

THE EFFECTS OF FLOW VELOCITY ON CRYSTALLIZATION FOULING IN FALLING FILM BLACK LIQUOR EVAPORATORS

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ABSTRACT

In pulp mills, fouling can be a significant problem in the so-called black liquor evaporation plant. This is a multistage evaporation plant that actually works as a crystallizer because, as the black liquor becomes more concentrated, large amounts of sodium salts, particularly sodium carbonate and sodium sulphate, will saturate and precipitate from the solution. The precipitated crystals may form on the heat transfer surface or can adhere to it, or they can remain in the solution. Black liquor is a complex viscous alkaline solution of organic and inorganic components. Also, because the proportions of the constituents in the black liquor vary depending on wood raw material and cooking conditions, it is difficult to predict when and where the sodium salts will precipitate.

In this paper, fouling measurements in a 4.5 m falling film research evaporator are presented. The results are mainly based on heat transfer measurements, both local and average, and these are presented in the form of fouling resistances. A number of experiments are presented, aiming at evaluating the effects of the flow velocity on the formation and removal of a crystalline fouling layer on the evaporator surface. The results show that the cleaning effect created by the physical shear of the falling film on the fouling layer is not important.

INTRODUCTION

Fouling is an important issue for the pulp and paper industry. One of the most important problem areas is the so-called black liquor evaporation plant. Black liquor, which is a residual stream from the pulp production process, needs to be recycled for both environmental and economic reasons. In the liquor recovery cycle, the black liquor is concentrated in a multistage evaporation plant prior to combustion in a recovery boiler where the chemicals needed for the pulping process are regenerated and, at the same time, steam is produced.

Black liquor is a complex viscous alkaline solution of organic and inorganic components. Fouling of the evaporators is mainly caused by the precipitation of inorganic water-soluble sodium salt in the black liquor. The sodium scales are mostly in the form of double salts of

sodium carbonate and sodium sulphate. In a survey of North American pulp mills performed by Schmidl and Frederick (1998) 35% of the investigated mills were reported to have problems with soluble sodium scales. The $\text{Na}_2\text{CO}_3\text{-Na}_2\text{SO}_4$ system will form different salts depending on the sodium carbonate/sodium sulphate ratio and also depending on the temperature (Shi et al., 2003; DeMartini and Verrill, 2007). The crystal species generally encountered in black liquor evaporators are either Burkeite or Sodium Sulphate Dicarboxylate and these crystals have different propensity to form scales on the heat transfer surface (Gourdon et al., 2009). Grace (1976) and Hedrick and Kent (1992) have both provided models for predictions of the solubility of the sodium salts in black liquor. However, predicting when these crystals will form or deposit on the heat transfer surface in the evaporators is difficult because of the complex composition of black liquor. The modelling is also complicated as the composition of the crystal species is not constant. The composition of the black liquor also varies from mill to mill due to different cooking conditions and wood species. Different substances in the black liquor will affect the solubility and crystallization behaviour of these salts. A number of other sodium salts exist (for example, sodium hydroxide) that will increase the total sodium content and thus lower the solubility (Green and Frattali, 1946). Other substances like calcium and the organic part of the black liquor may also affect the crystallization of sodium carbonate and sodium sulphate (Grace, 1975; Shi et al., 2003b). One other important feature that may contribute to Burkeite's and Dicarboxylate's propensity to form scales is that both have inverse solubility with temperature. This means that the solubility will be the lowest closest to the hot heat transfer surface. Thus, in black liquor evaporators, supersaturation, which is the thermodynamic driving force of the crystallization (Mersmann, 1999), is generated in two ways: (i) through evaporation, increasing the solution concentration, and (ii) by solution superheating on heat-transfer surfaces.

Bott (1995) describes the general fouling process with three steps: (i) induction, (ii) steady growth and (iii) plateau. Many anti-fouling strategies use the approach of trying to increase the duration of the induction period. During the

initiation period, certain conditions required for deposition, such as crystal nucleation and surface conditioning, are established (Helalizadeha et al., 2000). Förster et al. (1999) presented two successful anti-fouling approach methods: (i) modifying the characteristics of the heat transfer surface and (ii) adjusting the hydrodynamics of the flow conditions.

The mechanism of crystallization fouling relates to many subjects such as momentum, heat and mass transfer, chemical kinetics, material science, etc., which makes it difficult to explain in mathematical terms (Helalizadeha et al., 2005). Fouling on the surfaces of the black liquor evaporators commences either as the sodium salts nucleate on the surface or when already formed crystals adhere to it. The crystallization mechanism continues through both secondary nucleation and crystal growth. Besides these mechanisms, fouling can also be generated through adhesion of crystals to the surface and by cohesion or agglomeration driven by crystal-crystal attraction forces.

During evaporation of black liquor using an annular test section, Müller-Steinhagen and Branch (1997) obtained induction times in the range of hours. They observed that the induction period decreased with increased heat-transfer surface temperature or decreased liquor flow rate, while the scaling rates increased with increased surface temperature and decreased bulk temperature, but were not affected by liquor flow rates.

Cleaning of the evaporator surface is, of course, also an important part of the pulp mill operation. In the black liquor evaporators with the most severe fouling, the cleaning is frequently performed during the continuous operation of the mill. The mechanism during cleaning can, in general, include both dissolving the crystal deposits and removing the crystals either by breaking the adhesion bonds between the crystal and the surface or by breaking the cohesion bond between crystals. The thermodynamic driving force of the dissolution is the concentration difference between the concentration in the wash solution and the solubility. The solubility, in turn, depends on the temperature and the composition of the fluid. The mechanical removal of deposits is dependent on physical properties such as temperature and flow rate (Plett, 1985).

In this work the influence of flow velocity on the crystallization fouling of sodium carbonate and sodium sulphate from evaporation of black liquor is investigated. Measurements of the fouling behaviour for different operating conditions are performed in a free-falling film evaporator to isolate the influence of flow velocity on the fouling mechanisms. The aim is to illustrate the total effect of the flow rate but also, more importantly, to illustrate the pure mechanical effect, i.e. not considering the consequence of changing the concentration profile over the heat transfer surface. The effects of this on the cleaning process will also be discussed.

APPARATUS AND EXPERIMENTAL METHOD

Apparatus

The experimental part of this work was performed in a pilot evaporator and a schematic of the experimental set-up is seen in Figure 1. The evaporator was designed to be large enough to produce results relevant to industrial conditions, but also small enough so that a barrel of black liquor is sufficient to run it. The evaporator is a falling film type, heavily instrumented and designed especially for black liquor evaporation at a wide variety of operating conditions. The main component of the evaporator is a vertical tube, 60 mm in diameter and 4.5 m long, with the falling black liquor film on the outside. The active heat transfer area of the evaporator tube is 0.848 m². In order to resemble industrial conditions in which squirting from one tube can hit another, a liquor redistribution system has been mounted along the heat transfer surface, so as to minimize the amount of black liquor dropping beside the evaporator tube. The liquor is heated with saturated steam condensing on the inside of the tube. The heating steam is distributed along the inside of the evaporator tube through an internal steam tube. The black liquor is fed to the top of the evaporator using a circulation pump and then flows down the tube and is partially evaporated. The produced vapour is separated from the black liquor in a flash tank. The bottom of the flash tank is connected to the circulation pump. The black liquor vapour is fed to a condenser which regulates the pressure. The produced condensate can either be recirculated to the flash tank to keep the dry solids content constant, or be ejected.

The research evaporator is designed for a wide pressure range from full vacuum to 12 bar. The evaporator is fitted with 21 Pt-100 elements at different positions measuring temperatures. To determine local heat fluxes in the evaporator tube, thermocouples are soldered to it at different heights. The measurement possibilities in the evaporator, besides temperatures and pressures, include the following:

- Flow rate and density of the circulating black liquor (Endress & Hauser Coreolis mass flow meter)
- Viscosity of the circulating black liquor (Marimex, Viscoscope)
- Refractive index of the circulating black liquor (K-Patent PR-23-SD)
- Heating steam condensate volumetric flow (timing known volume using VEGASWING level switches)
- The mass flow of produced liquor vapour condensate (Mettler-Toledo balance)
- Particle counts (Lasentec FBRM D600L)
- Filtered and unfiltered samples

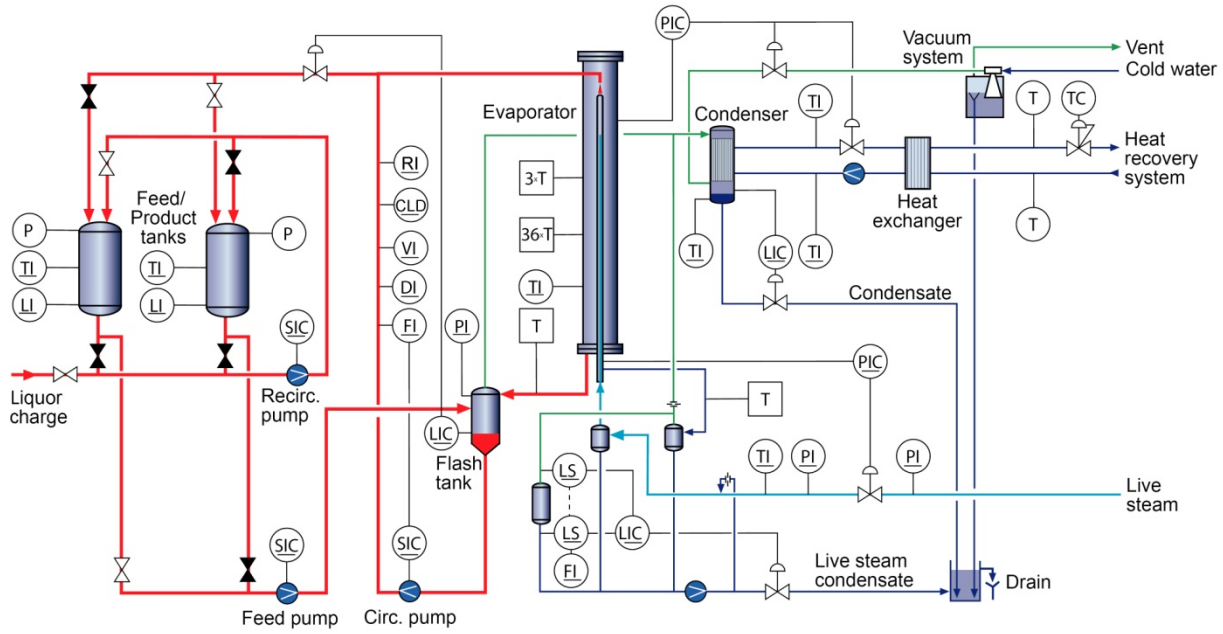


Fig. 1. Flow sheet of the research evaporator.

Further details about the research apparatus and measurement equipment are given in Gourdon (2010) and Johansson et al. (2005).

Evaluation Methods

In this work the fouling resistance

$$R_f(t) = \frac{1}{h_o(t)} - \frac{1}{h_o(t=0)} \quad (1)$$

is used to examine the fouling behaviour on the heat transfer surface. Both average and local measurements are performed and analysed. Here h_o is the outside heat transfer coefficient (in $\text{W}/\text{m}^2\text{K}$) and t is the time (in min). $h_o(t=0)$ thus represents the initial “clean” heat transfer coefficient. By looking at local fouling resistances one can determine when and where deposits form on the evaporator tube, i.e. whether some areas are more favourable to fouling than others, or whether there is a homogeneous formation along the heat transfer surface.

Equation (1) presumes that the heat transfer coefficient for the black liquor falling film is considered constant over time. Heat transfer coefficients are, however, dependent on physical properties such as viscosity and thermal conductivity. During evaporation, if for example the concentration increases, the heat transfer coefficient will, as a result of this, decrease mainly because of the increased viscosity. To isolate the consequences of fouling, this effect is accounted for by adjusting the heat transfer coefficient with the viscosity. For the same reason, the heat transfer coefficient is also adjusted for any change in the circulating mass flow rate. The falling film heat transfer coefficient is often described as having an exponential dependence on the mass flow rate and the viscosity:

$$h_o \propto \Gamma^a \mu^b \quad (2)$$

where Γ is the circulation mass flow rate in ($\text{kg}/\text{m s}$) and μ is the dynamic viscosity in (Pa s). For black liquor under the conditions studied in this work, Johansson et al. (2007) have suggested setting the parameters a and b to 0.26 and -0.41 respectively. The heat transfer coefficient, independently of changes in physical properties, can thus be expressed as:

$$h_{o,adj}(t) = h_o(t) \cdot \frac{\Gamma(t=0)^a}{\Gamma(t)^a} \cdot \frac{\mu(t=0)^b}{\mu(t)^b} \quad (3)$$

From the fouling resistance, fouling growth rates during the period of steady growth can be calculated as $\Delta R_f/\Delta t$; see Figure 2. ΔT is the temperature difference between the falling black liquor film and the condensation temperature of the heating steam (in $^\circ\text{C}$).

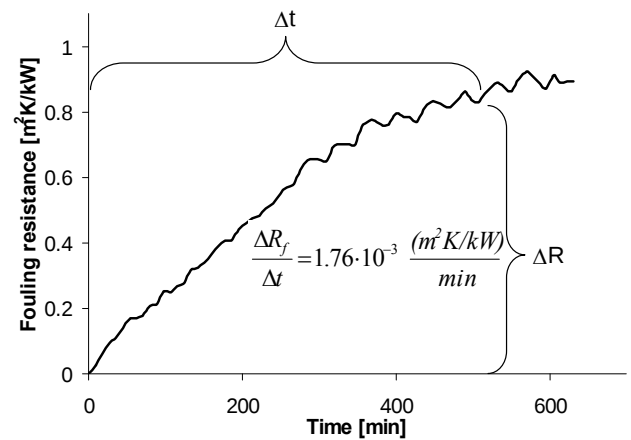


Fig. 2. Typical variation of the fouling resistance with time. Results from evaporation of black liquor with the following experimental conditions: $\Delta T = 13.7^\circ\text{C}$ and $\Gamma = 1.31 \text{ kg}/(\text{m s})$.

Experimental Procedure

The experimental results presented here are from evaporation of black liquor originating from a Swedish Kraft pulp mill using softwood. In order to get the wanted composition, the black liquor was, prior to the experiments, spiked with sodium carbonate and sodium sulphate. After adding the chemicals, the black liquor had a Na_2CO_3 / ($\text{Na}_2\text{CO}_3 + \text{Na}_2\text{SO}_4$) ratio of 0.854 and a total sodium concentration of 218 g/kg dry solids. The chemical composition of the liquor is described in detail in Gourdon et al (2008).

The research evaporator experiments were performed in batch mode. To resemble actual industrial conditions, the concentration (or actually the density) was kept constant during the experiments. During all experiments the pressure on the black liquor was kept at 135 kPa which corresponds to a temperature of about 120°C. The heating steam was controlled to obtain a constant saturation temperature throughout the experiments.

Thin black liquor was continuously fed to the evaporator system from two 0.3 m³ tanks. To keep a constant system volume, thick black liquor is recirculated to the original thin liquor tanks. The vapour condensate produced is mixed with the thick black liquor before being pumped back to the tanks. The drawback of running with a closed system is that, when precipitation occurs, the composition of the liquor will change. To avoid having varying feed concentrations, one could use a continuous feed of fresh black liquor, but this would require inconveniently large amounts of black liquor.

RESULTS AND DISCUSSION

The varied operating conditions together with some basic results for the set of experiments are summarised in Table 1. The mass flow rate is per unit of circumferential length, i.e. the tube wetting rate. The falling film Reynolds number is defined according to Schnabel and Palen (1998) as:

$$\text{Re} = \frac{4\Gamma}{\mu} \quad (4)$$

The solids fraction is defined as:

$$x = \frac{m_s}{m_s + m_w} \quad (5)$$

where m_s is the mass of dry solids in the liquid (either in dissolved or in solid state) and m_w is the mass of water. The solids fraction increase can thus be calculated from a combination of energy and water balance over the evaporator tube. The boiling in the black liquor causes a perfectly distributed film to be significantly disturbed, and large amounts of black liquor are thrown away from the tube; see Figure 3. The deposit thickness presented in Table 1 is measured with a calliper on samples taken 4 m from the evaporator tube top after the completion of the experiment. A photograph of a typical scale deposit on the evaporator tube is shown in Figure 4. In the picture a sample has been taken out and the deposit is also seen to crack.

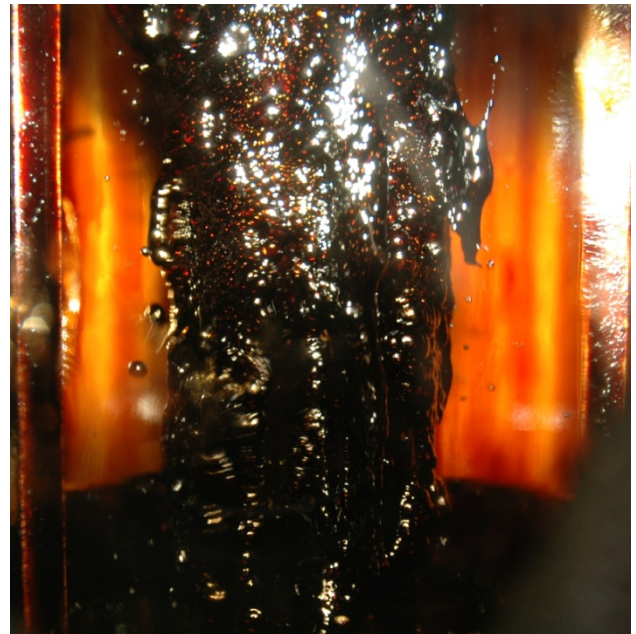


Fig. 3. Photograph of the black liquor falling film from inside the pilot evaporator. The film is heavily disturbed and contains numerous small bubbles. Liquid is frequently detached from the falling film either as small bubbles (seen to the left) or as large liquid chunks (seen to the right).

Table 1. Operating conditions and basic results for the set of experiments.

			1	2	3	4	5	6	7
Circulation mass flow rate	Γ	kg/(m s)	0.19	0.71	1.31	1.87	3.74	1.31	1.31
Reynolds number	Re		110	410	750	1070	2140	750	750
Temperature difference	ΔT	°C	14	14	14	14	14	11	26
Initial solids fraction increase	Δx_0	g/kg	39.0	10.2	8.4	5.5	3.1	5.1	12.2
Final solids fraction increase	Δx_{final}	g/kg	11.9	5.2	3.5	2.6	0.6	3.5	5.8
Deposit thickness		mm	3.4	3.5	5	5	2.4	6	6



Fig. 4. Scales on the evaporator tube after an evaporator experiment (exp #3). Deposit thickness is around 5 mm.

Effect of Mass Flow Rate

The effects of changing the mass flow rate are multiple. An obvious change will be to the Reynolds number of the falling film and thus to the heat transfer coefficient, which is roughly proportional to the mass flow rate to the power of 0.26 (Johansson et al., 2007). Also, as the Reynolds number increases, the turbulence of the falling film will generally increase. The dependence of the fouling growth rate on circulation flow rate is presented in Figure 5. The fouling rates are mean values over a time period between 5 and 11 h. The flow rates investigated in this study are all in the region between fully laminar and fully turbulent (Johansson et al., 2009). The flow of the falling film in this region is described as having pronounced rippling and surface waves of partially laminar and partially turbulent nature. These flow rate effects will influence the shear rate and thus possibly also the rate of adhesion and removal of crystals from the surface. The increased turbulence can, however, have opposing effects (Bott, 1997). As the turbulence also will enhance the mass transfer, the rate of crystal deposition can also be promoted.

The other main effect of changing the mass flow rate is the change in mass fraction increase (or concentration increase) between the inlet and outlet of the evaporator tube. This means that decreasing the flow rate will result in a steeper concentration gradient which, in turn, means that a

specific concentration will be reached higher up along the heat transfer surface of the falling film.

For the experiments presented in Figure 5, both the fouling rate and the value at which the heat transfer coefficient levelled out (reached the plateau state) were influenced by the circulation flow rate. Up to about 2 kg/(m·s), high flow rates are positive, having both a lower fouling rate and a higher final heat transfer coefficient. For the highest flow rate (3.7 kg/(m·s)) the fouling rate was not lower than for 1.9 kg/(m·s), indicating that a level is reached where it is no longer beneficial to increase the mass flow rate further to decrease the fouling rate.

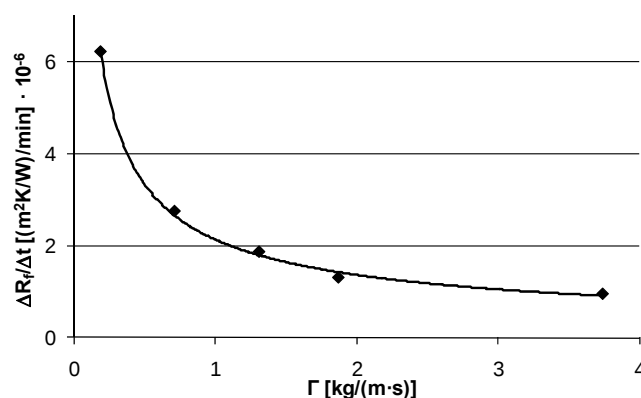


Fig. 5. Average fouling resistance growth rates for different mass flow rates.

Effect of Temperature difference

A second method for changing the mass fraction increase over the heat transfer surface is to increase the heat flux. The main method for changing the heat flux is to change the temperature difference between the heating steam and the black liquor. The evaporator is normally not operated using a fixed heat flux; rather it is the temperature difference between the black liquor and the heating steam that is controlled. Consequently, because the overall heat transfer coefficient will decrease due to fouling, the heat flux will change in the course of the experiments. In Figure 6, the fouling rates for three different temperature differences are presented. Based on the base case ($\Delta T = 14^\circ\text{C}$), the levels of the high and low temperature differences were chosen as to roughly halve and double the initial ("clean") heat flux for evaporation, i.e. after compensating for all heat losses. From Figure 6 it is seen that all temperature differences led to fouling and all experiments had an overall heat transfer coefficient levelling out with time. Again, the fouling rates presented are mean values over the first time period of the experiments where the fouling rate was relatively constant. This time period was reasonably long and varied between 8 and 11 h. It is clear that a high temperature difference gave a higher fouling rate. A high temperature difference also gave a lower final heat transfer coefficient.

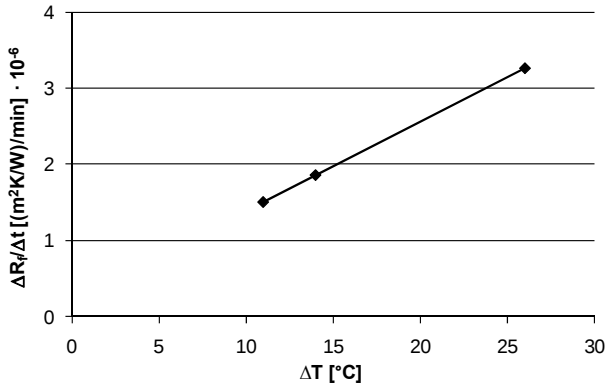


Fig. 6. Average fouling resistance growth rates for different temperature differences between the heating steam and the black liquor.

Local Fouling Rates

The local fouling resistances for three of the mass flow rates (base case and a high and low flow) are presented in Figures 7, 8 and 9. The five different local fouling resistances are labelled according to their distance from the top of the evaporator tube, i.e. from the inlet. Looking at local fouling resistances will enable the determination of the distribution of the crystals along the heat transfer surface, i.e. whether some areas are more favourable to fouling than others or whether there is a homogeneous formation along the heat transfer surface. From the local measurements (especially in Figure 9) it can be seen that the scale starts to form at the bottom of the evaporator tube and then expands upwards. A surface not suffering from fouling starts to foul only when the area beneath it has fouled.

For the lowest flow rate in Figure 7, only the highest level at 2.4 m is delayed and by only around 4 h. The reason for the simultaneous fouling on the lowest levels is probably very rapid scaling growth, probably also even during start-up. For the base case in Figure 8 the behaviour is similar, with the exception that both the top levels now have an initiation time of around 4 h. For the high mass flow rate in Figure 9 there is, however, a large difference in the fouling behaviour; the local initiation times are now very dependent on the vertical position. The initiation times for the three highest levels are also considerably longer than for the base rate. This demonstrates how the fouling grows from the bottom up.

Another way of illustrating this is shown in Figure 10 where the local initiation times are displayed for five of the experiments – base case, and high and low mass flow rate and temperature difference. The initiation time is here defined as the time from the start of the experiment until a fouling resistance of $1 \text{ m}^2\text{K/kW}$ is built up. Figure 10 shows how the low mass flow rate and the high temperature difference cause almost immediate scaling on all levels. For the high mass flow rate and low temperature difference, increasing initiation times are observed in counter-direction to the flow. The base case has a behaviour in between. The variation of the fouling growth rate with the mass flow rate and the heat flux presented in the previous sections is, consequently, not mainly a result of a thicker layer of deposits; it rather represents how high up the heat transfer

surface the scale reaches. The conclusion is that the scaling behaviour and scaling rate are affected by the locally obtained concentration.

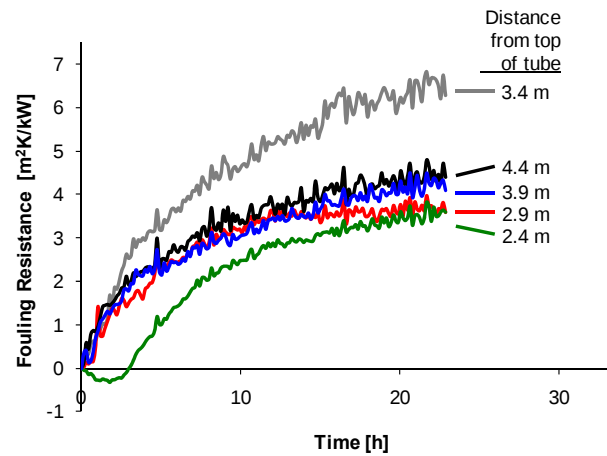


Fig. 7. Local fouling resistances at different vertical positions for experiment 2 with $\Gamma=0.71 \text{ kg/(m s)}$ and $\Delta T=14 \text{ }^\circ\text{C}$.

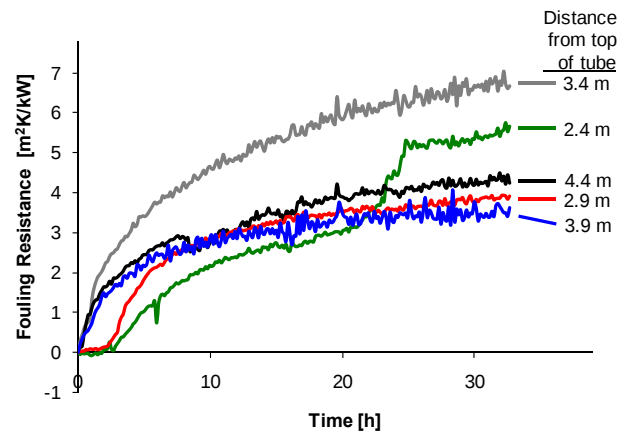


Fig. 8. Local fouling resistances at different vertical positions for experiment 3 (base case) with $\Gamma=1.31 \text{ kg/(m s)}$ and $\Delta T=14 \text{ }^\circ\text{C}$.

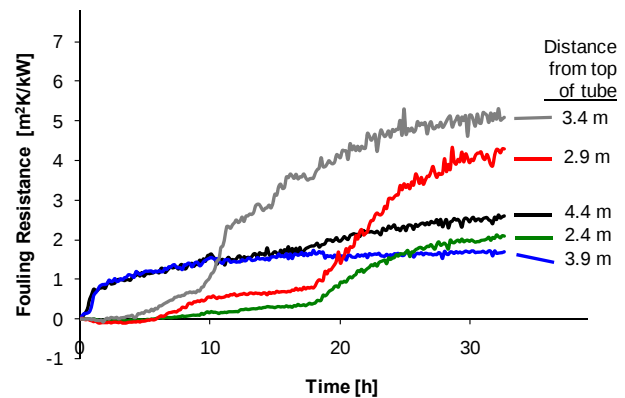


Fig. 9. Local fouling resistances at different vertical positions for experiment 5 with $\Gamma=3.74 \text{ kg/(m s)}$ and $\Delta T=14 \text{ }^\circ\text{C}$.

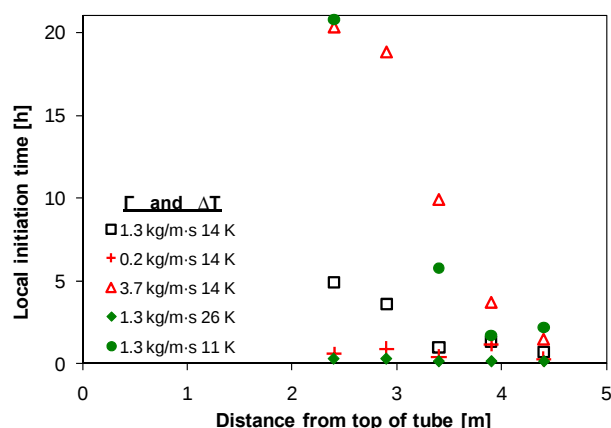


Fig. 10. Initiation time at different vertical positions along the heat transfer surface for the base case and for high and low mass flow rates and temperature difference.

Physical shear force

To evaluate the pure cleaning effect of the shear force produced by the flowing fluid, separated from the effect of the mass fraction increase, the fouling rates for all experiments are presented in Figure 11 as a function of the mass fraction increase. The mass fraction increases presented are at the initiation of each experiment (i.e. for a clean surface) and, as scale forms, these will consequently decrease and reach the final values presented in Table 1. The general idea is that if the trends for both the mass flow rate dependence and the temperature difference dependence are similar, the effect of shear force is negligible. Vice versa, if the trends are diverging and the fouling rate is more dependent on the mass flow rate, the effect of the shear force of the flow would be significant.

From Figure 11 it is seen that the fouling rate appears to have a close to linear relation to the increase in mass fraction, and that the results of different mass flow rates and temperature differences are similar. This implies that the physical shear of the flow on the scale particles must be low; otherwise the scale growth would have been different.

Other results also indicate that the effect of shear force is limited. Helalizadeha et al. (2000) discussed that a linear fouling resistance, which was the case for the experiments presented here, is generally characteristic of hard and adherent deposits and indicates either that the deposition rate is constant and there is no removal, or that the difference between deposition rate and removal rate is constant. This is in contrast to soft or fragile deposits which tear off easily due to the shear force of the flow.

The conclusion is that the fouling in the falling film black liquor evaporator is controlled by the crystallization chemistry and thermodynamics – and that the operating conditions do not, mechanically, affect the fouling but they will change the locally obtained concentration, which in turn will affect the fouling.

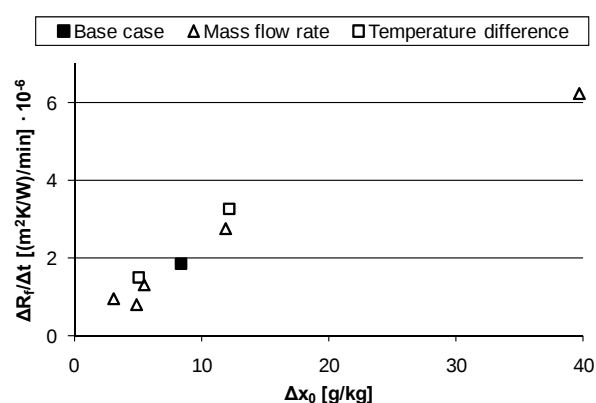


Fig. 11. Average fouling resistance growth rate as a function of the initial solids mass fraction increase (Δx_0) over the evaporator tube.

Industrial Implications

A typical pulp mill produces about 1 000 tonnes of pulp per day. In the process over 10 000 m³ of black liquor will be processed every day and this will result in a crystal mass production of approximately 200 tons per day in the evaporation plant. All of this crystal mass has the potential to scale the evaporator surfaces. In the pulp industry it is common to increase the flow velocity as a mean to increase heat transfer and to avoid scaling. The drawback is that the operating cost, and possibly also the investment cost, of the liquor circulation equipment is increased. This research has shown that increasing the flow rate will decrease the scaling rate but only because the concentration gradient is changed over the heat transfer surface, not because of increased shear force exerted by the flow on the fouling layer. Thus, any other means of changing the concentration profile would achieve similar result. One alternative is to change the temperature difference in the evaporator. However, in existing multistage black liquor evaporation plants, the temperature difference between the heating steam and the black liquor is not a parameter that can be adjusted in the individual evaporators. The individual evaporator's temperature difference will be defined by a number of parameters in the overall system, such as the total temperature difference between the temperatures of the live steam and surface condenser.

The results presented in this paper will also have implications on the washing of the evaporators as they also indicate that the cleaning process is mainly driven by dissolution. Thus the cleaning time, or efficiency, is determined not by the flow rate but rather by the concentration, over time, of the washing fluid.

Another means for decreasing the concentration increase would be to reduce the length of the tubes and instead increase the number of tubes. This could reduce the fouling, but since it is a design parameter, this can only be applied for new evaporators. The drawback of having more but shorter tubes is that the investment cost of the evaporator will increase considerably.

CONCLUSIONS

The pilot falling film evaporator experiments presented in this work have shown the dependence on mass flow rate and temperature difference in the sodium carbonate and sodium sulphate crystallization fouling. The fouling was found dependent on both these parameters and showed a relationship between the obtained mass fraction increase over the heat transfer surface and the fouling rate. The shear force of the flow, which depends on the mass flow rate, was shown to have little effect on the fouling rate.

The results of local fouling resistance measurements showed that the fouling was non-homogeneous and that the crystal deposition started from the bottom and grew upwards in counter-direction to the flow. The growth most likely represents crystal precipitation on the existing scale and agglomeration of existing crystals into the scale formed lower on the tube. A low flow rate or high temperature difference will reach a specific mass fraction increase higher up on the heat transfer surface, and this will increase the fouling rate.

NOMENCLATURE

- a* Parameter in eq. 2 and eq.3, dimensionless
- b* Parameter in eq. 2 and eq.3, dimensionless
- h* Heat transfer coefficient, W/m²K
- m* Mass, kg
- Re* Falling film Reynolds number, dimensionless
- R_f* fouling resistance, m²K/kW
- t* Time, min or h
- x* Mass fraction, g/kg
- Γ* Mass flow rate, kg/(m s)
- μ* Dynamic viscosity, Pas
- ΔT* Driving temperature difference, K
- Δx* Mass fraction increase, g/kg

Subscript

- adj mass flow and viscosity adjusted
- o outside
- 0 initial

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