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DEPOSIT FORMATION IN EVAPORATION OF A PULP MILL EFFLUENT

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ABSTRACT

A preliminary study was undertaken of the fouling of clarified wastewater from a "zero"-liquid discharge bleached chemi-thermo-mechanical pulp mill. This work concerned the fouling process which occurs in mechanical vapour recompression evaporators which comprise the first stage of the evaporation and concentration system. The clarified wastewater contains dissolved and suspended solids, both of which increase as the liquor is concentrated. Solids contain roughly 20% mineral matter and the remainder was organic material.

Thermal fouling measurements were made in a countercurrent double-pipe exchanger in which liquors of three different concentrations were heated by condensing steam. The decline in heat transfer coefficient was tracked over periods of several days at fixed steam temperature, and fluid velocity. Fouling increased with both liquor concentration and steam temperature. Soft, sludge-like deposits which contained mainly organic material were found. The inorganic fraction was about 25%, and consisted primarily of calcium, magnesium and silicon. The sources of the inorganic fraction in the deposits are discussed, and deposit analyses compared with those of the solids present in the liquor.

INTRODUCTION

As pulp mills move towards complete water recycling ("zero" liquid discharge) they have to increasingly treat wastewaters on site, in order to generate process water of quality equal to that previously supplied from outside sources. Different versions of "zero-effluent" processes are described by Young (1994a,b). Granfeldt and Suhonen (2003) discuss the bleached chemical-thermo-mechanical pulping (BCTMP) process, a simplified flowsheet of which is shown as Figure 1. Here, wood chips are first impregnated with pulping chemicals such as sodium hydroxide and sulphites, before undergoing a two-stage mechanical refining process which yields the pulp stream for peroxide bleaching, and a wastewater stream. The latter is then combined with the wastewater from the bleaching and washing process into a combined wastewater stream

which is then treated. Among chemical species in the wastewater are inorganic salts which originate with the wood, and the salts from the pulping and bleaching chemicals. Organic species in the wastewater are the degraded wood components from the pulping, refining and bleaching stages.



Figure 1 Simplified flowsheet for a bleached chemi-thermomechanical pulp mill.

Figure 2 shows a typical mill wastewater system, consisting of a clarifier, which produces an organic sludge, and the clarifier overflow which contains dissolved organic solids, and some suspended solids, depending on how well the system is operated.



Figure 2 Schematic of a typical BCTMP wastewater treatment plant

The overflow from the clarifier is evaporated to produce distillate for recycling to the pulping process, and a

stream which is further concentrated to 70 wt.% solids for combustion in the recovery boiler. The carbonate boiler ash may be expected to contain inorganic salts such as the sodium and silicates from pulping, and calcium and magnesium from the wood. The wastewater treatment system is not completely "zero liquid effluent" because of the water losses in the sludge, and other minor losses elsewhere.

The evaporator system shown consists of several mechanical vapour recompression (MVR) evaporators in parallel or in series which raise total solids concentrations from about 2 wt. % to about 20 wt. %, followed by multiple effect evaporators which raise the solids content further to roughly 35%. While all parts of the evaporator train are subject to fouling, the MVR units in particular are problematic. Mill experience suggested that depending on the operation of the clarifier, the MVR units can undergo a 50% decline in heat transfer coefficient over periods from a few weeks to several months. This experience prompted the present work, the objectives of which were to investigate the causes of the fouling problem, what conditions promoted fouling, and how fouling could be mitigated.

EXPERIMENTAL METHODOLOGY

The experimental methodology comprised three steps: (i) characterization of the MVR feed liquor, (ii) batch evaporation and deposition in a boiling flask, (iii) preliminary fouling experiments in a steam heated recirculation flow loop, with detailed characterization of solids.

It was evident that the MVR feed liquor samples contained some suspended solids - these were determined by vacuum filtration through a filter of 3-micron pore size. To determine total solids, a drying time of 68-h at 105°C was needed to obtain reproducible total solids values. Significantly shorter drying times were found to produce a gel-like residue. Solids, and deposits from subsequent deposition and fouling experiments, were characterized by thermo-gravimetric analysis (TGA), ultimate analysis, scanning electron microscopy (SEM) with electron dispersive X-ray (EDX) measurements, and X-ray diffraction (XRD). Inductive coupled plasma (ICP) methods were used on concentrated liquors, solids and deposits.

Liquors from 2 to 16 wt% solids concentrations were prepared for characterization by evaporation in a jacketed flask with condensate recovery. The batch reactor was then equipped with a submerged electrical heater, and liquor (2 wt. % solids), was injected in steps to raise the total solids to 23 % at constant volume to check for deposit formation. Deposits were observed to form at the three-phase interface of liquor, vapour and reactor wall, rather than on the submerged heater surface. These deposits and liquors were then characterized.

Thermal fouling experiments were carried out in a recirculation flow loop (Li *et al.*, 2007) equipped with a vertical double-pipe heat exchanger, whose dimensions are given in Table 1.

Table 1 Dimensions of Heat I	Exchanger Test Section
Annulus inner tube	
Length (mm)	835
Inside. Dia. (mm)	8.0
Outside Dia. (mm)	9.5
Annulus outer tube	
Length (mm)	692
Inside Dia. (mm)	25.4
Outside Dia. (mm)	28.5
Flow area (cm ²)	4.36
Heat transfer area (cm ²)	206

Saturated steam was maintained at constant pressure in the inner tube of the double-pipe exchanger; deposits formed on the outside of this 9.5 mm OD tube. Inlet and outlet temperatures were measured for both fluids. The procedure was as follows: About 8-L of liquor was placed in the feed tank. Flow was started around the loop and the liquor temperature raised to the desired value using the feed tank heater. The steam was then turned on to the test section, and data logging began. In a typical experiment, under mildest conditions, the inlet temperature of the wastewater was set at 93°C, which yielded an outlet temperature of about 99°C. The average of inlet and outlet steam temperatures, T_s, was about 113°C (160 kPa). In subsequent runs, the average steam temperature was raised to ~137°C (P ~330 kPa), and the inlet liquor temperature raised to 97°C. The fluid pressure at the probe was typically 240-310 kPa, such that only sub-cooled boiling would occur. Thus the concentration of solids in the liquor did not change with time. Run durations were from 22 hours to 142 hours. Occasionally there was a drift of operating conditions overnight when the unit was left unattended. With constant steam pressure in the test unit as fouling occurred, the heat flow and hence the outlet liquid temperature decreased. Fouling was tracked based on heat flow to the liquor, a log-mean temperature driving force with an average steam temperature, and a heat capacity for the liquor assumed equal to that of water (Equations 1-4):

$$Q = m_L C_{F_L} (T_{L,out} - T_{L,in}) \tag{1}$$

$$\Delta T_m = \left[T_{L,out} - T_{L,in} \right] / \ln \left[\left[T_s - T_{L,in} \right] / \left[T_s - T_{L,out} \right] \right] (2)$$

$$U = Q/[A\Delta T_m] \tag{3}$$

$$R_{f} = 1/U - 1/U_{c} \tag{4}$$

where U_C is the value of the overall heat transfer coefficient under clean conditions. The initial fouling rate was determined from the slope of the linear portion of the plot of 1/U versus time.

RESULTS and DISCUSSION

Table 2 lists properties of the MVR feed sample, and the resulting concentrated liquors from the batch evaporation experiments. The original MVR feed contained 2.8 wt.% total solids, and 0.43% suspended solids. The presence of suspended solids suggests that the clarifier operation was not perfect, and indicates that the MVR feed could contribute to particulate fouling in the evaporator train. As the total solids concentration is raised, the fraction of the total solids which is present as suspended solids increases. Both density and apparent viscosity (measured in a rotary viscometer) increase as the water is evaporated from the MVR feed.

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Effluent	MVR	Medium	High
EIIIuein	Feed	Conc'n	Conc'n
Total solids	2.76	7.77	16.56
(wt.%)			
Susp. Solids	0.43	1.55	3.62
(wt.%)			
Dissol. Solids	2.33	6.22	12.74
(wt.%)			
Density	1020	1050	1100
(kg/m^3)			
Dyn.Visc. at	1.32	1.91	4.36
25°C (mPa.s)			

Table 3 shows results from thermo-gravimetric analysis of the total and suspended solids from the liquors, as well as the deposits from the batch evaporation experiments described above. The procedure for these analyses was similar to that for "proximate analysis" of solid fuels. The sample is heated in nitrogen to 900°C, and held at that temperature for 10 minutes, to obtain volatile content and non-volatile "fixed carbon + ash". Air is then introduced such that the carbonaceous matter is burned, and the remaining material represents the ash. For the present cases, small positive or negative changes in weight were found when the air was introduced, which suggests that the carbonaceous fraction of the non-volatiles was low. Hence it appears that the 21% non-volatile content was mineral matter, and that the suspended and total solids and the batch deposits were similar in composition, with roughly 78 wt% volatile matter.

 Table 3 Thermo-gravimetry of Solids and Batch Deposits

	Volatile	Non-volatile	Change	Mineral
Sample	to 900°C	to 900°C	in air	matter
	(Wt.%)			
Total	78.7	21.3	+3.3	21.3
solids				
Susp.	76.1	21.9	-2.7	19.2
solids				
Batch	79.7	20.3	+5.0	20.3
deposits				

Thermal fouling experiments were carried out at low $(113^{\circ}C)$ and high $(136-7^{\circ}C)$ steam temperatures, with solids concentrations equivalent to MVR feed, feed with 70% of water evaporated (~8 wt. % solids), and with 84 % water evaporated (~15.0 wt. % solids). Inlet liquor bulk temperatures were initially set at 93°C, and then raised to 97°C in later runs. These conditions were chosen to approximate a reasonable range of conditions in the multiple vapour recompression evaporators.

Declines in clean heat transfer coefficient were negligible to slight at 2.8 wt% solids, steam temperature of 113° C, and with velocities varying from 0.28 to 0.53 m/s. A significant drop in heat transfer coefficient from 2.15 kW/m²K to 1.45 kW/m²K occurred over 40-h when the temperatures of the steam and liquid inlet were raised, at a low superficial velocity, as seen in Figure 3.



Figure 3 Decline in U with time for 2.8% total solids at T_L = 97°C, T_s = 136°C, V= 0.2 m/s

The effect of these changes in temperature on R_f versus time are shown in Figure 4. For the data at $T_s = 114^{\circ}C$ (Fig. 4a), the above-mentioned slight decrease in heat transfer coefficient gives barely detectable R_f values (~0.025 m²K/kW) after about 10-h, and no further increase to 24-h. At 136°C steam temperature (Fig. 4b), R_f values a factor of ten higher (~0.22 m²K/kW) are reached after about 36-h. The scatter of the data permits only an estimation of fouling rate. Initial fouling rate is about 8E-07 m²K/kJ at $T_s = 114^{\circ}C$, and 13E-07 m²K/kJ over the period 0-30 hours at 136°C, which is an approximate doubling of the fouling rate for the 22°C increase in steam temperature.

The effect of solids concentration on fouling was studied at the more severe operating conditions of $T_s = 136-137$ °C, and $T_{L, in} = 97$ °C, as shown in Figure 5. At 15% total solids, fouling is rapid and severe, yielding R_f of 0.6 m²K/kW after about 30-h, whereas at 8% solids, R_f reaches only half of this value, 0.25 m²K/kW. For 2.8% solids, R_f also reaches 0.2 m²K/kW, but at a slower rate than for 8% solids. Initial rates for the two runs at lower percentage solids are difficult to assess, but are of the order of 20E-07 m²K/kJ, whereas at 15%, the rate is about 35E-7 m²K/kJ.



Figure 4 Fouling resistance versus time for liquor of 2.8 % solids at (a) $T_s=114^{\circ}C$, $T_{L,in} = 92^{\circ}C$, and (b) $T_s = 136^{\circ}C$, $T_{L,in} = 97^{\circ}C$.

When the tube was removed from the test section, deposits were found to be soft and gel-like, and easily removed. They were generally uneven over the tube length, being thickest at the hot end of the double-pipe exchanger. Figure 6 shows a photograph of a heavy, rough deposit at the hot end of the test section. Examination under magnification showed the presence of holes in the deposits, which was attributed to boiling on the metal tube surface, as seen in Figure 7.

Deposits were characterized using thermo-gravimetric analysis, elemental analysis, and SEM-EDX. Liquors and some deposits were also analyzed by ICP methods. Tables 4 and 5 present some results. Generally, there were wide ranges of compositions found, as shown in Table 4. Deposits averaged 73 % wt. volatile material at 900°C, and 26 wt.% mineral matter. The organic fraction of the deposit averaged 43 % wt. carbon and 5.7 wt. % hydrogen, with an atomic ratio H/C of 1.6. The total liquor solids differed from the deposits, being lower in carbon and hydrogen content, lower in H/C ratio, and higher in oxygen+ nitrogen.



Figure 5 R_f versus time at a steam temperature of 136-137°C for liquors of different total solids concentrations (Wt.% Solids : $\blacklozenge = 15$, $\blacksquare = 8$, $\blacktriangle = 2.8$)



Figure 6 Deposit at hot end of test section for 142-hour run for 2.8% Solids at T_s = 136°C, $T_{L,in}$ = 97°C, V = 0.2 m/s



Figure 7 Close-up photo of deposit surface showing evidence of boiling underneath the deposit (magnification ~40 times)

 Table 4 Elemental and Thermo-gravimetric Analyses of Deposits and Total Liquor Solids

	Deposit	Deposit	Total Liquor
	Range	Average	Solids
% wt. Volatile*	60-85	73	79
% wt. C	39-50	43	30
% wt. H	4.9-6.9	5.7	3.7
% O+N (diff.)	19-32	25	45
H/C (atomic)	1.5-1.7	1.58	1.47
% Minerals	16-34	26	22

* at 900°C

The mineral content of the deposits was over 25% on average, therefore the make-up of the inorganic fraction was of interest. The deposits were analyzed using EDX and XRD. The values given in Table 5 represent the average surface analyses of several spots from EDX analysis. Calcium plus magnesium accounts for 6.4 % of the deposit from the 2.8 % solids stream, decreasing to 3.1 % for the deposits from the 15% solids stream. Silicon, presumably from the NaSiO₃ added in peroxide bleaching (Fig. 2) is present in deposits at 3-6% wt. Carbon decreases, and oxygen increases in deposits as the percentage solids in the stream increases. The Total Liquor Solids samples show lower metals and silicon content than for any of the deposits, except for sodium + potassium. This is not surprising, as metals which produce insoluble salts should accumulate in the deposits, whereas sodium and potassium which produce soluble salts are at considerably lower concentrations in the deposits. These analyses show that as the percentage solids in the liquor is raised, the deposits become closer in composition to that of the total solids. As seen above in Table 2, as percentage solids in the stream increases, so does the concentration of suspended solids and perhaps the tendency to cause particulate deposition. If particulate fouling increasingly occurs as concentration becomes higher, deposit composition should approach that of the solids.

Table 5 EDX Analyses of Deposits and Total Liquor Solids

Percent	Deposit	Deposit	Deposit	Total
By	2.8%	8%	15%	Liquor
Weight	Solids	Solids	Solids	Solids
% (Ca+Mg)	6.44	5.2	3.1	2.3
% (P+S)	1.8	1.3	1.7	1.0
% Si	3.5	6.3	3.1	0.2
% (Na+K)	0.9	2.9	8.7	13.8
% O	28	34	39	47
% C	58	50	44	34
O/C atomic	0.36	0.51	0.66	1.0

Zhang, et al., 2002 reported calcium oxalate deposits in re-circulating process water, however no information on evaporator deposits was reported. The XRD results obtained on the deposit samples of the present work can only be considered as qualitative, due to the sample size limit and the presence of large amounts of amorphous material. XRD analysis of the deposit samples showed that calcite (CaCO₃) weddellite lime (CaO), and $[Ca(C_2O_4).2H_2O]$ were present in all three deposit samples. A significant amount of whewellite (CaC2O4.H2O) was found only in the deposit from the 15% solid stream, while ankerite $[Ca(Fe^{2+},Mg,Mn)(CO_3)_2]$ was present in deposits from both the 2.8% and 8% solids streams. Enstatite (MgSiO₃) was identified in deposits from both 8% and 15% solids streams, but was not detectable in the 2.8% solid stream deposit, in which thenardite (Na₂SO₄) was found.

The weight-loss behaviour in the thermo-gravimetric analyzer is shown in Figure 8. The similarity of the weightloss curve versus temperature (up to 800°C) for the deposits from fouling runs at different percentage solids is evident. As the percentage solids increases, the curves for the deposit approach that of the suspended solids. The total solids thermo-gram is somewhat different, showing very little weight loss between 600 and 700°C.



Fig. 8 Thermo-gravimetric analysis of total solids (TS), suspended solids (SS), and Deposits (D-TS)

CONCLUSIONS

A preliminary study of fouling in BCTMP pulp effluent steams has shown that:

Increasing liquor total solids from 2.8 to 16 % was found to increase the suspended solids from 0.4 to 3.8 %. This increase would favour particulate fouling as the extent of evaporation increases throughout the evaporator system.

The heat transfer coefficient decrease with time became larger as the steam temperature was raised from 113 to 137°C and percent total solids was raised from 2.8 to 16%,

Thermal fouling resistance at a given time, and fouling rate increased both with steam temperature and solids concentration.

The order of magnitude of fouling rates was approximately similar to that observed in MVR evaporators, although the present tests were run at low velocities and Reynolds numbers.

Fresh deposits were soft and non-crystalline; they contain about 30 % mineral matter and 70 % organic material volatile at 900°C. As percentage solids in the liquor increases, deposit analyses approach those of the total solids. On average, deposits analyzed over 5 % (Ca +Mg), 4.6 % Si, and had H/C of 1.6, and O/C of 0.4.

Further experimentation, including flow effects are required to confirm a working mechanism of fouling.

NOMENCLATURE

- A external area of inner tube of test section (m^2)
- P saturation pressure of steam (kPa)
- Q heat flow (kW)
- R_f thermal fouling resistance (m²K/kW)
- T_L liquor temperature (°C or K)
- T_s steam temperature (°C or K)

- U overall heat transfer coefficient, based on A (kW/m^2K)
- V bulk liquid velocity (m/s)
- Re Reynolds number based on equivalent diameter

Subscripts In inlet Out outlet C clean

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