleaning cycles for heat transfer equipment undergoing fouling and ageing. *Chemical Engineering Science, 66*(4), 604-612.

Kaila, J., Jaakkola, H., & Veitola, J. (2004). *Practical Experiences From Very High Dry Solids Concentrator.* Paper presented at the International Chemical Recovery Conference.

Karlsson, E., Gourdon, M., Olausson, L., & Vamling, L. (2013). Heat transfer for falling film evaporation of black liquor up to very high Prandtl numbers. *International Journal of Heat and Mass Transfer, 65*, 907-918.

Leite, B. S., Andreuccetti, M. T., Leite, S. A. F., & D'Angelo, J. V. H. (2014). Study of sodium salts solubility in eucalyptus black liquor to understand and prevent scale formation in evaporators. *Chemical Engineering Transactions, 39*, 451-456.

Masse, M. A., Kiran, E., & Fricke, A. L. (1986). Freezing and glass transition phenomena in polymer-diluent mixtures. *Polymer, 27*(4), 619-622.

Mersmann, A. (2001). *Crystallization technology handbook*. New York, USA: Dekker, Inc.

Mullin, J. W. (2001). *Crystallization*. Oxford, England: Butterworth-Heinemann.

Nikkanen, S. (1993). Liquor heat treatment and high-dry-solids firing. *Bioresource Technology, 46*(1), 173-176.

Novak, L. (1979). *Sodium salt scaling in connection with evaporation of black liquors and pure model solutions.* (PhD Thesis), Chalmers University of Technology, Göteborg, Sweden.

Numrich, R., & Müller, J. (2010). Filmwise Condensation of Pure Vapors. In VDI-GVC (Ed.), *VDI Heat Atlas*. Berlin: Springer.

Olausson, L., Andersson, U., Gourdon, M., & Vamling, L. (2011). Method and apparatus for controlling incrustations in multi stage evaporation train for black liquor, WO/2011/102761.

Olsson, M. R. (2009). *Simulations of Evaporation Plants in Kraft Pulp Mills: Including Lignin Extraction and Use of Excess Heat.* (PhD Thesis), Chalmers University of Technology, Göteborg, Sweden.

Picot, J. B., Mortha, G., Rueff, M., & Nortier, P. (2012). A thermodynamically consistent model for burkeite solubility. *Chemical Engineering Science, 68*(1), 383-391.

Rosier, M. A. (1997). Model to predict the predpitation of burkeite in the multiple-effect evaporator and techniques for controlling scaling. *TAPPI Journal, 80*(4), 203-209.

Sandén, B., & Pettersson, K. (2014). *System Perspektives on Biorefineries*. Göteborg, Sweden: Chalmers University of Technology.

Sandquist, K. (1983). *Rheological properties of black liquor and fouling of heating surfaces at high dry solids content.* (PhD Thesis), Chalmers Univeristy of Technology, Göteborg, Sweden.

Schmidl, W., & Frederick, W. J. (1998). *Current trends in evaporator fouling.* Paper presented at the International Chemical Recovery Conference, Tampa, USA.

Schnabel, G., & Schlünder, E. U. (1980). Wärmeübergang von senkrechten Wänden an nichtsiedende und siedende Rieselfilme. *Verfahrenstechnik, 14*(2), 79-83.

Shi, B. (2002). *Crystallization of solutes that lead to scale formation in black liquor evaporation.* (PhD Thesis), Georgia Institute of Technology, Atlanta, USA.

Shi, B., Frederick, W. J., & Rousseau, R. W. (2003). Nucleation, growth, and composition of crystals obtained from solutions of Na_2CO_3 and Na_2SO_4. *Industrial & Engineering Chemistry Research, 42*(25), 6343-6347.

Shi, B., & Rousseau, R. W. (2001). Crystal properties and nucleation kinetics from aqueous solutions of Na_2CO_3 and Na_2SO_4. *Industrial & Engineering Chemistry Research, 40*(6), 1541-1547.

Silva, C. L. Q., Penna, W., Araújo, A. C. B., Brito, R. P., Vasconcelos, L. G. S., & Alves, J. J. N. (2009). Model fine tuning for prediction of hydrocyclone performance - An industrial case study. *International Journal of Mineral Processing, 92*(1-2), 34-41.

Smith, J. B. (2000). *Sodium salt scaling in falling film black liquor evaporators.* (PhD Thesis), Georgia Institute of Technology, Atlanta, USA.

Svarovsky, L., & Thew, M. T. (1992). *Hydrocyclones: Analysis and Applications*. Letchworth, England: Springer Netherlands.

Söderhjelm, L., Virkola, N.-E., & Fagerström, P. (1985). *Evaluation of Black Liquor Fouling Tendency by a Laboratory Method*. Paper presented at the International Chemical Recovery Conference, New Orleans, USA.

Wadsborn, R., & Rådeström, R. (2009). Modeling of the solubility of different inorganic sodium salts in black liquor under varying conditions. *TAPPI Journal, 8*(3), 9-13.

Vakkilainen, E., Holm, R. (2000). *Firing Very High Solids Black Liquor in Recovery Boilers*. Paper presented at the TAPPI Engineering Conference, Atlanta, USA.

Valmet (Producer). (2015). Evaporator and Recovery Boiler Energy Efficiency. *Technical Paper Series*. Retrieved from http://www.valmet.com/globalassets/info-center/downloads/white-papers/other-services/wpo_evaprecoveryboil.pdf

Welty, J. R., Wicks, C. E., Rorrer, G., & Wilson, R. E. (2009). *Fundamentals of momentum, heat, and mass transfer*. New York: John Wiley & Sons Ltd.

Verrill, C. L., & DeMartini, N. A. (2006). *Evaporator boilout guidelines.* Paper presented at the TAPPI Engineering, Pulping and Environmental Conference, Atlanta, USA.

Verrill, C. L., & Frederick, W. J. (2006). *Evaporator fouling 101 - Sodium salt crystallization and soluble-scale fouling.* Paper presented at the TAPPI Engineering, Pulping, Environmental Conference, Philadelphia, USA.

Verrill, C. L., & Giehl, F. T. (2004). *Manipulation of Crystallization to Resolve Severe Concentrator Scaling* Paper presented at the International Chemical Recovery Conference, Charleston, USA.

Vinograd, J. R., & McBain, J. W. (1941). Diffusion of electrolytes and of the ions in their mixtures. *Journal of the American Chemical Society, 63*(7), 2008-2015.

Zeebe, R. E. (2011). On the molecular diffusion coefficients of dissolved CO_2, HCO_3 and CO_3 and their dependence on isotopic mass. *Geochimica et Cosmochimica Acta, 75*(9), 2483-2498.

Zhao, X., & Chen, X. D. (2011). *A Critical Review of Basic Crystallography to Salt Crystallization Fouling in Heat Exchangers.* Paper presented at the Heat Exchanger Fouling and Cleaning Conference, Crete Island, Greece.

Appendix A – Solubility calculation

The solubility is calculated from the data from the solubility measurements described in Section 4.5 according to the following procedure.

The original samples consist of water, *W*, and dry solids, where the latter can be divided into a natural content of sodium salts, S_0, and a residual, *R*:

$$DS_{in} = \frac{R+S_0}{R+S_0+W}.$$

In the filtrate, the dry solids also contain the amount of salt required to reach saturation, *S*:

$$DS_{out} = \frac{R+S_0+S}{R+S_0+S+W}.$$

Combining these two gives the following expression for the amount of salt required to reach saturated conditions:

$$S = \frac{1}{DS_{out}-1}(R+S_0)\left(1-\frac{DS_{out}}{DS_{in}}\right) \qquad \text{(kg)},$$

or per kg of dry solids in the original sample:

$$s = \frac{1}{DS_{out}-1}\left(1-\frac{DS_{out}}{DS_{in}}\right) \qquad (\text{kg/kg}_{\text{DS}}).$$

The natural content of salt has to be added in order to calculate the solubility limit, and was analysed for the black liquor used in this study. The relation between salt and the dry solids in the initial black liquor is given by:

$$\frac{S_0}{R+S_0} = 0.154.$$

The solubility limit, $c*$, was calculated as:

$$c^* = \rho\frac{S+S_0}{R+W+S+S_0} = \rho\frac{(S+S_0)/(R+S_0)}{(R+W+S+S_0)/(R+S_0)} = \rho\frac{s+0.154}{1+\left(\frac{1}{DS_{in}}-1\right)+s} \qquad (\text{kg/m}^3).$$

Appendix B – Cleaning model

Implementation of the cleaning model described in Section 5.2.