CHALMERS

Experimental investigation and modelling of sodium scale dissolution with black liquor

A pilot plant investigation

Master's Thesis within the Innovative and Sustainable Chemical Engineering programme

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MASTER'S THESIS

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Cover:
Development of a black liquor falling film on a sodium scale layer.

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ABSTRACT

In this thesis the dissolution of sodium scales with black liquor has been investigated. The experimental part was carried out at a falling film pilot plant evaporator at the division of Heat and Power Technology at Chalmers University of Technology. In order to study the dissolution, a scaling layer was build up by evaporation of a saline solution which was then washed off by black liquor at different temperatures and flow rates. During washing the outgoing dry solid content of the wash liquid was measured along with the scaling layer thickness.

The dissolution rate constant was found to be lower than in previous research carried out by dissolution with water at corresponding temperature and flow rate. The dissolution was dependant on the concentration difference between the saturation concentration and the concentration of the bulk liquid, the flow rate and the temperature of the washing liquid. The dissolution seems to be decreasing with increasing viscosity, but since temperature affects the viscosity, the solubility and the dissolution rate constant the effect of only the viscosity cannot be confirmed.

In contrast to previous work the results suggests that the amount of wash liquid needed to dissolve a given amount of scales decreased with increasing temperature and flow which suggest that there might be beneficial to wash at a high wetting degree and at a high temperature.

Key words:

Black liquor, black liquor solubility, sodium scaling, evaporator cleaning, dissolution rate, falling film

Experimentell undersökning och modellering av natriuminkrusters upplösning i svartlut
Ett pilotskale försök
Examensarbete inom masterprogrammet *Innovative and Sustainable Chemical Engineering*

MARTIN PETTERSSON
KARIN ÖHRMAN
Institutionen för Energi och Miljö
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Chalmers tekniska högskola

SAMMANFATTNING

I detta examensarbete har natriuminkrusters upplösningshastighet i svartlut studerats genom försök gjorda i en fallfilms indunstare vid avdelningen för Värmeteknik och Maskinlära vid Chalmers Tekniska Högskola. Genom att indunsta en saltlösning byggdes ett lager av inkruster upp längs indunstarröret som sedan löstes upp av svartlut vid olika temperaturer och flöden. Under tvätten mättes inkrustertjockleken och torrhalten på den från indunstaren utgående tvättvätskan.

Upplösningshastigheten var lägre, vid motsvarande temperatur och flöde, än tidigare studier rapporterat för upplösning med vatten. Temperatur och flöde påverkade både upplösningshastigheten och tvättförloppet. Upplösningshastigheten verkar minska med ökad viskositet, men eftersom temperaturen påverkar viskositeten, lösligheten och upplösningshastighetskonstanten så kan inte påverkan av bara viskostet säkerhetsställas.

I kontrast till tidigare studier verkar det som att mängden tvättvätska nödvändig för att lösa upp en given mängd salt minskar med ökad temperatur och flöde, vilket tyder på att det kan vara fördelaktigt att lösa upp inkruster vid hög temperatur och högt flöde.

Nyckelord:

Svartlut, natriumsalters löslighet i svartlut, natriuminkruster, tvättning av indunstare, upplösningshastighet, fallfilm

Contents

Preface

In our thesis the dissolution of sodium salt scales with black liquor has been experimentally investigated. It was performed as part of the Master programme *Innovative and Sustainable Chemical Engineering* at the division of Heat and Power Technology at Chalmers University of Technology.

We would like to thank our examiner Dr. Mathias Gourdon and supervisor doctoral student Erik Karlsson for all support and advices. During our thesis work we enjoyed the practical experience gained running the pilot plant evaporator.

Finally we would like to thank everyone at the division of Heat and Power Technology for all the pleasurable coffee breaks.

Göteborg April 2013

Martin Pettersson

Karin Öhrman

Notations

Greek letters

δ_{bulk}	Thickness of the bulk	[m]
δ_x	Thickness of the laminar boundary layer	[m]
Γ	Wetting degree	[kg / ms]
ΔA	Surface area of a discretized cell	[m^2]
Δt	Time step	[s]
ΔT	Temperature difference	[°C]
μ	Dynamic viscosity	[Pas]
ρ	Density	[kg / m^3]

Roman letters

c_b	Bulk concentration	[kg$_{\mathrm{salt}}$ / kg$_{\mathrm{solution}}$]
c_{in}	Inlet concentration	[kg$_{\mathrm{salt}}$ / kg$_{\mathrm{solution}}$]
c_{out}	Outlet concentration	[kg$_{\mathrm{salt}}$ / kg$_{\mathrm{solution}}$]
C^*	Solubility limit	[kg$_{\mathrm{salt}}$ / kg$_{\mathrm{solution}}$]
d	Scale thickness	[m]
D_{tube}	Tube diameter	[m]
DS	Dry solid content	[kg$_{\mathrm{dry\ solids}}$ / kg$_{\mathrm{solution}}$]
DS_{end}	Final dry solid content	[kg$_{\mathrm{dry\ solids}}$ / kg$_{\mathrm{solution}}$]
DS_{in}	Initial dry solid content	[kg$_{\mathrm{dry\ solids}}$ / kg$_{\mathrm{solution}}$]
DS_{out}	Final dry solid content	[kg$_{\mathrm{dry\ solids}}$ / kg$_{\mathrm{solution}}$]
k_c	Dissolution rate constant	[kg$_{\mathrm{salt}}$ / m^{2}s]
L	Tube length	[m]
$\dot{m}_{BL,in}$	Mass flow rate of black liquor	[kg / s]
$\dot{m}_{BL,N}$	Mass flow rate of black liquor from N:th step	[kg / s]
$m_{m,0}$	Initial mass of black liquor to sample m	[kg]
m_m	Mass of black liquor in sample m	[kg]
$\dot{m}_{\mathrm{water}}$	Mass flow rate of water	[kg / s]
r	Dissolution rate	[kg$_{\mathrm{salt}}$ / m^{2}s]
R	Residual in black liquor	[kg / kg]
R_0	Residual in black liquor	[kg]
R_{mn}	Residual in sample m	[kg]
Re	Reynolds number	[-]
s	Amount of salt added to reach saturation	[kg$_{\mathrm{salt}}$ / kg$_{\mathrm{R+s0}}$]
s_0	Initial salt in black liquor	[kg$_{\mathrm{salt}}$ / kg$_{\mathrm{solution}}$]
$s_{0,m}$	Initial salt in sample m	[kg]
s_m	Amount of salt in sample m	[kg$_{\mathrm{salt}}$]
s_n	Amount of salt dissolved in the n:th step	[kg]
T_i	Inlet temperature of wash liquid	[°C]
T_{salt}	Operating temperature for saline solution	[°C]
T_{vap}	Operating temperature for vapour	[°C]
W	Water in black liquor	[kg$_{\mathrm{water}}$ / kg$_{\mathrm{R+s0}}$]
W_0	Water in black liquor	[kg]
x	Mole fraction Na_2CO_3 / ($\mathrm{Na_2SO_4} + Na_2CO_3$)	[mol / mol]

1 Introduction

The forest has always had a great importance to Sweden's economy. In 2011 the export of pulp, paper and sawn timber was worth 128 billion SEK, which is 11% of Swedens export (Skogsindustrierna 2012). The average Kraft pulp mill has a high energy demand, but is largely self sufficient and a net exporter of electricity (Brännvall et. al. 2008). Black liquor, which is a mixture of spent cooking chemicals and dissolved organic material, is incinerated in a recovery boiler to produce energy and recover cooking chemical. In order to achieve high efficiency, the liquor must be evaporated to higher solid content, which is performed in an evaporation plant. One difficulty that arises is at higher solid content the inorganic components may precipitate on the heat transfer area, which leads to a lower heat transfer and a decrease in efficiency (Theliander 2008a).

The contamination process of heat transfer areas is referred to as fouling; another often used term is scaling which refers to a hard crystal-like form of fouling. The type of fouling formed is dependent on the concentration of the black liquor and operating conditions (Theliander 2008a). The most frequently encountered types of fouling when evaporating black liquor are calcium and sodium scales (Shi 2002).

There are methods for calculating how often to clean the evaporators, for example the method proposed by Ishiyama et al (2011) but cleaning measures are often carried out on a periodical basis even without significant loss of efficiency (Schmidl 1998), resulting in unnecessary cleaning and loss of up time for the process. Soluble scales are removed by boil out with fresh water, condensate or weak black liquor. Insoluble scales are removed by hydroblasting and acid cleaning (Clay 2008). Not much is known about the factors affecting the cleaning methods used by industry.

In previous work performed at the division of Heat and power technology at Chalmers by Broberg and Åkesjö (2012) studied the dissolution of sodium scaling with water.

1.1 Objective

The objective of this master thesis was to investigate the build-up of a reproducible scaling layer and study and model the dissolution of soluble scales with black liquor. The validation of the model was done through experimental investigations in a pilot plant evaporator located at the division of Heat and Power technology at Chalmers. The factors of interest were temperature and flow rate at one concentration of the black liquor and the results were compared with previous work on dissolution with water.

1.2 Method

In this thesis an experimental method was used to investigate the dissolution of sodium scales with black liquor in a pilot plant evaporator. The data collected was evaluated using a model in MATLAB. Before the experimental part was carried out a literature study of the research area was performed. The modelled values were compared with previous work from the dissolution of sodium scales with water.

2 Background

2.1 Kraft pulping process

The alkaline Kraft process is the most common pulping process in Sweden (Skogsindustrierna 2012). The aim of the Kraft process is to liberate fibres from the wood matrix. This is done by removal of the lignin, which is the glue that holds the fibres together. In the Kraft process wood chips are treated at elevated temperature in cooking liquor. The cooking liquor, white liquor, is an alkaline solution containing sodium hydroxide, NaOH, and sodium sulphide, Na_2S. The wood chips are treated until a certain delignification is achieved. After the cooking stage the fibres are separated from the spent cooking liquor, referred to as weak black liquor. The liberated fibres are further refined to pulp and the weak black liquor is sent to the chemical recovery cycle. In the recovery cycle black liquor is evaporated then sprayed and incinerated in the recovery boiler. Smelt produced by the incineration is dissolved with wash water from the lime mud wash. Non-process elements are removed before the stream is further treated in the causticizing plant to strong white liquor (Theliander 2008a). A schematic diagram of the Kraft pulp process can be seen in Figure 2-1.

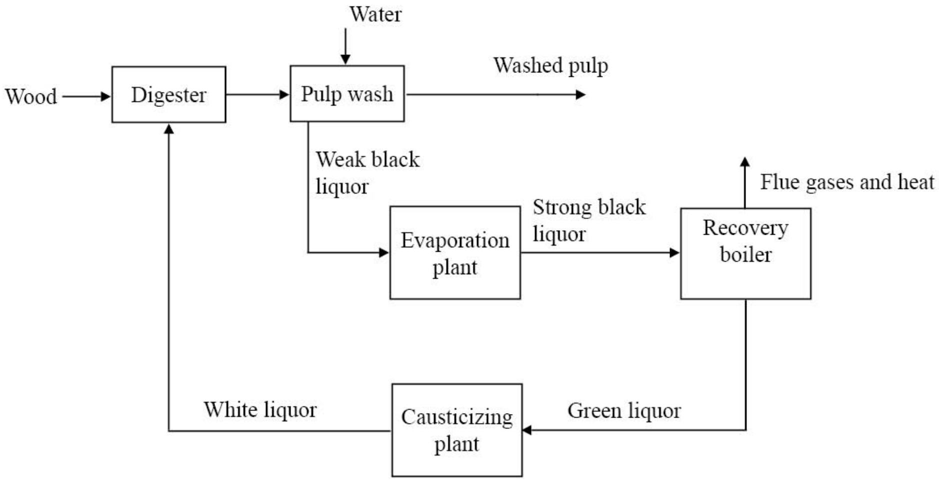

Figure 2-1 Schematic diagram of the Kraft plant.

2.1.1 Black liquor evaporation

Before recovering energy and the cooking chemicals in the recovery boiler the weak black liquor has to be evaporated. This is usually done by feeding black liquor to a multistage evaporation plant of which the first effect is heated with live steam and the following are heated with the vapour from the previous step. The cascade use of vapour increase the energy efficiency of the evaporation and a modern pulp mill has up to seven effects (Ek 2009). The dry content is hereby increased from 15-20% to 70-80 % (Brännvall 2008).

The evaporator equipment that has become the most common and that is currently the standard type used in black liquor evaporation is the falling-film evaporator. In this apparatus the liquor is feed on top creating a film, due to gravitational forces, on the heat transfer area (Brännvall 2008). Falling film evaporator can have the black liquor film either on the outside or the inside of the evaporator tubes.

2.1.2 Black liquor

Black liquor is a viscous alkaline solution consisting of both organic and inorganic components. Primarily the organic components are degraded lignin, various carbohydrates, and extractives. Inorganic compounds consist of various ions such as Na^+, K^+, Ca^{2+}, OH^-, SO_4^{2-}, CO_3^{2-}, $S_2O_3^{2-}$, HS^-, and Cl^-. The approximate composition of the major elemental constituents in black liquor is shown in Table 2-1.

Table 2-1. Approximate composition of black liquor (Theliander 2008a).

Element	Amount (weight %)
Carbon	34-39
Oxygen	33-38
Sodium	17-25
Sulphur	3-7

The properties of black liquor depend of raw material, process conditions, process equipment, and after treatments (Vakkilainen 2000). The chemical composition of the black liquor will influence the physical properties. Density and viscosity is among the most important properties for black liquor evaporation. Black liquor viscosity increases with increasing dry solid content and decreases with increasing temperature. The density is strongly influence by the concentration, and at low concentrations it is close to that of water at the same temperature (Gourdon 2009).

2.2 Falling film theory

As with all fluid dynamics, the Reynolds number can be used to categorise the flow behaviour of black liquor in a falling film evaporator. There are two definitions commonly used for the Reynolds number, in this thesis Equation 2-1 will be used. It is calculated from the wetting degree, which is displayed in Equation 2-2. The wetting degree is based on the mass flow rate of black liquor and the outer perimeter of the tube, it is used to facilitate the comparison to other falling film evaporators.

$$Re = \frac{4\Gamma}{\mu} \tag{2-1}$$

$$\Gamma = \frac{\dot{m}}{\pi D_{tube}} \tag{2-2}$$

The transition to turbulent flow occurs at the approximate Reynolds number of 4000 and completely laminar flow takes place below approximate Reynolds number of 20. Between those values there is a region of flow with pronounced rippling with surface waves of partially laminar and partially turbulent flow (Johansson 2008).

2.3 Crystallization

The solubility depends on the type of solute and temperature. The most common behaviour is that increased temperature leads to an increased solubility. A system with inverse temperature dependency will have lower solubility as the temperature increases.

The driving force of crystallization has experimentally been shown to be the supersaturation (Seader 2006). The degree of supersaturation is the difference between the solubility limit and the concentration. By supersaturating a solution it reaches the solubility limit and transits into the metastable zone shown in Figure 2-2. In the metastable zone crystals can grow from existing crystals and impurities but not form spontaneously. When the solution is concentrated further, it transits to the labile zone where spontaneous nucleation of small crystal occurs (Seader 2006).

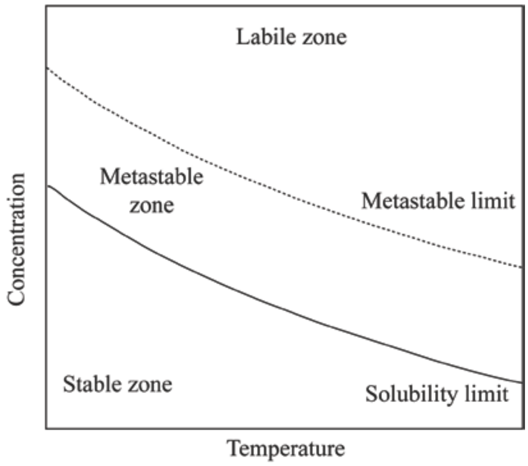

Figure 2-2 Solubility diagram for an inverse temperature dependent system.

Nucleation can either be primary or secondary, depending on if the supersaturated solution contains any crystal surfaces or impurities. Primarily nucleation requires a high degree of supersaturation and is the primarily mechanism in precipitation (Seader 2006). At the point of primarily nucleation a large number of particles form rapidly and the concentration of the solute typically drops below the metastable limit (Frederick 2004a).

Once crystals are attached to a heat-transfer area, scales will continue to grow as long as the solution is supersaturated (Frederick 2004a).

2.4 Evaporator fouling

During concentration of black liquor in an evaporation plant the inorganic salts will exceed their solubility limit and start to precipitate. Once scales start to form it poses a serious problem due to the rapid decrease in overall heat transfer coefficient with increasing thickness of scaling (Brännvall 2008).

2.4.1 Black liquor fouling

Black liquor evaporators may be subjected to the following types of fouling, calcium carbonate scaling, sodium carbonate or sulphate scaling, soap or fibre scaling, and aluminium or silicate scaling (Vakkilainen 2000). If fouling is formed the kind of fouling is dependent on concentration of the black liquor and operating conditions of the apparatus. Precipitation of organic material like soap may be avoided by efficient removal of tall oil prior to evaporation and operating at a reasonably high pH to avoid precipitation of lignin (Brännvall 2008).

The most frequently encountered types of scaling when evaporating black liquor are calcium and sodium scales (Shi 2002). Calcium carbonate scaling occurs by the release of calcium ions when the organic compounds in the black liquor decompose at temperatures above 120°C (Brännvall 2008). Since calcium scaling is temperature activated it can be avoided by heating the liquor prior to evaporation. After thermal deactivation calcium will exist as calcium carbonate and will not participate as scaling (Shi 2002).

2.4.1 Sodium salt scaling

Sodium carbonate and sodium sulphate is common in black liquor. Therefore they have been shown to be the major contributor to scaling on heat transfer areas when evaporating black liquor (Shi 2001).

When concentrating black liquor over the solubility limit for sodium carbonate and sodium sulphate there is the possibility of formation for at least five different crystal species (Frederick 2004b). Only two of them, burkeite and dicarbonate, are important with respect to fouling (Frederick 2004a). The approximate compositions of burkeite and dicarbonate are $2Na_2SO_4 \cdot Na_2CO_3$ and $Na_2SO_4 \cdot 2Na_2CO_3$ (Gourdon 2009a).

The sodium salts may crystallize on or adhere to the heat transfer surface or crystallize in the black liquor (Gourdon 2009a).

The formation of sodium salts in black liquor evaporation mainly takes place by two mechanisms, agglomeration of fine particles at the heat transfer surface after primary nucleation and crystal growth from existing crystals in a supersaturated solution (Frederick 2004a). Burkeite and sodium carbonate have reversed solubility with increasing temperature resulting in an increased probability of precipitation at the heat transfer area (Shi 2002). In falling film evaporators scaling has been shown to grow from the bottom of the evaporator (Gourdon 2009a).

In Figure 2-3 adapted from Gourdon (2009a), the different crystal regions as a function of liquid compositions are illustrated. The solvent free mole fraction is expressed as in Equation 2-3.

$$x = \frac{[Na_2CO_3]}{[Na_2CO_3]+[Na_2SO_4]} \qquad (2\text{-}3)$$

The region where the most severe scaling occurs is considered to be in the dicarbonate region or where both burkeite and dicarbonate crystallise (Frederick 2004a). Both burkeite and dicarbonate crystallise in $0.68 < x < 0.82$ and many evaporators are operated within this region (Frederick 2004b).

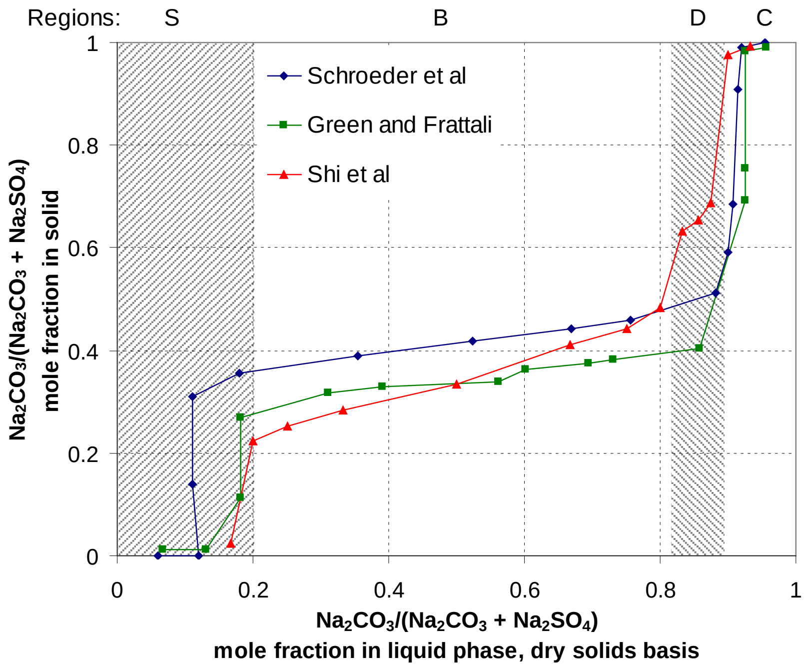

Figure 2-3 Solid compositions regions for the formed crystals as a function of solute compositions for the aqueous solutions. The four regimes are sulphate (S), burkeite (B), dicarbonate (D) and carbonate (C). Equilibrium data was obtained by Gourdon (2009) from Schroeder et al. (1936), Green et al. (1936) and Shi et al. (2003). Figure adapted from Gourdon (2009a).

Dicarbonate fouling on heat transfer areas can be minimized with a high number of suspended crystals (Clay 2008). To minimize fouling operating conditions should be kept over the crystallisation point and changes in operation conditions should be slow (Clay 2008). Gourdon (2009a) showed that a higher tube wall temperature gave rise to a higher fouling rate. At a lower temperature difference the surface crystal fraction growth is higher for a given molar ratio (Gourdon 2009a).

2.5 Evaporator cleaning in industry

For the pulp and paper industry not much has been found on how to efficiently remove fouling instead a larger focus has been on how to minimise fouling. W.R. Grace & Co. patented in 1970 (Engman 1970) a method for inhibiting and removing scaling from black liquor evaporators by addition of a water soluble polymer.

The most common cleaning measures are, for soluble scales, boil out and, for insoluble scales, hydroblasting and acid cleaning (Clay 2008). Boil out can be performed with fresh water, condensate or weak liquor. During boil out the evaporator do not work at full capacity and often effects are bypassed. Boil out liquor is often transferred back to the weak liquor system although it is crucial to return the stream slowly in order to avoid massive nucleation and rapid fouling events (Clay 2008).

Since the 1980’s boil out and acid cleaning frequency has gone down but hydroblasting frequency has gone up (Schmidl 1998).

There are methods for calculation how often an evaporator should be washed. Ishiyama et al (Ishiyama 2011) have proposed a model introducing the economic effect of two different cleaning methodologies, solvent cleaning and mechanical cleaning. Cleaning measures are, however, often performed on a regular basis, even without significant loss of performance, as a measure of prevention (Schmidl 1998).

In a study by Gourdon (2011) he proposes that the cleaning process is mainly driven by dissolution and that the cleaning efficiency is determined by the concentration of wash liquid over time.

2.6 Related work

In a previous master thesis at the division of Heat and Power Technology, Broberg and Åkesjö (2012) investigated the dissolution rate of sodium scaling using pure water. Their main conclusion was that the most accurate description of the dissolution rate followed the first order model, with respect to the concentration difference between the solubility limit and the bulk concentration, further described in Section 2.6.1. They found that the dissolution rate constant, k_c, was dependant on temperature, but not on the wetting degree and suggested that there might be a linear relationship between the rate constant and the temperature.

2.6.1 First order dissolution model

The driving force in the first order dissolution model is the difference in concentration between the solid-liquid interface, where the concentration is the saturation limit C^*, and the concentration in the bulk C_b. The dissolution rate for the first order dissolution model is displayed in Equation 2-4.

$$r = k_c(c^* - c_b) \tag{2-4}$$

Figure 2-4 illustrates the concentration gradient in the film. The dissolved salts are transported by diffusion through the boundary layer and into the bulk liquid which is considered to be perfectly mixed and much thicker then the boundary layer. In order to assess the difference, the initial concentration C_0 has to be taken into consideration.

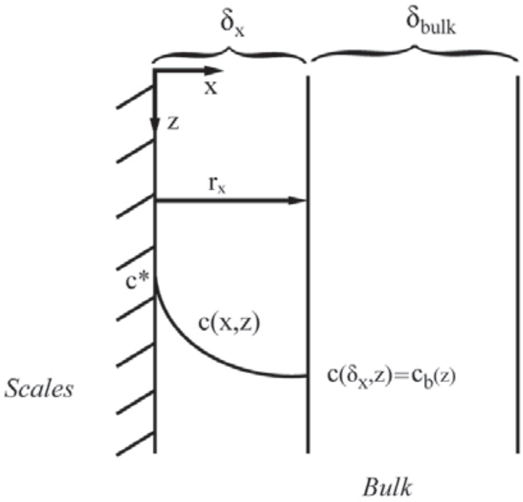

Figure 2-4 Illustration of concentration gradient resulting in the driving force for the dissolution.

3 Experimental method and work

In order to experimentally evaluate the dissolution of sodium scales with black liquor a pilot plant evaporator was used. To find the solubility of sodium salts in black liquor a series of solubility experiments were performed as describes in Section 3.1. The experiments at the pilot plant consisted of two parts: one where scaling was build up, described in Section 3.3, and one where the formed scale was cleaned with black liquor, described in Section 3.4.

3.1 Solubility measurements

The driving force for first order dissolution model is the difference between saturation and the bulk concentrations which displays the need to measure the saturation limit for the salt at the desired black liquor dry solid content. The equipment used for the solubility measurements is displayed below in Figure 3-1. The measurement was carried out by adding Na_2CO_3 and Na_2SO_4, in molar ration 17:3, to the black liquor sample and thereby supersaturating the sample at a temperature with a higher solubility than the temperature of interest. The sample was feed to the evacuated vessel (1) and allowed to equilibrate in an oven or a water bath at the temperature of interest. After at least eight hours, the two valves (2 & 4) were opened and the sample was filtered, by applying pressurized air to the vessel, through a sintered steel filter (3) with a pore diameter of 2 μm where the precipitated crystals are separated from the filtrate which is a saturated solution. The filtrate was collected in a container (5) from which the difference in solubility could be determined by measurement of dry solid content. Dry solid content was measured according to TAPPI standard (TAPPI 2009).

Figure 3-1 Solubility measurement equipment. 1 – Sample vessel 2,4 – Valves 3 – Filter housing 5 –Filtrate container. Picture adapted from Gourdon (2009a).

From the initial dry solid content of the black liquor and the dry solid content of the saturated black liquor the difference between the initial and saturation concentrations i.e. the dissolution potential can be calculated, see Appendix A.

3.2 Pilot plant evaporator

The pilot plant evaporator was built in cooperation between Chalmers and Metso Power AB. It is of the falling film type where the black liquor is falling on the outside of a single tube, heated on the inside by condensing steam. The evaporator was built to be large enough to give results which would be applicable to the industry, but small enough to be run on only one barrel of black liquor (Gourdon 2009a).

The 4.5 meter long tube, mounted vertically, has an outer diameter of 60 mm and a heat transfer area of 0.848 m^2. At the top of the tube a specially designed flow distributor is mounted to ensure a uniform falling film. For research purposes the evaporator is designed to have the possibility of different operation modes.

In order to visually examine the flow and inspect the onset of scaling, sight glasses are mounted at three different heights along the tube as displayed in Figure 3-2.

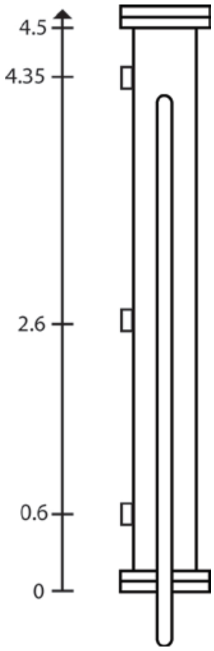

Figure 3-2 Schematic of the evaporator displaying the height of the sight glasses.

During evaporation the concentration will increase since water is removed. There is no direct method to monitor how the concentration changes but it is measured indirectly by the density of the circulating fluid which is measured by a density meter. A focused beam reflectance measurement, a Lasentec FBRM D600L, is mounted in the feed circulation pipe. It provides a possibility to measure the number of particles and the particle distribution in the solution. An overview of the pilot plant is shown in Figure 3-3.

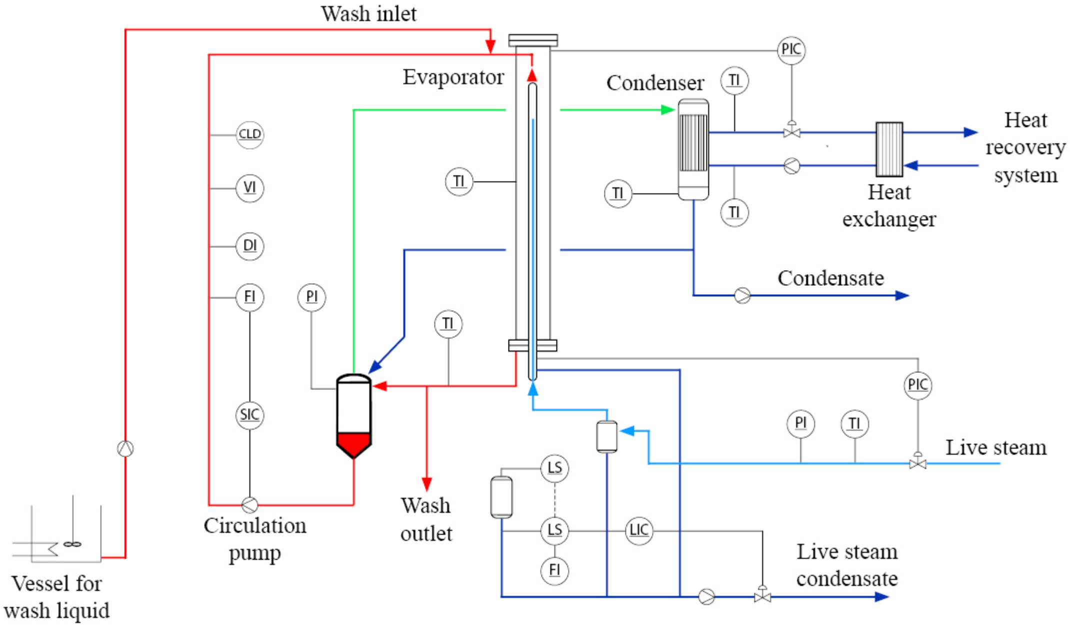

Figure 3-3 Schematic diagram for the pilot plant evaporator.

Six pairs of thermocouples are mounted along the tube in order to monitor the temperature difference over the tube wall. Since the temperature difference will decrease when a scaling layer is formed, the thermocouples can be used to monitor whether the scaling layer is growing. Although the thermocouples can be used as an indication, the measurements are not precise enough for providing data for thickness estimation.

3.3 Scaling layer build up

In order to investigate the dissolution rates, a scaling layer had to be created. Sodium salt scaling is one of the most prominent in black liquor fouling and therefore the one investigated. A sodium salt scale should be easier to form since the main mechanism is crystallisation. Black liquor fouling is hard to control and it would not be certain that the fouling at the heat transfer area would have formed in a similar manner in each experiment. Therefore the formation of the scaling layer was done by evaporation of a sodium carbonate and sodium sulphate solution. Water was removed from the circulating solution by heating the evaporator with steam, which condenses on the inside of the evaporator tube. When the solution was evaporated the concentration increased and eventually passed the metastable limit. The concentration of the sodium salt solution was monitored using the density. In order to form scales on the tube the number of particles was kept low by adding fresh solution to the system or by recirculating condensate. Another reason for the addition of fresh solution and condensate was to keep the level in the liquid vapour separator above critical level for operation.

The sodium salt solution which was used to produce scaling has a molar composition of 17:3 in carbonate to sulphate ratio which is just above the region where both burkeite and dicarbonate is formed as seen in Figure 2-3. In order to prevent crystallisation in the storage tanks and in the inlet when the solution is feed to the system, the concentrations was kept well below the saturation limit which was 0.3 kg salt/kg solution at 40 °C (Shi 2002), which was the temperature at which the solutions were prepared.

During the experiments the scaling layer occasionally cracked and detached from the tube. When this happened the experiment was restarted by dissolving the formed scales with deionised water. After all scales were dissolved the evaporation was restarted.

Scales were formed during different operating conditions, all operation parameters are listed in Appendix B in chronological order for all experiments.

A clear indication that scales formed was the temperature differences of the thermocouples; if scaling was formed the temperature differences were decreased due to the insulating properties of the scaling layer. The start in decreasing difference began for the thermocouples mounted at the bottom of the tube since scales are known to grow from the bottom up (Gourdon 2009). Another indication was the decrease in overall heat transfer coefficient for the tube. The most important confirmation that scales were forming was by visual inspection of the tube at the sight glasses.

3.4 Washing

When a sufficient scaling layer was achieved the evaporation was stopped. Before the washing part started, the evaporator was cooled to the desired wash temperature.

The black liquor was heated to the desired temperature using an electrical heater. To have uniform conditions during the washing a stabile temperature was required. Before the washing experiment black liquor was circulated in order to heat the feed pipes as well as to achieve a steady flow. Due to evaporation during heating a sample of the wash liquid was taken in order to measure the ingoing dry solid content.

When the equipment and black liquor had the right temperature, the flow of black liquor was fed over the tube in order to dissolve the sodium scales.

Video cameras were mounted at each sight glass level to visually monitor the removal of the scales. The video cameras also documented commentary made during the experiment and supplied information of whether the flow was evenly distributed or if all parts of the tube were washed similarly.

The scaling thickness was measured during the washing at the middle and bottom sight glasses by a rod with a flat metal disc which was inserted through the outer wall of the evaporator to the tube. The difference in distance was read by a vernier calliper and documented during the washing. For the top sight glass the tube was visually inspected for scaling.

Two different methods were used to gather the information needed to evaluate the dry solid content of the wash liquid out of the evaporator. The first method consisted of a coriolis flow and density meter connected to the outlet of the evaporator by a long rubber tube. In this method the meter sampled data every fifth second in order to give continuous measurements. To validate the density measurements and get a correlation between density and dry solid content a few samples of wash liquid was collected. The second method was the same method used by Broberg and Åkesjö (2012) where the wash liquid was collected at the bottom of the evaporator in containers of one litre. The time it took to fill each container was noted. After the washing the containers' weight and density was measured. The dry solid content in a selection of containers was measured in order to verify the estimation of dry solid content made from the density in each container. The inlet flow for the experiments was measured by the time it took to fill the samples and taking an average from these values.

3.4.1 Conditions and limitations

In order to be able to compare the results with Broberg and Åkesjö (2012) washing temperatures were chosen in the same interval, 40-80°C.

Limitations for the wetting degree was set by the wash liquid pump, the lower wetting degree was set due to insufficient wetting of the tube below this limit. The upper limit was set to avoid extensive spatter of black liquor.

4 Model development for scale dissolution

A schematic illustration of the expected dry solid content of the washing liquid against time is shown below in Figure 4-1. The washing is divided into three regimes. The initial phase is not of interest, due to the long contact time during development of the flow as well as dissolution of scales not situated on the tube and mixing. The tail is not considered due to residual scales in the bottom which leading to the wash liquid does not reach the inlet concentration, even though the tube is considered clean. The goal of the model was to find a good fit in the region of interest and to accurately describe the decreasing scale thickness along the tube.

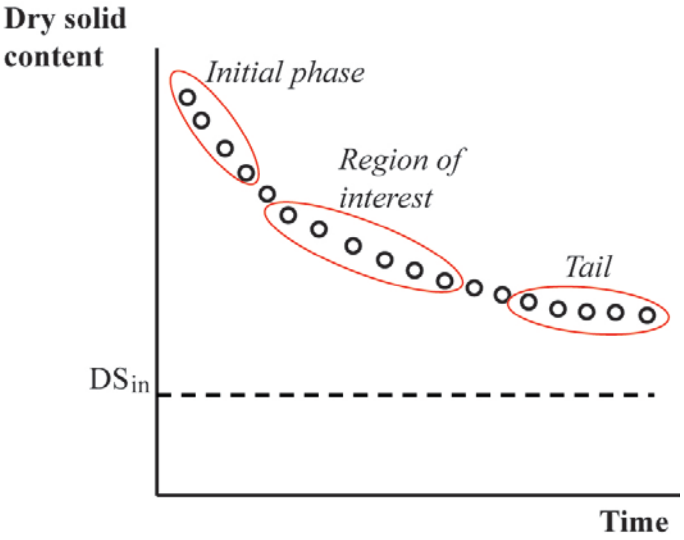

Figure 4-1 Schematic illustartion of washing behavior and regions of interest.

In order to model the dissolution, the evaporator tube is discretized in small time steps and short tube segments where the tube is assumed to have rotational symmetry and for each tube segment the local scaling layer thickness is estimated as described in Section 4.1. For each time step, the amount of salt dissolved from the tube was calculated by the dissolution rate in each tube segment, using Equation 2-4. The amount of scales dissolved was added to the wash liquid which increased the bulk concentration to the next tube segment, and the scaling layer thickness decreased accordingly. The dissolution rate constant k_c was found by making additional simulations with different values for k_c until the best fit between the measured values was found.

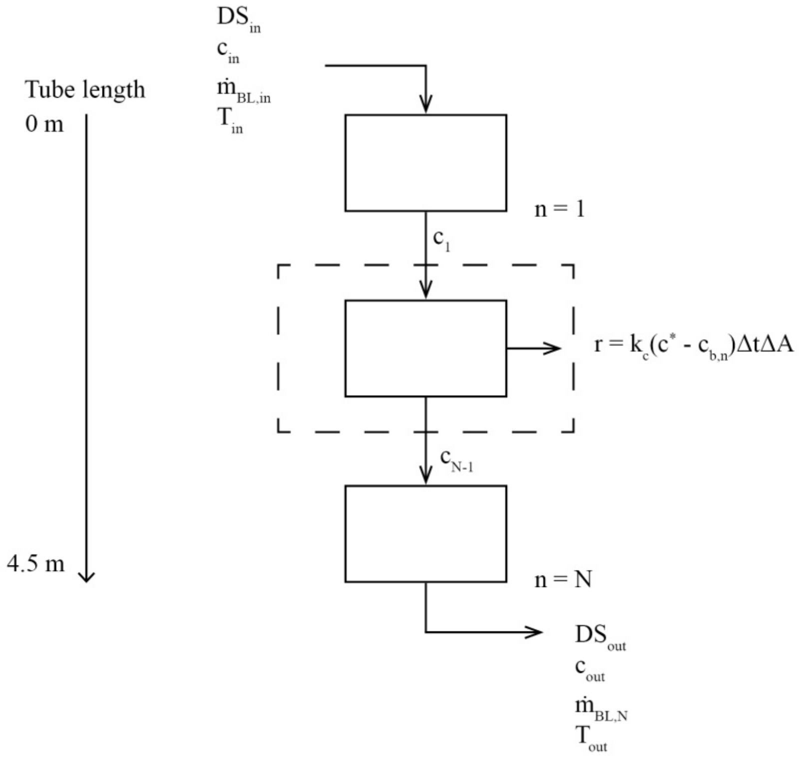

Figure 4-2 Calculating method for the model calculations.

In order to make these calculations, a few assumptions had to be made which are shown below.

- **The scale is dry**

  Therefore the scaling does not contribute with water to the flow during washing.

- **Constant inlet flow**

  The inlet flow is constant over the whole washing sequence and has a uniform distribution over then tube.

- **Constant properties in each cell**

  The dissolution rate and the contact area are constant in each time step and tube segment

- **Smooth scaling layer**

  The roughness of the scaling layer and the increase in contact area is not considered.

In order to compare the calculated and experimental results the dry solid content in each discrete time step has to be calculated. The only component that changes along the tube is the amount of dissolved salt to the wash liquid. With the other components constant over the tube the outlet dry solid content from step n can be calculated by summation of the amount of dissolved salts in the previous steps as shown in Appendix C.

4.1 Scaling distribution

The information on the scale thickness along the tube was unknown except for the two measured points. The thickness of the scaling layer was assumed to decrease exponentially from the middle sight glass to the top. The distribution in-between the middle and the bottom sight glasses as well as the end of the tube and the bottom sight glass was determined by fitting a polynomial to the two measured points to achieve a reasonable scaling distribution. The volume of scales was calculated using the trapezoid method which in turn was compared to the total mass of dissolved salt, as calculated in Appendix D. The quotient of the dissolved salt and the volume corresponded to a density, which if it is close to the tabulated density of 2570 kg/m^3 (Foshag 1935) shows a god fit between the real distribution and the model. The value of the density along with observations and measurement during washing was the basis for choosing the most appropriate distribution.

The different distributions which were evaluated are displayed in Table 4-1. The exponential model which was used is shown in Equation 4-2 and the coefficients where found using the two measured points.

$$d = Ae^{b*L} \tag{4-1}$$

Table 4-1 Description of the different scaling distributions used for modelling of the scaling dissolution.

Distribution model	Description
Linear (Dist I)	Linear relationship between top sight glass and middle sight glass as well as for the distance between middle and bottom sight glass but with different coefficients. Constant from bottom sight glass to the bottom of the column.
Exponential 1 (Dist II)	Exponential between top and middle sight glass. Linear between middle and bottom sight glass. Constant from bottom sight glass to the bottom of the column.
Exponential 2 (Dist III)	Exponential between top sight glass and middle sight glass as well as for the distance between middle and bottom sight glass but with different coefficients. Constant from bottom sight glass to the bottom of the column.
Exponential 3 (Dist IV)	Exponential between top sight glass and middle sight glass as well as for the distance between middle and bottom sight glass but with different coefficients. Linear from bottom sight glass to the bottom of the column with a slope extrapolated from the values for the middle and bottom sight glass.
Exponential Linear (Dist V)	Exponential between top and middle sight glass and linear between middle sight glass and bottom of the column.

5 Experimental results and discussion

The experimental results are divided in three sections; Determination of solubility, Scaling layer build up and Washing. In total 10 scaling layer experiments and 4 washing experiments were performed due to the fact that not all scaling layer experiments were successful. Reasons for this will be discussed in Section 0.

Since not every scaling layer experiment led to a wash experiment the correlation between scaling layer and wash experiments is shown in Table 5-1.

Table 5-1 The correlation between scaling layer experiments and washing experiments.

Scaling layer experiment	Wash experiment
S1	
S2	E1
S3	
S4	E2
S5	
S6	E3
S7	
S8	E4
S9	
S10	

5.1 Determination of solubility

The procedure described in Section 3.1 Solubility measurements was used to determine the solubility of sodium sulphate and sodium carbonate at the desired wash temperatures. In Table 5-2 the amount of salt added to reach saturated conditions as well as the saturation concentration is shown. The calculations are described in Appendix A.

Table 5-2 Solubility limit for black liquor at two different temperatures.

T [°C]	Saturated [kg_{salt}/kg_{DS}]	c^* [$kg_{salt}/kg_{solution}$]
40	1.609	0.289
80	1.465	0.271

The difference in the two points was approximate 7% and in order to investigate if the temperature dependant solubility affects the result of the model, a sensitivity analysis has to be performed. The result is described in Section 7.1.

5.2 Scaling layer build up

In all 10 scaling layer experiments were performed. The different parameters had influence on the scaling and operation of the equipment.

Some of the difficulties experienced when forming scales were; cracking and detachment of the scaling layer, sedimentation of particles resulting in plugging of the circulation pump and non uniform formation of scales at the tube wall. Some of the operating conditions during the scaling layer build up seemed to be less favourable for the formation of scales.

For experiments S1 and S2 the temperature was kept a few degrees higher than the wash temperature for the corresponding wash experiments. This was done in order to avoid the need for cooling of the evaporator to the desired wash temperature. The low temperature gave a slow build up and therefore constructing a thin scaling layer. These experiments indicated that scaling is more prominent at higher temperatures.

In S3 and S4 the strategy was to use the same operation parameters as Broberg and Åkesjö (2012). The build up was faster for these experiments than for the two previous.

S5 had almost the same operation conditions as S3 and S4 but at the end of the experiment the temperature of the saline solution was increased due to that the formation of scales was too slow.

In theory a high temperature difference between the fluid and the heat transfer area will produce more scaling but a lower temperature difference in the nucleation stage of the evaporation will give higher surface crystal growth. Therefore the strategy for S6, S8, S9 and S10 was to begin with a larger temperature difference to initially increase the density faster but change to a lower difference before the metastable limit was reached. After the metastable limit was reached, the temperature difference was increased. This strategy worked well for the formation of scales.

In S7 the temperature difference was high during the whole experiment. For this experiment, the density increased without reaching a peak, mentioned by Gourdon (2009a), which would indicating that the concentration dropped below the metastable limit due to primary nucleation., But the number of particles in the solution was high indicating nucleation of particles. The experiment did not result in a good scaling layer, this could be a result of crystal growth on the existing particles in the fluid.

The temperature difference between the steam and the fluid affects the scaling. A high temperature difference over the metastable limit seemed to give rise to a larger number of particles and a lower degree of scaling initially. A higher difference after passing the metastable limit, however, gave rise to a higher degree of scaling. In experiments S4, S5, S9 and S10 the scaling layer cracked and fell off. In S4 the experiment was not restarted which resulted in that the flow redistributors grew full of scales and the flow was hindered. For S4, S5, and S9 the number of particles was high when the scaling fell off. This was not the case for S10 where the number of particles was low. This indicated that there were more factors influencing the cracking of the scales than the number of particles. One possible explanation could be that the tube wall was contaminated with a surface active substance before the experiments took place due to wide range of applications of the pilot plant.

Many of the experiments, initially after passing the metastable limit, produced a large number of particles. The high number of particles gave rise to an increased work performed by the circulation pump probably due to sedimentation in the pipe.

In the last scaling experiment, S10, the carbonate-sulphate ratio was shifted to higher amounts of sodium carbonate. As a result the formation of scales was faster and the number of particles in the solution was lower than in the other experiments. This indicates that a higher carbonate-sulphate ratio would produces more scaling.

The constructed scaling layer had different appearance depending on the position on the tube and between the experiments. The scaling layer for S8 is shown below in Figure 5-1. At the bottom sight glass the scaling had a rougher surface and was thicker than at the middle sight glass. In S6 the scaling at the middle sight glass had a rougher surface compared to S8.

The scaling layer was not uniformly distributed along the tube; in most of the experiments the scaling was thicker at the bottom sight glass. At the middle sight glass the scaling was much thinner and probably did not stretch much higher than the sight glass, which was confirmed by visual inspection. In experiment S4 the scaling layer was thicker at the middle sight glass, which differed from the expected behaviour described by Gourdon (2009a) but observed before by Broberg and Åkesjö (2012).

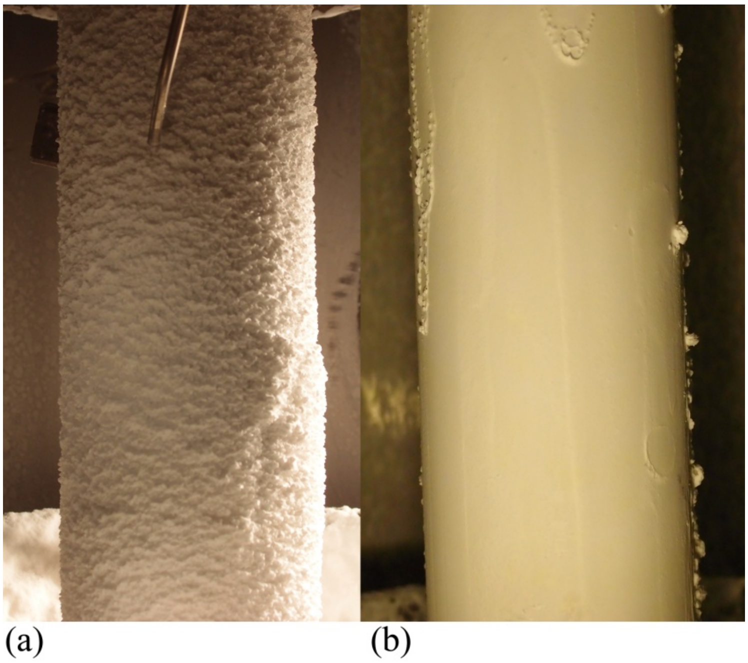

Figure 5-1 Scaling layer for S8 experiment at two height of the tube (a) bottom sight glass, (b) middle sight glass.

5.3 Washing

After successful scaling build up the constructed scales were dissolved with black liquor at different temperature and wetting degrees.

5.3.1 Washing method

For the washing procedure two different methods were used. In the first two experiments the outlet flow of wash liquid was measured with a flow meter and a few 250 ml samples were collected for analysis of the dry solid content where the sampling time was measured. The expectation was to get continuous measurements but there were difficulties with this method of measuring, for example fluctuations in the data measurements. There was as well possibility for mixing in the outlet tube since the meter was not in direct connection to the outlet of the evaporator. In this method it was not only spatter of the wash liquid that limited the flow but the flow meter. A high flow gave rise to unsteady flow measurement probably due to mixing of air and liquid in the flow meter, resulting in no useful data of the flow and density. The flow measurements did not give any reliable results and therefore the flow for experiment 1 and 2 was measured by the sampling time.

The second method, where all the wash liquid were collected in containers of one litre, provided average for the washing conditions during the time it took to fill the sample. The filling time for each container was fairly equal during the experiments except for the first container, which took longer to fill for both washing experiments 3 and 4. This was probably due to an initiation time needed to develop the contact between the scaling layer and the wash liquid.

In washing experiments 1 and 2 the experiment was stopped when measured thickness reached a constant value and the density of the wash liquid had levelled out. In experiment 3 the criteria for stopping the washing was set to the number of existing containers. For experiment 4 more containers were used since the scaling layer was thicker. More containers could have been used for both experiment 3 and 4 but since the region of interest was the dissolution part of the washing the amount was considered sufficient.

In comparing the two different methods the second was the most efficient due to non consistent measurements by the flow meter in the first set-up.

5.3.2 Washing results

In Table 5-3 the operating parameters and results for the wash experiments are shown. The goal was to have both temperature and wetting degree of the wash liquid at a high and low level. However, the inlet flow for E4 was set lower than E2 due to spatter of the wash liquid. The inlet temperature was easy to control during the washing but the temperature along the tube deviated from the desired temperature due to cooling. The values used in the modelling were the temperature along the tube, which were averaged from the thermocouples along the tube. The average was used since the temperatures varied along the tube. For experiment 1 and 2 the temperature difference between top and bottom was 12°C and 17°C but decreased to a reversed temperature difference during the experiment. For experiment 3 the temperature difference was

15°C initially but changed a few degrees during the experiment. In experiment 4 the difference was initially below 5°C but the scales at the bottom of the tube were thick creating an insulating layer which gave rise to a larger temperature difference, 15°C, at the end of the experiment.

Table 5-3 Operating conditions and results for the wash experiments.

	E1	E2	E3	E4
Inlet temperature	41	42	81	82
Temperature of wash liquid [°C]	49	47	73	68
Flow [kg/h]	170	248	163	211
Wetting degree [kg/ms]	0.25	0.37	0.24	0.31
Wash time [min]	8.5	10	9.4	13.9
Amount of wash liquid used [kg]	16.7	37.8	25.0	46.1
Amount of scales dissolved [kg]	0.5	1.7	2.2	5.4

The deviations between the temperatures in the corresponding experiments were relatively low. The desired values for the wash liquid were 40°C and 80°C but instead resulted in 50°C and 70°C. Insufficient cooling before experiment 1 and 2 is the reason that the temperatures are higher than desired. The opposite occurred in experiment 3 and 4 where the cooling was larger than needed and steam should have been used to prevent the further cooling and keeping the desired wash temperature.

As can be seen in Figure 5-2 the dry solid content of the outgoing wash liquid seemed to have an exponential decrease. This was consistent for all 4 experiments. This might depend on the distribution of scales over the tube; it may as well be affected by residual salt in the bottom of the evaporator.

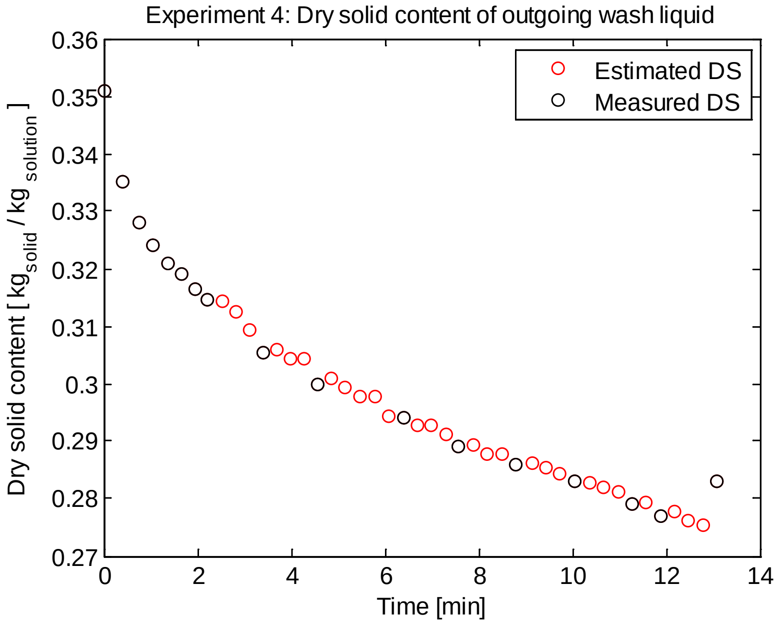

Figure 5-2. Dry solid content of outgoing wash liquid in experiment 4.

For one of the wash experiments, E4, the washing time was not sufficient to clean the tube fully. The scaling layer was much thicker than for the other experiments due to favourable operating conditions in the build up of the scaling layer. In Figure 5-3, the remaining scaling layer after washing for E4 is shown. A complete cleaning of the thick scaling layer would have required more wash liquid than was available. It had as well required more containers for the wash liquid. Measurements on the scales, which were chiselled from the tube, showed a thickness for the remaining scales of 4 mm.

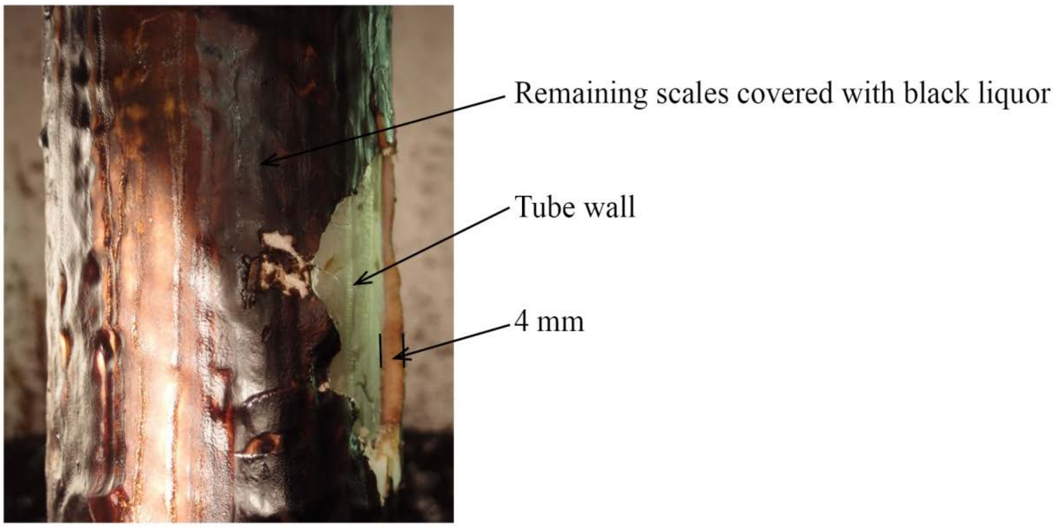

Figure 5-3 Remaining scaling layer after washing with black liquor for experiment 4. On the right side of the tube a part of the scaling was chiselled away exposing the steel tube.

6 Modelling results and discussion

6.1 Scaling distribution

In order to evaluate the proper distribution, the amount of salt dissolved during washing is divided by the volume of scales as mentioned in Section 4.1. The result is tabulated in the Table 6-1 and the bold values correspond to the distribution used. In the first experiment, the density is far from the value in literature. It can be explained by the thin scaling layer, due to the low temperature which was used during build up, which give rise to larger measurement errors. A contributing factor is that the inlet concentration of the black liquor is not known due to the absence of an initial sample which was taken in the later experiments. The lack of an initial sample leads to difficulties estimating the salt concentration because the amount of salt in the samples is calculated using the inlet dry solid content, as can be seen in Appendix D.

Table 6-1 The scaling density for different distributions mentioned in Section 4.1. Bold values corresponds to the distribution used in the simulations.

Experiment	Dist I	Dist II	Dist III	Dist IV	Dist V
E1	949	1057	**1066**	1056	1041
E2	1905	2306	2309	2309	**2321**
E3	1795	2024	**2066**	2033	2033
E4	2434	2453	3218	3181	**2367**

6.2 Dissolution rate constant

In order to accurately describe the dissolution, multiple simulations where performed for different values of the dissolution rate constant, k_c, to find the constant which best correspond to the dissolution behavior during washing. In order to fit the dissolution rate constant, appropriate regions of interest had to be found for the different experiments as mention in Section 4 and they are tabulated in Table 6-2. The region of interest began where the change in outgoing dry solid content were not too steep and ended where the dry solid content had levelled out. The fit between the experimental data and the model was only evaluated in these regions. Three criterions to evaluate the model fit were used; scale thickness at the bottom and middle sight glass and the dry solid content in the outgoing wash liquids variance with time.

Table 6-2 Approximate regions of interest for the evaluation of dissolution rate constant.

	Start [min]	End [min]
E1	1.5	3.5
E2	2	6
E3	2	7
E4	2	10

For all experiments the experimentally determined values are compared with the modelled values for three different values of the dissolution rate constant, one which have the best fit along with one higher and one lower value which gives appropriate interval for the dissolution rate constant ± 0.01 kg/m^{2}s.

6.2.1 Experiment 1

In Figure 6-1, the modelled result is compared to the experimentally determined values of the outgoing wash liquid dry solids content for experiment 1. The few sample points is due to that the density meter should have been used during experiment 1 and 2, but unfortunately did not satisfy our demands and hence only the samples were used.

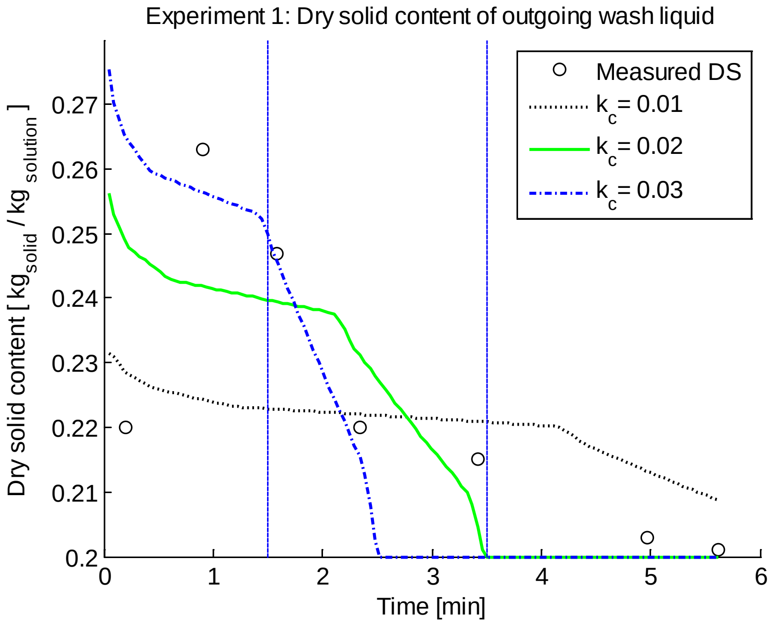

Figure 6-1 Results for experiment 1, showing three different values for the dissolution rate constant and the measured dry solid content for the outgoing wash liquid plotted against time. The region of interest is marked as the interval between the blue vertical dashed lines.

Below, in Figure 6-2, the measured scale thicknesses are compared with the model estimates at the both sight glasses. The lower dissolution rate constant, 0.01, gives a better fit in the middle sight glass but the higher value, 0.03, gives a better fit in the bottom sight glass as can be seen in Figure 6-2. In Figure 6-1 , the middle value, 0.02, gives the best possible fit between the points and is therefore chosen as the most appropriate one.

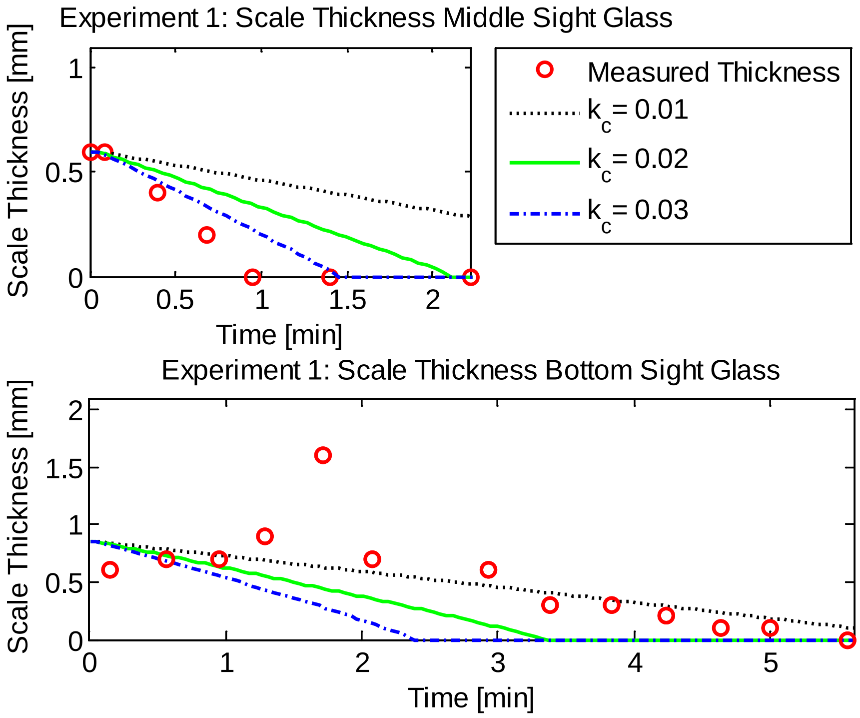

Figure 6-2 Modelled and measured thickness at the middle and bottom sight glass for experiment 1.

In experiment 1 the scaling layer was thin, as a result the thickness measurements had a higher uncertainty. This reflected in the modelling results and it was hard to get a good fit, as can be seen in both figures previously mentioned.

6.2.2 Experiment 2

In experiment 2, the amount of sample points were few, due to the use of the same method of measuring as in experiment 1. The scaling layer was thicker, resulting in better measurement of the thickness, which gives a density closer to the values found in literature, as can be seen in Table 6-1.

In Figure 6-3 the modelled dry solid content of the outgoing wash liquid for three values of the dissolution rate constant is plotted together with the experimental points for experiment 2. The concentration drops sharp at one point, for each value of the dissolution rate constant, and reach the inlet concentration, which shows that the tube is clean according to the model.

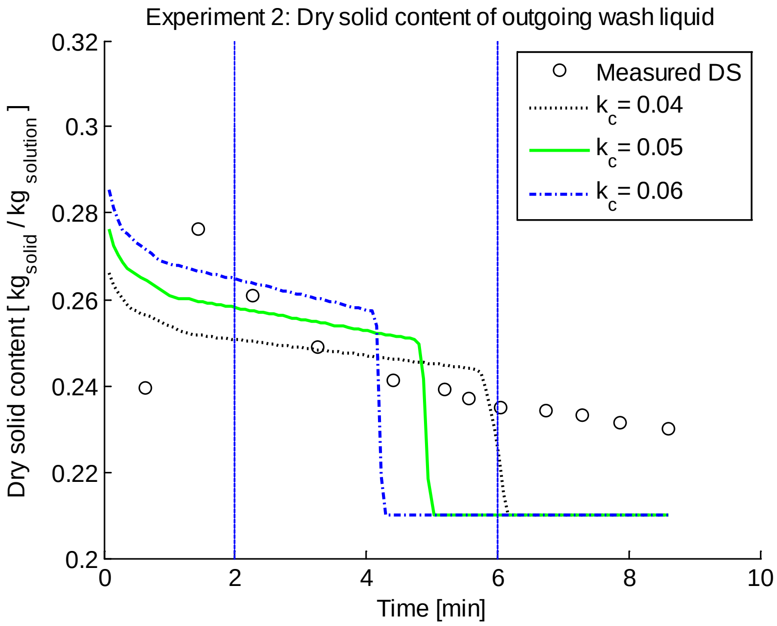

Figure 6-3 Results for experiment 2, showing three different values for the dissolution rate constant and the measured dry solid content for the outgoing wash liquid plotted against time. The region of interest is marked as the interval between the blue vertical dashed lines.

In Figure 6-4, where the modelled estimated thickness at the bottom and middle sight glasses for three values of the dissolution rate constant and the measured thicknesses are displayed. The higher value, 0.06, for the dissolution rate constant gives a better fit in the middle sight glass and the lower value, 0.04, gives a better fit in the bottom sight glass. The dissolution rate constant of choice, 0.05, performs quite well in both sight glasses.

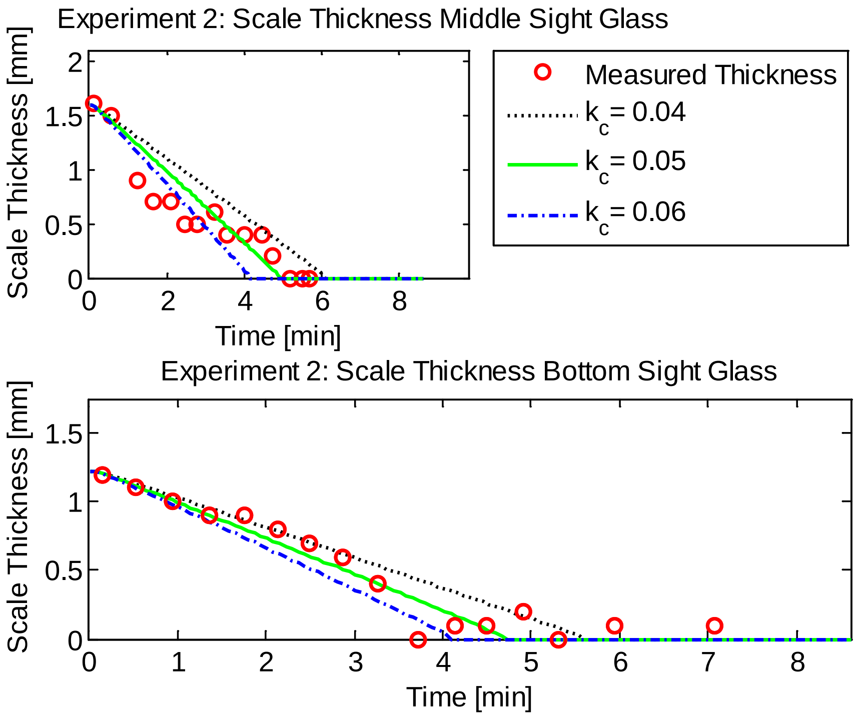

Figure 6-4 Modelled and measured thickness at the middle and bottom sight glass for experiment 2.

During the scaling layer build up experiment 2, the scale layer grew so thick that the flow redistributor situated at the bottom sight glass grew full of scales which hindered the flow. Therefore the scales situated in and below the redistributor were removed prior to washing which removed uncertainties regarding the thickness below the bottom sight glass. This yielded a density closer to the literature value as can be seen in Table 6-1.

6.2.3 Experiment 3

In experiment 3 the second experimental washing method was used which gave rise to an increased amount of sample points compared to previous experiments. The dry solid content was measured in approximate half of the samples and in the rest the dry solid content was estimated using the density. In Figure 6-5 the outgoing wash liquids' dry solid content is plotted together with the modelled result for three different values of the dissolution rate constant.

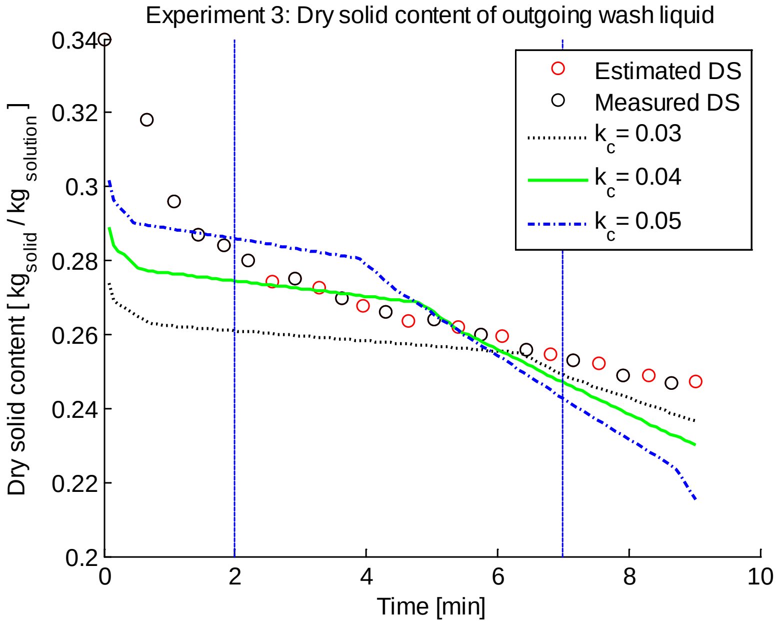

Figure 6-5 Results for experiment 3, showing three different values for the dissolution rate constant and the measured dry solid content for the outgoing wash liquid plotted against time. The region of interest is marked as the interval between the blue vertical dashed lines.

In Figure 6-6 the modelled estimation of the thickness for three values of the dissolution rate constant is shown together with the measured values. The lower value, 0.03, gives a better fit in the middle sight glass and the higher value, 0.05, gives a better fit in the bottom sight glass. However both the lower and the higher values shows less accuracy in the outgoing concentration of the wash liquid, as can be seen in Figure 6-5, and therefore the dissolution rate constant of choice is 0.04.

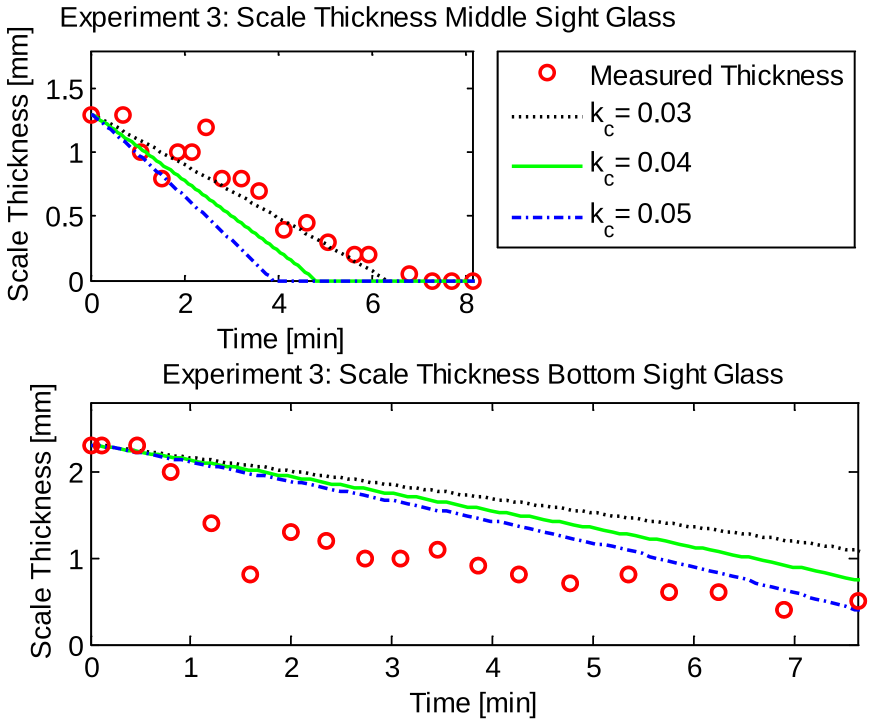

Figure 6-6 Modelled and measured thickness at the middle and bottom sight glass for experiment 3.

The drop in the outgoing wash liquid concentration, which was seen in Experiment 2, is absent in Figure 6-5 and in Figure 6-6 there are indications that there are scales remaining on the tube. This indicates that the tube was not clean according to the model, which was not confirmed by visual inspection. This might be due to overestimation of the thickness in the bottom sight glass.

6.2.4 Experiment 4

In experiment 4 the second method was used in the same way as in experiment 3 and hence the amount of samples were high as can be seen in Figure 6-7, where the modelled and measure dry solid content of the outgoing wash liquid are displayed for three values of the dissolution rate constant.

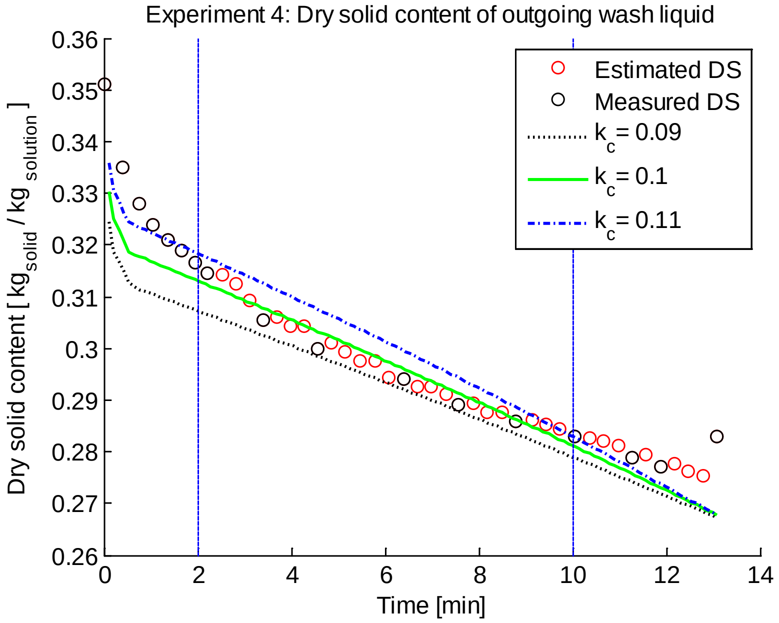

Figure 6-7 Results for experiment 4, showing three different values for the dissolution rate constant and the measured dry solid content for the outgoing wash liquid plotted against time. The region of interest is marked as the interval between the blue vertical dashed lines.

As can be seen in Figure 6-8, where the modelled and measured thickness is plotted for three values of the dissolution rate constant, the difference is quite small between the different values and shows a god fit with the experimental values in the bottom sight glass. In the middle sight glass the fit was not accurate for any of the three values of the dissolution rate constant. The dissolution rate 0.1 performs slightly better in the region of interest and is therefore the dissolution rate of choice.

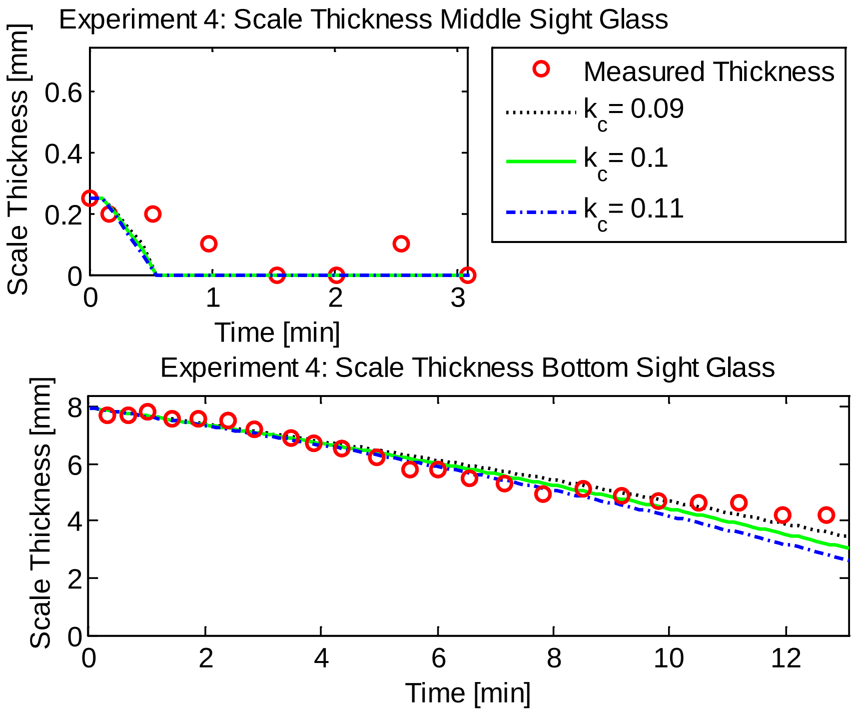

Figure 6-8 Modelled and measured thickness at the middle and bottom sight glass for experiment 4.

In experiment 4 the scale layer was very thick at the bottom sight glass which led to the amount of black liquor available for dissolution was not sufficient so the washing stopped with residual scales left on the tube. The thickness of the residual scales can be seen in Figure 5-3 and the thickness of the removed part was measured to 4 mm, which corresponds to the modelled and measured values during the washing. The thickness in the middle sight glass, however, was very thin which might contribute to the lack of fit with the model, due to measurement errors.

6.2.5 Experimental summary

In all experiments mentioned above, there was a conflict of achieving a good fit between the modelled and the experimental values for all three criteria. The best fit for each experiment was chosen by a compromise between all three parameters and could be determined with a certainty of ± 0.01 kg/m^2s, as can be seen in the sections 6.2.1-6.2.4. A summary of the experiments is displayed below in Table 6-3 along with the parameters of washing for each experiment.

In the measurements where the thickness of the scaling layer was below 1 millimetre, there seems to be an increased probability of errors. The thickness measurements can have given a systematic error due to crystal growth on the metal disc or difference in the thickness on the clean tube.

In order to calculate the Reynolds number, displayed in Table 6-3, the viscosity was approximate by using a correlation for the initial dry solid content and density for the black liquor (Vakkilainen 2000). The Reynolds number indicates that the flow should be in between laminar and turbulent flow, and visual inspection yields that the flow was non-laminar.

Table 6-3 The transport coefficient, Reynolds number and the conditions during washing.

	E1	E2	E3	E4
k_c [kg_{salt} / m^2s]	0.02 ± 0.01	0.05 ± 0.01	0.04 ± 0.01	0.1 ± 0.01
Temperature [°C]	49	47	73	73
Wetting degree [kg/ms]	0.25	0.37	0.24	0.31
Viscosity [Pas]	0.0014	0.0016	0.008	0.009
Reynolds number	733	911	1151	1425

6.3 Comparison with Broberg & Åkesjö

The work mentioned in Section 2.6 by Broberg and Åkesjö (2012) where the dissolution was investigated using pure water is displayed below together with the result from this study.

6.3.1 Wetting degree

In Figure 6-9 the wetting degree and dissolution rate constant at ≈ 80 °C for water and black liquor is shown.

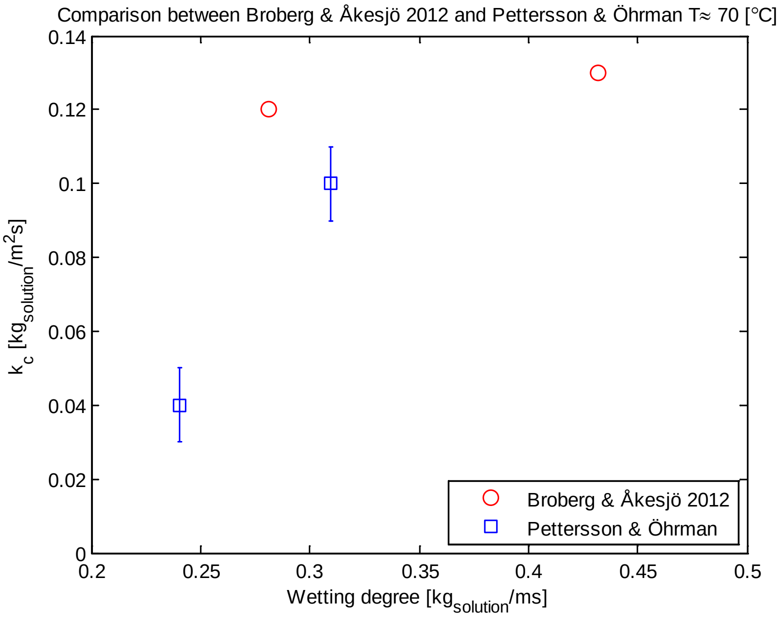

Figure 6-9 Comparison between dissolution rate constant and wetting degree at 80°C. The red dots represent values for water obtained by Broberg and Åkesjö (Broberg 2012). The blue crosses represent black liquor and the values were obtained by modelling of the experiments in this thesis.

As can be seen in Figure 6-9 the dissolution rate constant for water seemed to be more or less independent of the wetting degree. For the black liquor the dissolution rate constant is lower and a flow dependence could not be ruled out.

6.3.2 Temperature

Broberg and Åkersjö (Broberg 2012) suggested that for the dissolution of sodium scales with water the dissolution rate constant might have a temperature dependence and suggested a linear relationship between those two. In Figure 6-10 the dissolution rate constant is plotted against temperature. As for the water dissolution rate constant, the black liquor seemed to possess temperature dependence. However, the results are not conclusive enough to propose a relationship.

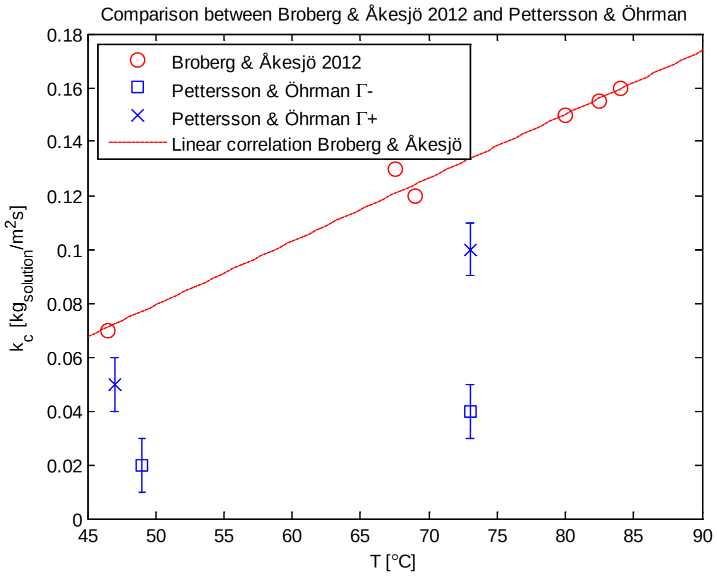

Figure 6-10 Comparison between dissolution rate constant and temperature during washing. The values for water, red circles, were obtained by Broberg and Åkesjö and the linear relationship proposed displayed as a red line. (Broberg 2012) Values for black liquor found in this thesis is displayed as blue crosses.

6.3.3 Viscosity

One big difference between black liquor and water is the viscosity which could affect the dissolution behaviour. In order to compare the dissolution rate constant and the viscosity, it was approximate by using the initial dry solid content and density for the black liquor (Vakkilainen 2000). The viscosity for pure water is estimated using commonly available engineering tables. In Figure 6-11 the viscosity and dissolution rate constant are compared for water and black liquor. There is, however, an uncertainty in the values used since the salt concentration will affect the viscosity for water. But the dissolution rate constant seemed to decrease with increasing viscosity.

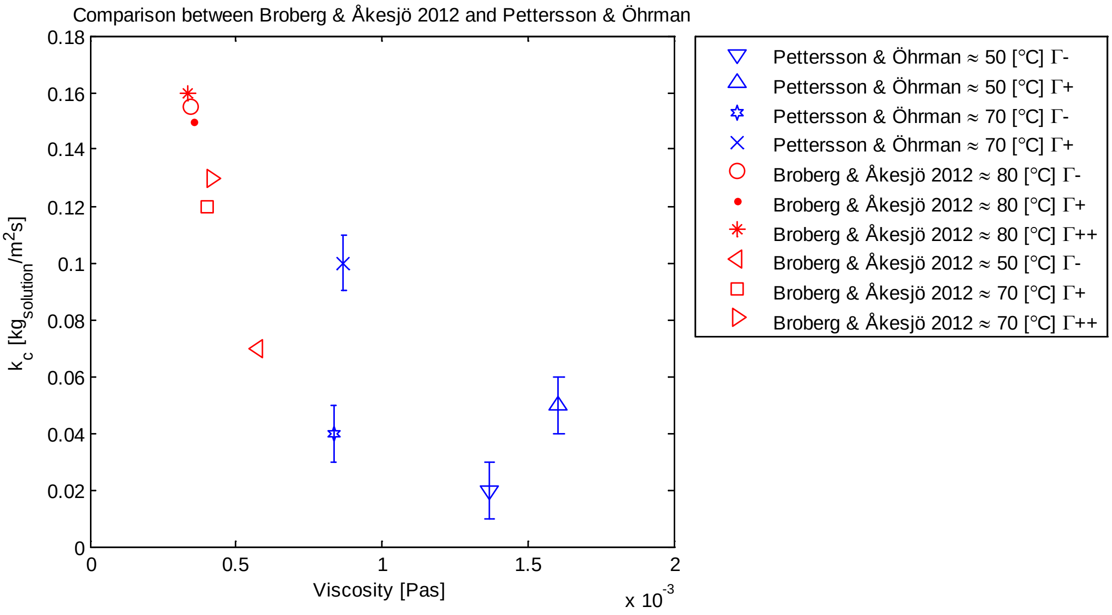

Figure 6-11 Estimated viscosity and dissolution rate constant at different temperatures for both black liquor and pure water.

7 Sensitivity analysis

In order to investigate how much the uncertainty of different variables affect the result of the model a sensitivity analysis was performed. The parameters were varied ±10% and the results are shown in the following sections.

7.1 Solubility

The first order dissolution model is dependent on the saturation concentration and in order to evaluate the sensitivity the solubility limit is varied. The variation between the measured solubility's was less than 10% and therefore the solubility is changed ± 10% in order to evaluate if the temperature along the tube or the values for the solubility affects the result. As can be seen in Figure 7-1 the solubility changes the appearance, but not significantly and should be confided in the given range of the dissolution rate constant and the models could be considered quite robust in respect to the temperature dependant solubility.

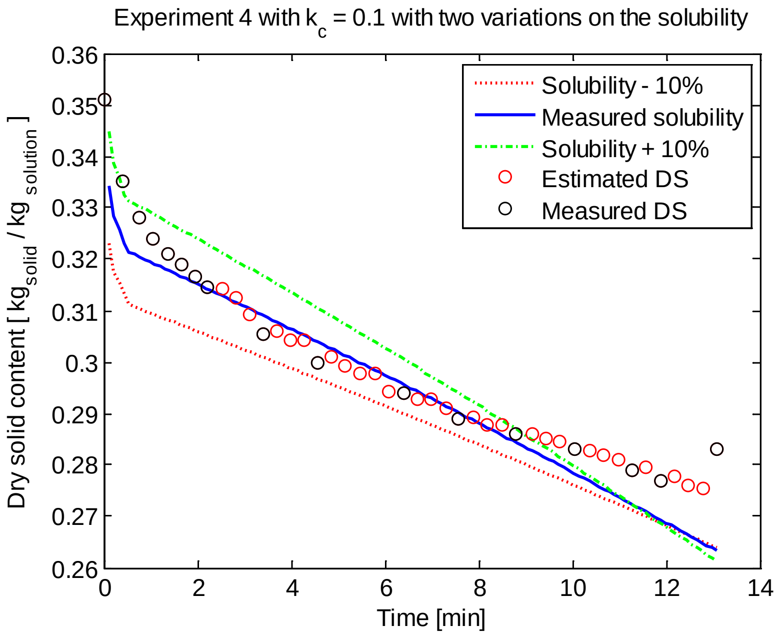

Figure 7-1 Sensitivity analysis with respect to solubility of sodium salts in black liquor.

7.2 Inlet flow

In order to evaluate the flow, the time it took to fill the sample containers where noted. The average flows, which were used in the experiments, and standard deviation are displayed in Table 7-1. In all experiments, except experiment 2, the deviation is below 10%.

In Figure 7-2 three cases where the inlet flow is varied ± 10% is plotted and it can be seen that the curve does change vertically. The change would not affect the chosen dissolution rate constant significantly.

The high deviation in experiment 2 can be explained by the high flow and the small volume of the sample containers which were used.

Table 7-1 The flow and standard deviation for the experiments.

Experiment	Average Flow [kg/h]	Deviation [kg/h]
1	170	4.12
2	248	48.2
3	163	11.4
4	210	7.35

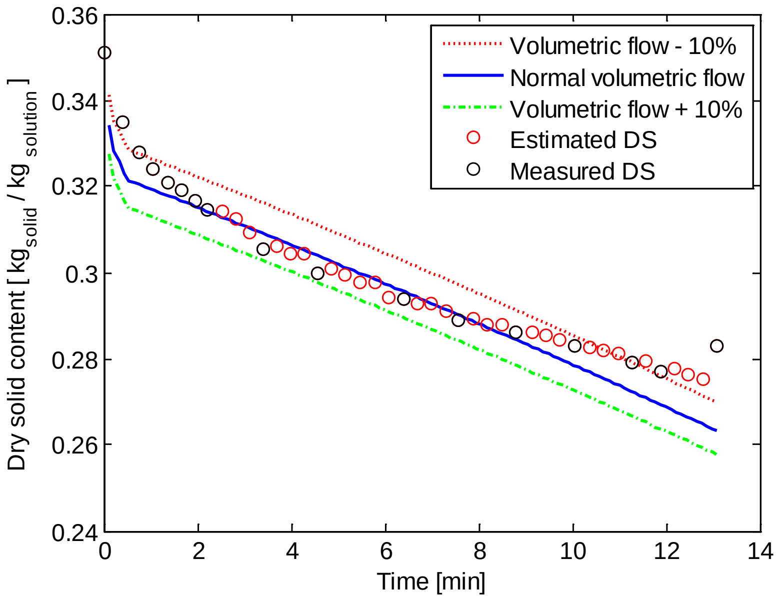

Figure 7-2 Sensitivity analysis with respect to black liquor inlet flow. Dissolution rate constant is kept constant for the different flows.

7.3 Mesh independence

Discretisation give rise to numerical errors, which decreases with decreasing time and spatial steps, but this also increase the computational costs and hence an optimum has to be reached where the accuracy is high and the computational cost is low. To check for mesh independence, where the size of the discrete steps does not affect the result, the time and length steps were increased and as can be seen in Figure 7-3 the result was equal for the cases where the tube steps are 5000 and 500 which shows that 500 tube steps was sufficient to reach a good result to a low computational cost.

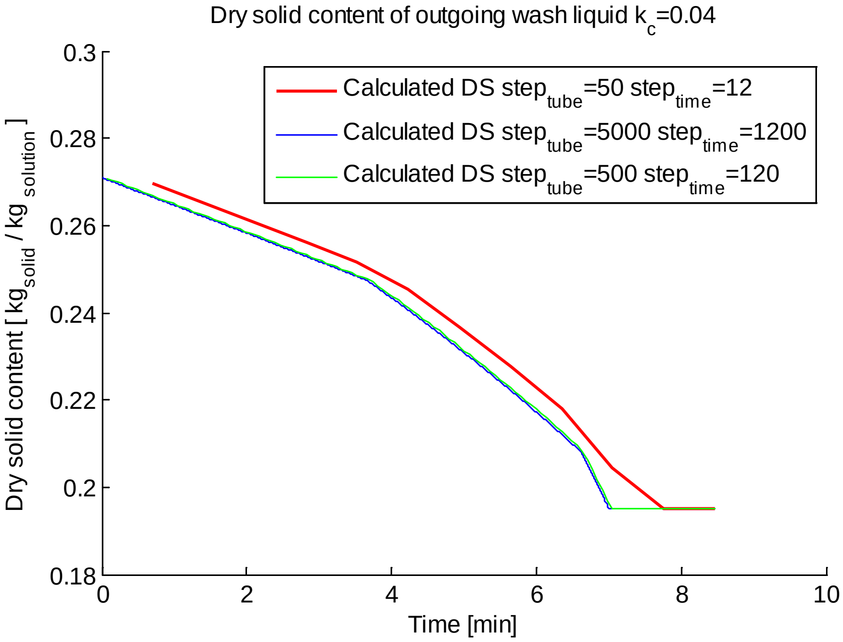

Figure 7-3 Dry solid content out from the evaporator as a function of time for different mesh sizes.

7.4 Sensitivity conclusion

The parameters which are described above do affect the result, but the effect is relatively small and thus should be confided in the suggested dissolution rate constant ± 0.01. The values for the dissolution rate constant differ between the experiments therefore an affect of temperature and wetting degree can be observed but not determined to which extent.

8 Conclusions

The formation of scales is a complex subject and it is hard to predict whether scales will form on the evaporator tube or anywhere else in the system. One difficulty during the formation of the scaling layer was the detachment of the scales from the tube wall. This happened inconsistent of number of particles and operating parameters. One possible explanation could be that the tube wall was contaminated with a surface active substance before the experiments took place.

A solution with higher carbonate to sulphate ratio gave rise to lower number of particles in the solution after passing the metastable limit and was probably more prone to scale the heat transfer area than to form crystals in the solution.

A high temperature difference over the metastable limit seemed to give rise to a larger number of particles and a lower degree of scaling initially. A higher difference after passing the metastable limit, however, gave rise to a higher degree of scaling. This could indicate that to avoid scaling it may be suitable to operate at a high temperature difference between the liquor and the steam until the metastable limit for the sodium salt has been passed. But since a high temperature difference benefits fouling a lower temperature difference would be appropriate above the metastable limit to avoid scale formation. Scales seemed to be more prone to form at higher temperatures thus it would be suitable to have lower temperatures in evaporators where scales are likely to form to reduce the onset of scaling.

The dissolution rate differs substantially from each other for the different experiments but seemed to have both a wetting degree and temperature dependence. They have all in common that they are well below the values found by Broberg and Åkesjö (2012), for the dissolution in pure water, at corresponding temperature and wetting degree.

The method of collecting the wash liquid in containers and measuring the dry solid content seems to be a suitable experimental method to investigate the washing behaviour. Although the thickness measurements may not be accurate they display the tendency of the dissolution process. Inaccuracy in the measurements may be an effect of the thin scaling layer and the accuracy was higher at thicker layers.

9 Further research

To further investigate the dissolution rate constant’s viscosity dependence, complementary studies with a higher dry solid content of the black liquor should be performed. A higher dry solid content would not only increase the viscosity but also the initial salt concentration, which would have to be taken into account. An interesting research topic could be to find a solution where the viscosity is increased without changing the initial salt concentration. To separate the effect of the black liquor and the decreasing driving force, by initial salt concentration, experiments with saline solutions water with the same dissolution capacity as in the black liquor could be carried out.

The tube has several thermocouples mounted, which could be used to estimate the local temperatures along the tube. This in turn could provide a more accurate data for the local solubility and therefore more accurate dissolution rate along the tube since they are temperature dependent. However that would require more solubility measurements in the desired temperature interval to propose a suitable relation between temperature and solubility.

Since there is an uncertainty in the existing way of measuring the thickness a new method should be developed. Scaling distribution along the tube is only estimated from the two known points, and it would be beneficial to be able to measure the thickness between these points and thereby evaluate the scaling distribution.

In the model used the initial roughness of the scaling layer has not been considered. It will result in an initial increase in the contact area but smooth out as scaling is dissolved. In further modelling it would be interesting to see if this increased contact area affects the results.

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Appendix

A. Solubility calculations

The dry solid content consist of the residual, R, and inlet concentration of salt, s_0. Dry solid content can be determined by drying which removes the water, W according to TAPPI standard (TAPPI 2009).

$$DS_{in} = \frac{R+s_0}{R+s_0+W} \qquad \text{(A-1)}$$

In the filtrate the dry solid contains the amount of salt needed to reach saturation as well.

$$DS_{out} = \frac{R+s_0+s}{R+s_0+s+W} \qquad \text{(A-2)}$$

On 1 kg of initial dry solids

$$R + s_0 = 1 \qquad \text{(A-3)}$$

The amount of water can be expressed as below in Equation A-5.

$$DS_{in} = \frac{R+s_0}{R+s_0+W} = \frac{1}{1+W} \qquad \text{(A-4)}$$

$$W = \frac{1}{DS_{in}} - 1 \qquad \text{(A-5)}$$

By combining with Equation A-2 the amount of salt, s, added to reach saturated conditions in 1 kg of solids can be calculated as displayed in Equation A-7.

$$DS_{out} = \frac{1+s}{1+s+\left(\frac{1}{DS_{in}}-1\right)} \qquad \text{(A-6)}$$

$$s = \frac{DS_{out}\left(1+\left(\frac{1}{DS_{in}}-1\right)\right)-1}{1-DS_{out}} \qquad \text{(A-7)}$$

To find the solubility limit, the amount of initial salt has to be taken in consideration. The initial concentration was found by an external chemical analysis, which gave the relation between salt and the dry solids in the initial black liquor displayed in Equation A-8.

$$\frac{s_0}{R+s_0} = 0.154 \qquad (A\text{-8})$$

$$s_0 = 0.154 * (R + s_0) \qquad (A\text{-9})$$

And 1 kg of Residual corresponds to $(R + W + s + s_0)$ kg solution which gives the saturation concentration C^*.

$$C^* = \frac{s+s_0}{R+W+s+s_0} = \frac{s+0.154*(1)}{1+\left(\frac{1}{DS_{in}}-1\right)+s} \qquad (A\text{-10})$$

B. Operation parameters for scaling experiments

Experiment	T_{salt} [°C]	ΔT [°C]	Flow [l/h]
S1	85	10	500
S2	48	10	500
S3	105	15	500
S4	105	15	500
S5	105	15	500
	120	15	500
S6	120	15	700
	120	6	700
	120	10	700
	120	25	700
S7	120	25	700
S8	120	15	700
	120	8	700
	120	25	700
	120	25	500
S9	120	15	500
	120	8	500
	120	25	500
S10	120	15	700
	120	8	700
	120	12	700
	120	15	700
	120	15	500
	120	18	500
	120	22	500
	120	14	400
	120	8	400

C. Dry solid content out of each cell

In order to compare the calculated and experimental results the dry solid content in each discrete time step has to be calculated. The only component that changes along the tube is the amount of dissolved salt in step n, $\mathrm{s_n}$, to the wash liquid. The other components, the residual, $\mathrm{R_0}$, the water, $\mathrm{W_0}$, and the initial salt amount, $\mathrm{s_0}$, are assumed to be constant over the tube. Then the outlet dry solid content from step n can be calculated by summation of the amount of dissolved salts in the previous steps as shown in Equation C-1.

$$\mathrm{DS_n} = \frac{\mathrm{R_0+s_0+\sum_1^n s_n}}{\mathrm{R_0+s_0+W_0+\sum_1^n s_n}} \qquad \text{(C-11)}$$

D. Salt dissolved in each sample

In order to estimate the amount of salt, s, dissolved during the washing in the samples, the dry solid content was measured, or estimated by using the density and a correlation between dry solid content and density. The amount of salt can be calculated as seen below.

The dry solids initially contain only residuals and the initial salt.

$$DS_{in}m_{m,0} = R_m + s_{0,m} \tag{D-1}$$

After the washing the dry solids contains dissolved salts as well.

$$DS_{m,out}m_m = R_m + s_{0,m} + s_m \tag{D-2}$$

The weight increase only consists of the dissolved salts.

$$m_m = m_{m,0} + s_m \tag{D-3}$$

$$m_{m,in} = m_m - s_m \tag{D-4}$$

If Equation D-4 is substituted into Equation D-1 the result is shown below in Equation D-5.

$$DS_{in}(m_m - s_m) = R_m + s_{0,m} \tag{D-5}$$

Then Equation D-5 is subtracted from Equation D-2 and rearranged to form Equation D-8.

$$DS_{n,out}m_m - DS_{in}(m_m - s_m) = R_m + s_{0,m} + s_m - \left(R_m + s_{0,m}\right) \tag{D-6}$$

$$m_m\left(DS_{m,out} - DS_{in}\right) + DS_{in}s_m = s_m \tag{D-7}$$

$$s_m = \frac{m_m\left(DS_{n,out} - DS_{in}\right)}{(1 - DS_{in})} \tag{D-8}$$

The total amount of dissolved salts is found by summation of all the samples.