

# Minimizing fouling in spiral heat exchangers at a BCTMP mill

WINNER OF THE  
NATIONAL STUDENT  
PROBLEM-SOLVING  
COMPETITION

By M.R. HAQUE

**Abstract:** This paper investigates the cause of calcium oxalate ( $\text{CaC}_2\text{O}_4$ ) fouling in spiral heat exchangers.  $\text{CaC}_2\text{O}_4$  solubility decreases with lowering temperature. The predicted precipitation rate due to temperature difference was consistent with the observed fouling rate. This observation suggests that the effluent supersaturates and forms precipitate (scale) upon contact with the cold heat exchanger surface. Suspended particles then accumulate and cause rapid fouling. This study recommends using physical separation methods and partial replacement of NaOH with  $\text{Mg}(\text{OH})_2$  during alkaline bleaching to reduce  $\text{CaC}_2\text{O}_4$  content and minimize fouling.

**H** HEAT EXCHANGER FOULING or scaling are general terms that involve the deposition of extraneous material on the heat transfer surface of a heat exchanger. Although both deposits commonly occur together, deposits from fouling are known as foulants, whereas deposits from scaling are known as scales. Scale is a hard mineral deposit that usually precipitates from the solution and grows in the same place. Foulants are often high in organics and are formed from suspended solids at a point other than where they deposit. Both types of deposits introduce a layer of heat resistance and reduce the operational capability of the heat exchanger. In severe cases, the deposit can be strong enough to interfere with effluent flow and increase the pressure required to maintain flow rate through the heat exchanger.

Deposits of inorganic salts are a common problem in domestic, commercial and industrial processes where 'dirty' water is used. Industrialized nations worldwide annually spend 30 billion \$US to deal with this problem [1]. The pulp and paper sector contributes significantly to this expenditure because of the buildup of inorganic and organic materials in the process water.

Calcium carbonate, calcium oxalate and calcium sulfate are the most persistent scaling components in the pulp and paper industry. These compounds have low solubility products and tend to deposit where abrupt temperature or pH fluctuations exist [2]. The effect of temperature change often makes heat exchanger surfaces ideal candidates for fouling. Frequent fouling of heat exchangers can cause significant fluctuations in plant operation and requires both time and manpower to clean up.

In order to take preventive measures to reduce the fouling frequency, it is important to identify the nature of the scaling component and understand the fouling mechanism. The mechanism subsequently exposes the relationship between fouling potential and temperature, pH or any other factor in the process. This thesis investigates an existing heat recovery system located in a pulp mill which has been plagued with frequent fouling problems.

## BACKGROUND

### *High Yield BCTMP Mill*

The undisclosed pulp mill is situated in Quebec (referred to as 'pulp mill' henceforth) and employs a bleached-chemo-thermo-mechanical pulping (BCTMP) process to convert wood chips to pulp. This is primarily a mechanical process, with production yields over 80%. Maple, birch or aspen wood are chipped and fed, along with water, to the refiners, as shown in Fig. 1. In the refiners, chips are converted to fiber under high shear stress and high temperature. The pulp stream is then washed and passed through a two-stage alkaline peroxide bleaching stage. Water is pumped to facilitate the flow of bleaching chemicals and to wash the bleached pulp at the last press. The pulp mill operates three highly closed water loops, as seen in Fig. 1. Water is recycled between the latency-washing, refining-washing, and washing-bleaching stages to conserve water and reduce environmental impact [3]. Water circulation, however, causes accumulation of chemicals such as oxalate, extractives, lignin, hemicelluloses, cellulose, calcium and magnesium. These chemicals deposit on downstream equipment (ex: heat exchangers) and cause fouling problems [3].

### *Heat Recovery System*

The heat recovery system was installed in 1994 as part of the pulp mill's initiative to recover thermal energy from the effluent discharged from the BCTMP process. The system plays a critical role in maintaining the high energy efficiency of the mill. The effluent is stored in a storage tank, from there it is pumped through the three spiral heat exchangers before being sent to an activated sludge plant (ASP) for treatment. A fluctuating effluent temperature between 70°C to 80°C represents the potential low grade thermal energy that is recoverable. The heat recovery system also helps maintain the downstream temperature required for ASP operation.

The original setup has undergone many changes to deal with malfunctioning equipment and constant fouling problems. The latest setup employs three heat exchangers (HEXs), as shown in Fig. 2. Cold river water at seasonal temperature

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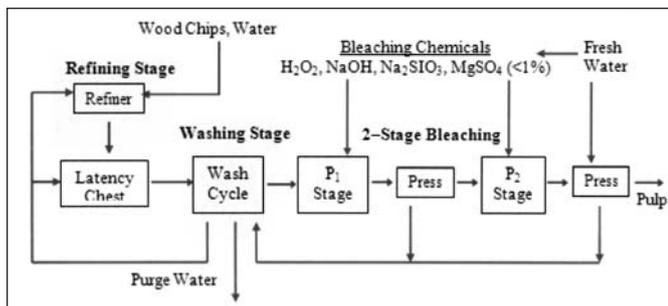


FIG. 1. Schematic of pulp flow in BCTMP mill (modified from Zhang et al [3]).

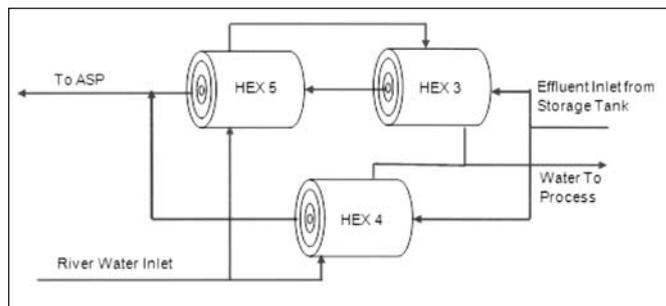


FIG. 2. Effluent flow configuration through the heat exchangers (HEXs) in the recovery system.

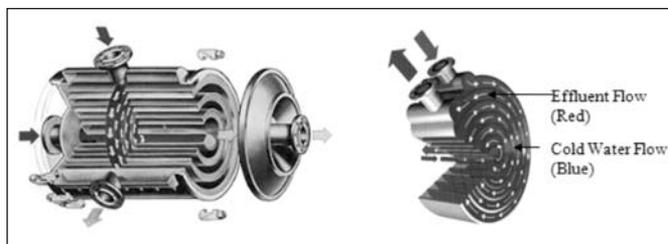


FIG. 3. Internals of a spiral heat exchanger [5].

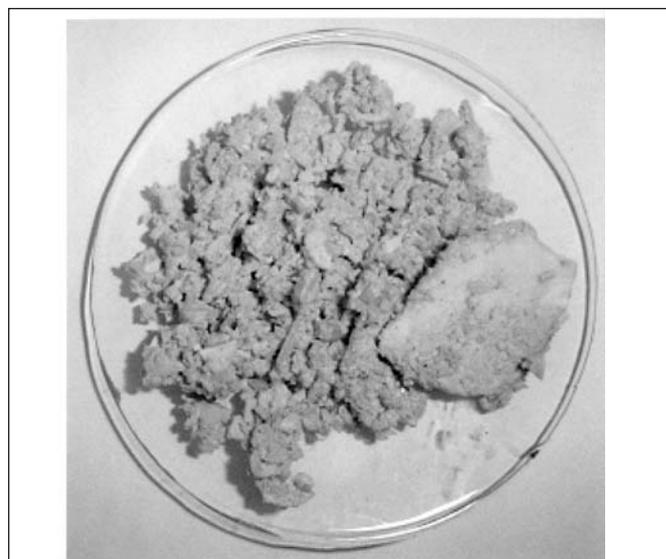


FIG. 4. Dried hard Scale sample.

is used as the coolant liquid. The heated river water is then sent to the mill for use.

The three heat exchangers at this mill are refurbished spiral units manufactured in 1973. The original manufacturer was American Heat Reclaiming Corporation (AHRC), which has since been bought by Alfa Laval Inc. Originally one of the heat exchangers was a larger unit, and hence two smaller heat exchangers were arranged in series to have comparable effect. In 2004, however, the larger heat exchanger broke down and was replaced with a smaller AHRC unit.

Spiral heat exchangers are made of two flat plates, which are wrapped around each other to create two concentric channels of rectangular cross section. The warm effluent and cooling water flow in countercurrent direction, Fig. 3, maximizing the heat transfer efficiency [4,5].

The rectangular single channel geometry means that the cross-sectional area decreases with settling solids, increasing velocity of the effluent. According to Alfa Laval, the high velocity sweeps and removes the settled solids. This increases the amount of solid that can be present in the effluent without fouling up the heat exchanger [4,5]. For this reason, spiral heat exchangers have been employed in fouling prone applications such as PVC slurry, oleum-processing etc. A decrease in channel spacing, however, decreases the maximum solids concentration that can be handled by the heat exchanger. It is possible that inadequate spacing is a reason for fouling in the AHRC heat exchangers.

The spiral heat exchangers have been experiencing severe fouling problems since installation. The pulp mill has observed the formation of porcelain like hard scales on the surface of the heat exchanger. It has also been observed that fiber, particulate matter and other foulants also deposit on the scale, eventually blocking up the heat exchanger, Fig. 4.

Every time a heat exchanger blocks up, it has to be bypassed and blasted with high-pressure water for scale removal. This results in a loss of heat transfer by the system. It has been estimated that \$400,000+ has been spent to improve the system with the intention of reducing fouling rate. Major work has been done to direct the effluent flow to a storage tank to maintain stable and constant flow rate. Despite the significant investment and effort, the rapid fouling problem remains. It has also been noted that HEX 5, as seen in Fig. 5 before and after cleaning, has been fouling up more often than the other two HEXs in the mill. A thor-

ough understanding of the cause of fouling has yet to be determined. Hence, a suitable solution to the problem still awaits.

**Previous Scale Analysis**

In order to determine the inorganic composition of the scale, X-ray fluorescence spectroscopy was performed after ashing dried scale samples. Table I displays the results of the scale analysis performed in 1998. It is seen that the inorganic portion of the deposits is mainly calcium salts. It was also found that calcium oxalate (CaC<sub>2</sub>O<sub>4</sub>) was the major form of calcium salt present in the sample. The analysis was showed that 70.4% of the deposit was made of calcium oxalate.

Additionally, calcium oxalate deposits have also been found at other points in the pulp mill. A study of calcium oxalate deposits has been performed in the disc filter shower and rejects press samples by Zhang et al [3]. This study provides a mechanism for the formation of calcium oxalate in a BCTMP mill. Relevant results from this study have been included in this thesis, which specifically tries to determine the cause of scaling in the spiral heat exchangers.

**OBJECTIVES**

The overall objective of this thesis is to determine the cause of fouling in the spiral heat exchangers and suggest practical measures to reduce formation of scale. Understanding the fouling mechanism would help identify effective solutions. The breakdown of objectives is as follows:

- a) Characterize the nature of the scale deposits
- b) Once the scale composition has been identified, speculate on the mechanism of scale formation
- c) Identify possible upstream processes, operating conditions or

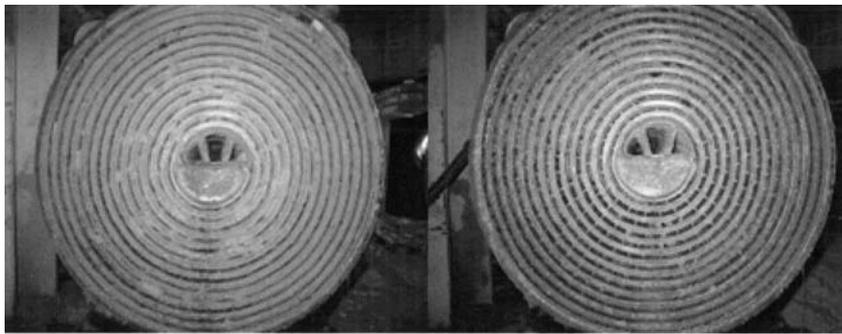


FIG. 5. Cross Sectional view of HEX5 before (left) and after (right) high pressure cleaning.

other factors which are unknown as of yet that contribute to the rapid scale formation d) Suggest possible measures to solve the frequent scaling problem, including separate handling and treatment of contributing streams in order to delay scale formation

## METHODOLOGY

A combination of process data analysis and thermal analysis (TA) experiments was performed to determine the mechanism of fouling in the heat exchangers. Thermal analysis was used to identify the main chemical present in the scale samples obtained from the pulp mill. Data analysis was used to find the effect of pressure, temperature and flow rate on fouling.

### Identifying Scale Components

Thermal analysis was chosen to confirm the suggestion that calcium oxalate is the main scale component. Investigation of calcium oxalate by thermal analysis is also well documented by other researchers [6,7]. This aids analysis of the thermograph trends and is further discussed later in this paper. Scale samples were collected from three points along the spiral heat exchangers, as shown in Fig. 6, to determine if the scale was the same along the heat exchanger. The samples were stored in airtight containers and oven dried at 85°C for 48 hours before using the thermal analyzer. TA Instruments Model No. Q600 (Simultaneous Differential Scanning Calorimeter and Thermogravimetric DSC/TGA Analyzer) was used.

A platinum crucible was tared and approximately 10 mg dried scale sample collected inside. An inert atmosphere was maintained with nitrogen flowing at 100 mL/min. The temperature setting was set to increase at 20°C/min up to 1000°C. The thermographs were recorded in the computer and displayed the change in mass loss (wt%) and heat flow (mW) as temperature increased. The heat exchanger scale sample thermographs were compared with reference calcium oxalate thermographs to confirm the type of scale.

### Determining Degree of Saturation of Solution

Once the type of scale was established, the

next step was to characterize the effluent flowing through the heat exchangers. It is well known that the saturation level influences the potential of a solution to form scales. Supersaturation has been mentioned as the primary cause of scale deposition. When the solubility of the deposited material is exceeded, the material precipitates and forms scales [8,9]. It was thus important to characterize the degree of saturation of the solution.

Figure 7 is a photograph of the effluent sample obtained from the pulp mill, showing the suspended particles which have settled to the bottom. The following experiment was performed to determine the amount of soluble and insoluble particles present in the solution.

The procedure begins with weighing an empty filter paper (Ahlstrom Filter, Grade 601, Size 9 cm). The stock effluent solution was then mixed thoroughly and 100mL transferred to a beaker. The effluent was filtered, followed by washing the residue with distilled water (without losing residue) to remove trapped substances. The filter paper with the residue was then carefully transferred onto a wash glass and dried overnight at 85°C. The final weight of the filter paper with dried residue was then recorded. A 10mg sample of the residue was then analyzed in the thermal analyzer to determine the calcium oxalate content of the suspended particles. A schematic of the procedure is shown in Fig. 8.

### Process Data Analysis

Process data spanning one year (October 1, 2004 to September 30, 2005) was analyzed. The data was obtained from the performance indicator (PI) system in the mill, which records real time data. The analysis was limited to temperature and flow rate readings around the heat recovery system. The temperature readings were used to investigate the effect of temperature on solubility. The flow rate trends were used to estimate the scale growth rate.

Figure 9 shows the process variables that were configured online around the heat recovery system of the pulp mill.

TABLE I. Scale analysis results.

Element	% Ash
Calcium	96.9
Silica	1.3
Magnesium	0.5
Aluminium	0.4
Iron	0.3
Manganese	0.2
Strontium	0.2

Manual temperature readings were collected during March 9<sup>th</sup> and 10<sup>th</sup>, 2006 and marked as MT in the diagram.

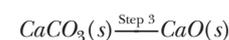
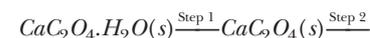
## RESULTS AND DISCUSSIONS

This section details the results obtained from the procedures mentioned above. Several research papers are cited that support the proposed mechanism of scaling.

### Composition of Scale Components

X-ray fluorescence spectroscopy initially suggested that calcium oxalate is the main scale component. To verify this result, thermographs obtained from the sample scale analysis had to be compared to reference calcium oxalate monohydrate thermographs. A thermograph displays the percent mass loss (wt%) and heat flow (mW) trend of a sample as temperature increases. Both mass loss and heat flow are characteristic for a given compound as decomposition occurs via a series of distinctive exothermic and/or endothermic steps. The thermograph for pure calcium oxalate monohydrate is shown in Fig. 10.

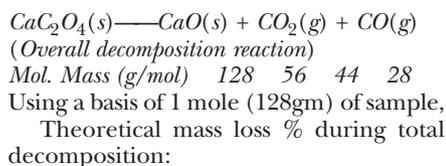
The thermograph shows three distinct steps for calcium oxalate decomposition. These correspond to the following sequence of reactions [6].



The dehydration step (step 1) corresponds to a mass loss of 10%, as indicated in Fig. 10. The decomposition to calcium carbonate (step 2) results in a mass loss of 18%, followed by 30% mass loss to calcium oxide (step 3). These steps are subsequently compared to the thermographs obtained from the actual scale samples, Fig. 11.

The second and third step, with corresponding losses of approximately 18% and 31%, match the reference thermograph in terms of percent mass loss and the temperatures at which the mass loss occur. This confirms that the scale sample does contain calcium oxalate. The insignificant mass loss in step 1 can be attributed to drying at 85°C. The drying possibly released the hydration water from the calcium oxalate before it was tested with the thermal analyzer. Thus only slight change in mass loss occurs at low temperature. The percentage of calci-

um oxalate in the scale is estimated by the following calculation.



$$\frac{\text{Mass of Gas Evaporated}}{\text{Total Mass of Sample}} \times 100\% =$$

$$\frac{(44 + 28)gm}{128gm} \times 100\% = 56\%$$

Actual mass loss % from thermal analysis experiment, Fig. 11: Step 2 + Step 3:

$$\frac{\text{Mass of Gas Evaporated}}{\text{Total Mass of Sample}} \times 100\% = 49\%$$

Percentage of calcium oxalate =

$$\frac{49}{56} \times 100\% = 87.5\%$$

Calcium oxalate has three different hydrated forms: monohydrate, dihydrate and trihydrate. Monohydrate is the most stable and has the lowest solubility [2]. Thus it can be speculated that calcium oxalate monohydrate (CaC<sub>2</sub>O<sub>4</sub>·H<sub>2</sub>O) is the main component (87.5%) of the heat exchanger deposit. The study by Zhang et al. also showed that the pulp mill disc-filter shower and reject press had calcium oxalate deposition [3]. This suggests that the mill has been experiencing calcium oxalate scaling problems elsewhere in the system and thus it is likely that in the heat exchangers, the scale type is indeed calcium oxalate.

**Determining Fouling Rate**

Once the type of scale has been determined, the next step involves quantifying fouling rate based on a few simplified assumptions. The flow rate trends over a one-year period through HEX 3 & 5 and through HEX 4 are plotted in Figs. 12 and 13.

The flow rate trend shows the extent of the fouling problem in the pulp mill. Maximum flow is achieved immediately after high pressure cleaning. Then the scaling material and foulants begin to deposit and slowly reduce the flow rate, eventually plugging up the heat exchanger. The deposit build-up reduces the flow channel area. This increases the pressure drop across each heat exchanger and reduces the flow rate through the system.

The change in flow rate over time is thus a function of fouling rate. A faster fouling rate leads to a steep decrease in flow. Subsequently a slower fouling rate takes longer to affect flow. The change in flow rate over time, the slope in Figs. 12 and 13, can thus be used to estimate fouling rate.

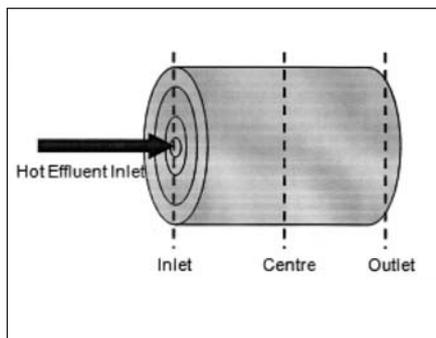


FIG. 6. Positions of sample scale collection.



FIG. 7. Pulp mill effluent.

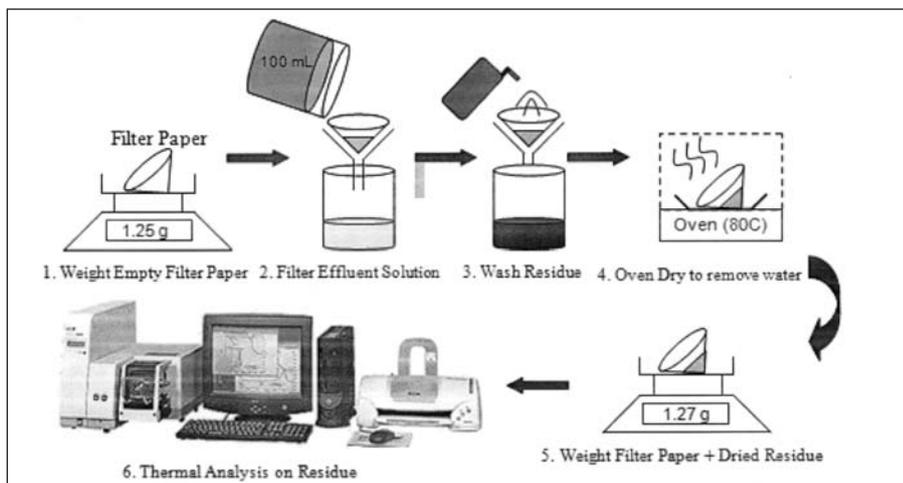


FIG. 8. Schematic of procedure to measure level of saturation of effluent solution.

$$\frac{d(\text{flowrate})}{dt} = f(\text{Fouling rate})$$

The following assumptions are made in order to quantify the fouling rate.

- The spiral heat exchanger surface is flattened into a rectangular cross section, Fig. 14
- Effluent velocity remains constant over time
- The fouling rate is constant over time

For a constant velocity, the volumetric flow rate is defined as

$$\text{Volumetric Flowrate} = \text{Velocity} \times \text{Unblocked Area}$$

The maximum flow occurs at time = 0, when the deposit thickness (t) = 0 and channel spacing (b) = 15.875mm (heat exchanger inner channel). As time increases, the t is increased by a constant value (fouling rate) until the channel completely blocks up. The fouling rate that best matches the actual flow rate profile with the theoretical profile, shown in Fig. 15, is selected as the correct estimated fouling rate. The same treatment is applied to analyze individual slopes for all data. The average results are presented in Table II.

It is seen that the series arrangement of HEX 3 and 5 foul up faster than HEX 4. This agrees with mill observations that

they have to clean HEX 5 more often. It is also seen that the fouling rate through HEX 3 & 5 increased after April 2005 and the average maximum flow after scale removal decreased after April 2005, note the boxed area in Fig. 12.

Both observations suggest that the heat exchanger cleanup procedure was changed in April 2005, inversely affecting the heat exchanger performance. The pulp mill confirmed that, before April, an external company cleaned the heat exchangers with a high-pressure water hose. Since April, the cleaning has been done internally with a lower pressure hose to reduce operating expenses. The effect of inefficient cleaning thus had significant impact on fouling rate. This is discussed in detail in a later section.

**Calcium Oxalate Formation**

Once it is confirmed that there is excess calcium oxalate passing through the heat recovery system, it is important to determine the source of the calcium and oxalate ions in the BCTMP process. Zhang et al. have done significant work on the formation of oxalate in a BCTMP mill with a similar configuration to our pulp mill [3]. They have investigated the BCTMP process and identified 3 sources of oxalate: input with wood, refining stage and bleaching stage.

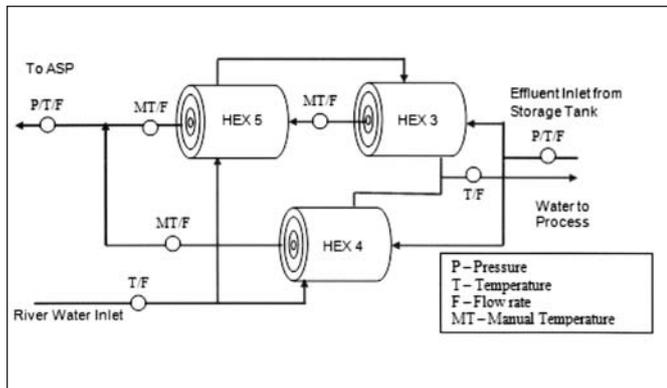


FIG. 9. Data points available around the Heat Recovery System.

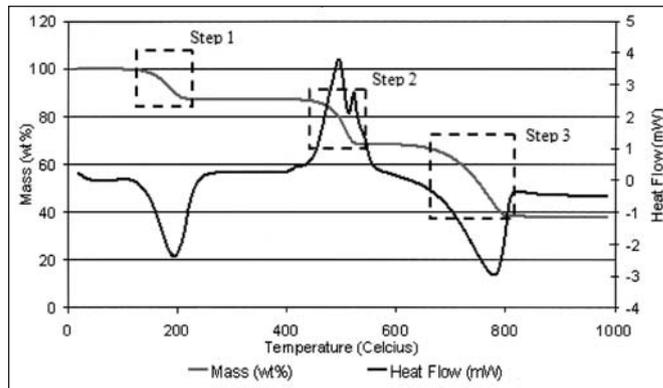


FIG. 10. Thermograph for decomposition of pure calcium oxalate monohydrate.

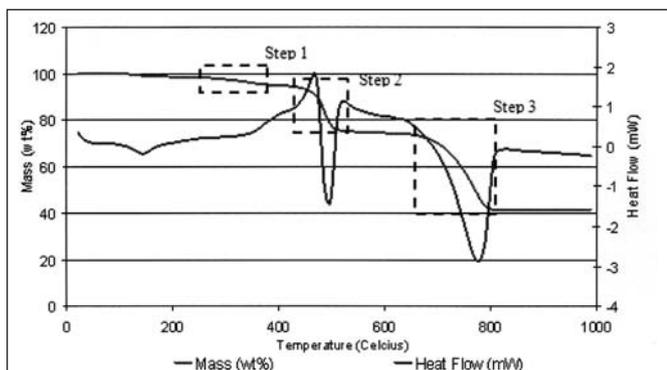


FIG. 11. Thermograph for decomposition of scale sample dried at 85°C from HEX5.

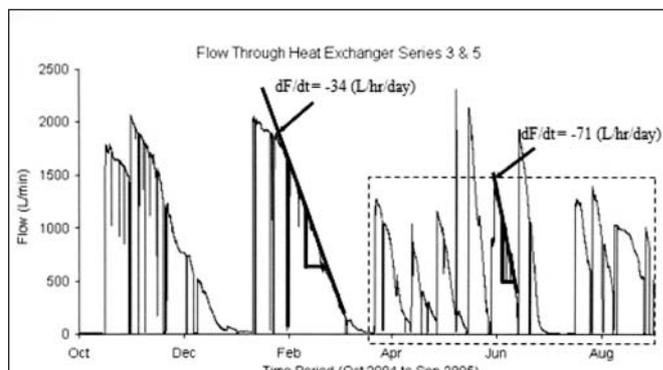


FIG. 12. Flow trend through HEX 3 & 5.

Their work shows that the input with wood and the refining stage contributed small amounts of oxalate. However, a significant amount was formed during peroxide bleaching. Other researchers have also confirmed peroxide bleaching as a major oxalate source in BCTMP mills [9,12]. The mechanism of formation has been described as an attack of hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) on oxalate precursors (OP) present with fiber in the pulp solution (Fiber-OP). Fiber-OP exists as Fiber-OP-H<sup>+</sup>, which is in equilibrium with Ca<sup>2+</sup> ions to form Fiber-OP-Ca<sup>2+</sup>. Ca<sup>2+</sup> ions enter the BCTMP process with hard water and wood. The oxidation of Fiber-OP with H<sub>2</sub>O<sub>2</sub> produces oxalates. The reaction chain is summarized in Fig. 16 [3].

**Effect of Temperature**

It is well known that crystals formed in one part of a system and carried elsewhere are less adherent than those crystals formed on site. Therefore, a change of operating condition that leads to precipitation within the heat exchangers is what causes stable scale formation. For a heat exchanger, temperature is most likely the key factor that would influence scaling.

Figure 17 shows the solubility curve for calcium oxalate. The solubility values are obtained from various sources compiled in the solubility handbook [10]. The data points can be fit with a straight line, suggesting a linear relationship between tem-

perature and solubility. Thus, contact with a lower temperature surface would reduce the solubility of calcium oxalate and then precipitate solids, causing build up of scale. The equation of the solubility-temperature graph is as follows.

$$\text{Solubility (g/L)} = 0.0001 \times \text{Temp}(\text{ }^\circ\text{C}) + 0.0051$$

The solubility graph can be used to determine the precipitation amount based on the temperature difference. The data for temperature difference is presented in Fig. 18.

Table III displays the precipitation rates formed across each heat exchanger. Using the temperature-solubility relationship, the temperature difference across each heat exchanger is converted to a solubility difference value. Maximum flow rate is assumed to be 2100L/min, from the average maximum flows achieved, Figs. 12 and 13.

$$\text{Precipitation Rate} = \Delta \text{Solubility} \times \text{Flowrate}$$

From the last column in Table III, it can be seen that HEX 5 has the highest precipitation rate. This once again agrees with the mill observation that HEX 5 needs to be cleaned more frequently. To confirm if the effect of temperature is significant, a theoretical fouling rate is calculated, based on estimates of fouling rates calculated earlier.

$$\begin{aligned} \text{Fouling rate (kg/day)} &= \text{Exposed Surface Area} \\ &\times \text{Fouling Rate (mm/day)} \times \text{Foulant Density} \\ \text{Exposed Surface Area} &= 90.9 \text{ m}^2 \\ \text{Fouling Rate} &= 0.07 \text{ mm/day, from Table II, HEX 4} \end{aligned}$$

Density is assumed to be 1500 kg/m<sup>3</sup> based on the visible structure of deposits, which appears to have the same structure as clay. Typical clay density is 1500 kg/m<sup>3</sup>. Using the above data, theoretical fouling rate for HEX 4 is found to be 9.54 kg/day. HEX 4 was considered because it is the only HEX in its line. The series arrangement on the other line makes it difficult to relate flow rate and fouling rate.

The underlying assumption in estimating fouling rate based on flow rate gradients is that deposit builds up uniformly across the entire heat exchanger surface. The fouling rate estimated from the flow rate gradient ignores the fact that deposited solids at a single point along the effluent flow channel are sufficient to constrict the flow. In reality, the deposit formation is not uniform. This is visible in Fig. 19. The real fouling rate is thus significantly lower than 9.54 kg/day. The overestimated fouling rate of 9.54 kg/day however provides a frame of reference for comparison with the precipitation rate due to temperature difference across HEX 4, which is 4.35 kg/day.

From previous calculations, Table III, it was found that 4.35 kg/day of calcium oxalate precipitated due to the change in

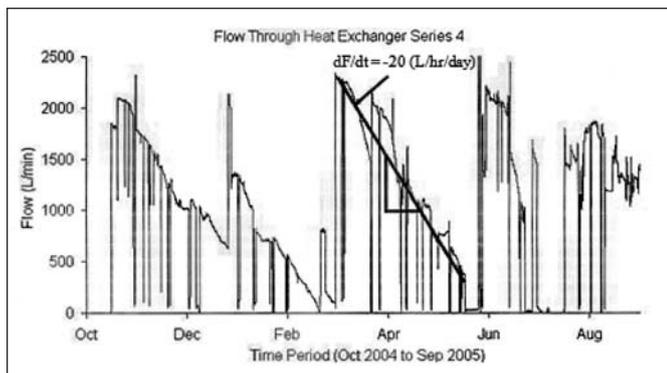


FIG. 13. Flow trend through HEX 4.

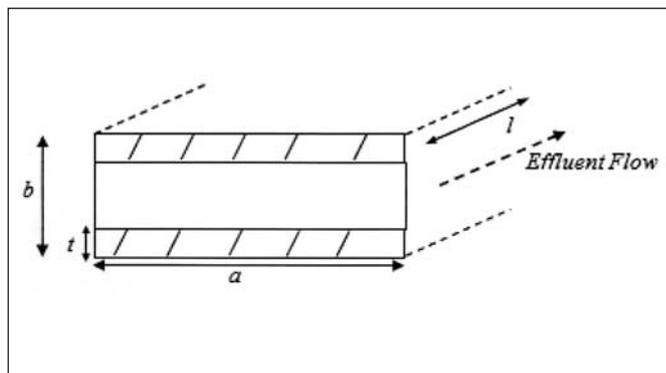


FIG. 14. Cross section of flattened heat exchanger channel.

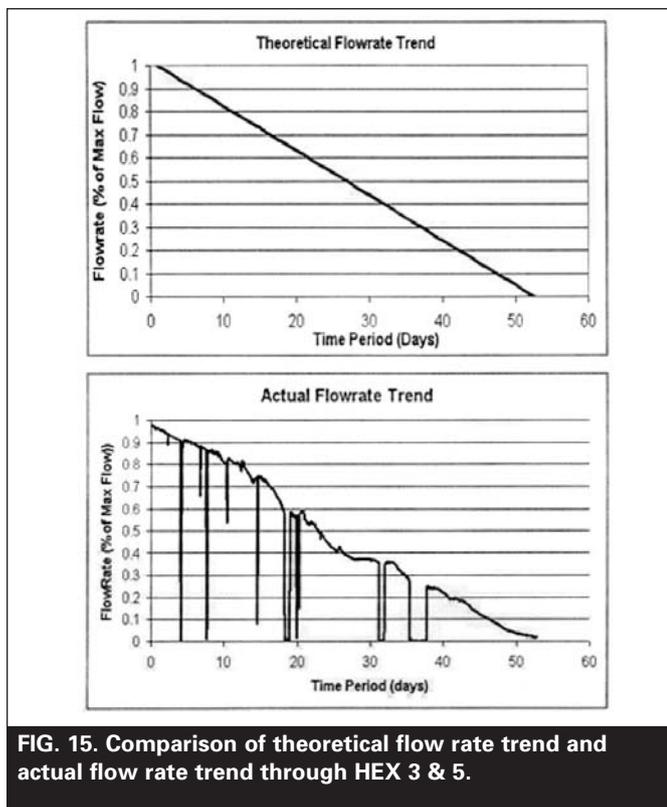


FIG. 15. Comparison of theoretical flow rate trend and actual flow rate trend through HEX 3 & 5.

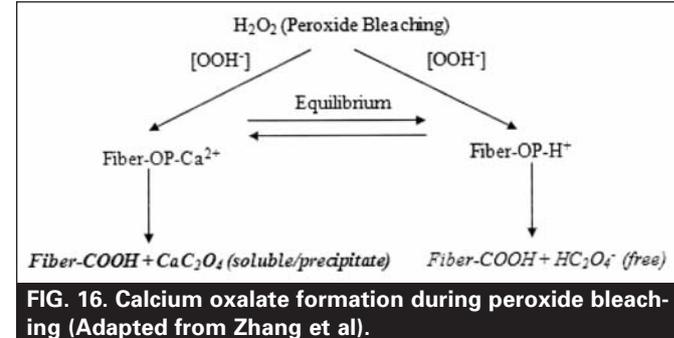


FIG. 16. Calcium oxalate formation during peroxide bleaching (Adapted from Zhang et al).

TABLE II. Summary of fouling rate through heat recovery system.

Data Analysis	Units	Heat Exchanger 3 & 5		Heat Exchanger 4
		Before April 05	After April 05	Nov 04-Apr 05
Flow after clean up (max)	l/hr	2100	1230	2100
Rate of flow decrease	(L/hr)/day	40	90	20
Fouling Rate	mm/day	0.14	0.3	0.07
Time to complete blockage	# of days	53	12	105

calcium oxalate solubility with decreasing temperature across HEX 4. The proximity of 4.35 kg/day precipitation rate and 9.54 kg/day theoretical fouling rate suggest that it is possible that temperature difference drastically affects calcium oxalate fouling. The difference between the precipitation rate and the fouling rate could be also explained by:

- The effect of suspended particles. The effluent contains significant amount of suspended particles, fibers, etc., Fig. 7. These suspended solids are likely to contribute to fouling and account for a significant portion of the difference between the two numbers.
- The analysis uses average values to estimate the temperature difference. Temperature fluctuations in the actual process could result in faster deposition of solids.

The fact that these numbers are not off by orders of magnitude suggests that temperature difference has a significant effect on the fouling rate. The next step is to characterize the level of calcium oxalate saturation, which leads to the following analysis.

**Effect of Saturation Level**

Several researchers have highlighted the importance of saturation level on the scaling mechanism [11,12,13]. The procedure to determine saturation level and the amount of suspended calcium oxalate in the effluent was detailed in an earlier section of

this paper. Results are presented in Table IV.

Table IV shows that the effluent has a high quantity of suspended calcium oxalate particles. The presence of suspended calcium oxalate particles suggests that the effluent is saturated with calcium oxalate. Therefore, the solubility graph of calcium oxalate can be used to determine the dissolved concentration. The amount of suspended calcium oxalate content is 72 times greater than the dissolved content. This means that the effluent is highly saturated.

It was earlier mentioned that suspended particles from one part of the system carried elsewhere are less adherent than those particles formed on the same spot. However, once the deposit forms, it is likely that the bombardment of suspended particles will inject additional mass into the scale and cause rapid fouling, Fig. 20.

$$\text{Undissolved Calcium Oxalate Particle Flow} = \text{Particle Density} \times \text{Maximum Flow}$$

$$0.90(\text{g/L}) \times 2100(\text{L/min}) \div 1000(\text{kg/g}) \times 1440(\text{min/day}) = 2700(\text{kg/day})$$

Approximately 2.7 tonnes of calcium oxalate in suspended particles are passing through the heat exchanger every day. This is a rather high number and, even if a fraction of this mass attaches to the scale, the contribution to fouling would be sig-

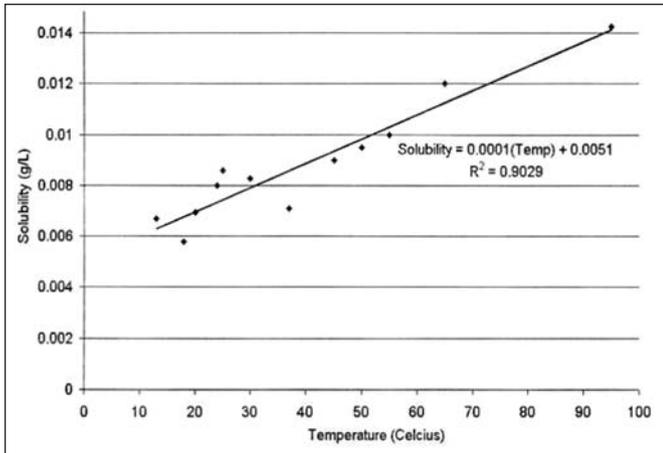


FIG. 17. Change in solubility with solution temperature for calcium oxalate monohydrate.



FIG. 19. Close-up of heat exchanger non-uniform deposit.

nificant. The overall high calcium oxalate content in effluent means that it is highly prone to fouling.

**Proposed Fouling Mechanism**

So far the sources of calcium oxalate have been identified and the effect of temperature and saturation level established. The results suggest the following fouling mechanism taking place.

The pulp mill contains three highly closed water loops. The continuous recirculation of water builds up organic and inorganic chemicals and thus the dissolved ions are saturated. Saturation of calcium and oxalate ions was confirmed while characterizing the effluent. The mechanism begins with the calcium and oxalate ions dissolving in the solution.

A key factor in scale formation is supersaturation to the point of crystallization. This is regarded as the primary cause of scaling [8]. Various researchers have shown that the growth rates of calcium oxalate crystals have a second order dependence on supersaturation [8,13]. Supersaturation is defined as a solution that contains a higher concentration of dissolved solute than the equilibrium concentration. The driving force of supersaturation is either a differential concentration at a fixed temperature or a differential temperature at a fixed concentration. However, a change in pH or pressure that can alter the solubility also affects supersaturation [8].

There is a proportional relationship between calcium oxalate solubility and effluent temperature, as noted earlier. It is thus likely that a decrease in temperature as the effluent passes through the heat exchanger causes a disruption in the thermodynamic equilibrium, which is necessary for supersaturation.

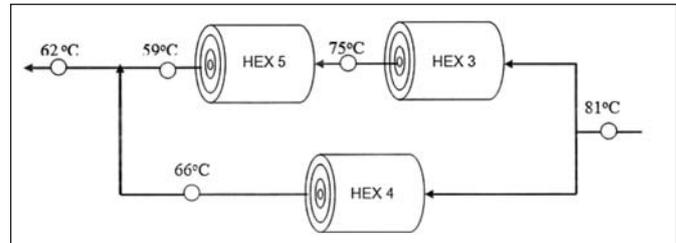


FIG. 18. Average temperature data across individual heat exchangers.

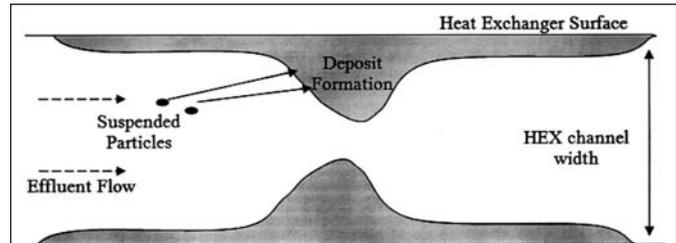


FIG. 20. Contribution of suspended particles to deposit formation.

TABLE III. Precipitation rates due to temperature difference across each heat exchanger.

	Temp In Celcius	Temp Out Celcius	ΔT Celcius	ΔSolubility g/L	Max. Flow L/min	Precip. Rate kg/day
HEX 4	81	67	14	0.0014	2100	4.35
HEX 3	81	75	6	0.0006	2100	1.84
HEX 5	75	59	16	0.0016	2100	4.72

Calcium oxalate is a sparingly soluble salt and needs a small degree of supersaturation to precipitate [9,12]. Thus, when the effluent temperature decreases, the solubility decreases and the solution become supersaturated before precipitating out.

The presence of suspended particles suggests that nucleation sites are not a limiting factor for precipitation. Adequate residence times due to insufficient effluent velocity mean that the precipitated calcium oxalate adheres to the heat exchanger surface and starts growing crystals.

Once the scale has formed, extraneous materials settle directly on top of the scale, resulting in rapid fouling. The high percentage of suspended particles and the temperature difference across the heat exchangers result in fouling. The higher the temperature difference, the faster the fouling rate will be. Figure 21 shows a summary of the proposed mechanism.

Other researchers have also suggested similar reasons for calcium oxalate scaling. Yu and Ni mention that precipitation of oxalates is strongly dependent on the solubility of CaC<sub>2</sub>O<sub>4</sub>, ion supersaturation, nucleation sites, precipitation rate and contact time. They have found that for a high yield mill, the factors that affect calcium oxalate solubility are also the key parameters that influence the scale growth rate. These factors are mainly temperature and pH fluctuations [9]. The effect of pH is probably negligible, as pH is constant across the heat exchanger.

**Effect of Heat Exchanger Scale Removal Efficiency**

It was shown earlier that the scale removal efficiency affected fouling rate. It is expected that inefficient scale removal would lower maximum flow rate and reduce the time required for plug up. This effect is seen from a detailed study of the flow rate trend through HEX 3 & 5, Table II and Fig. 12.

From Fig. 12, it is apparent that since April 2005 the pulp mill underwent changes that influenced maximum achievable flow

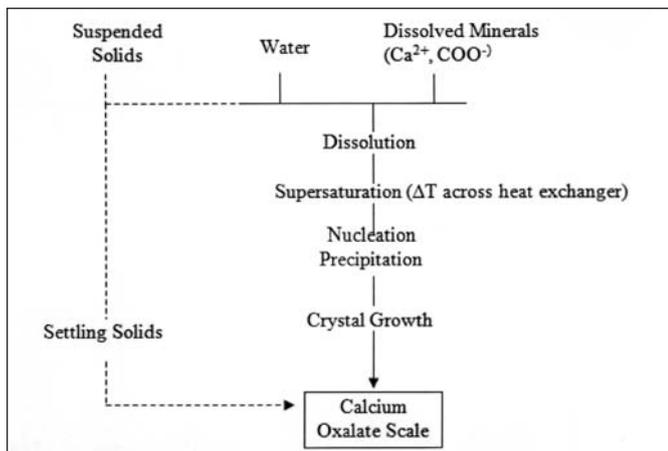


FIG. 21. Proposed calcium oxalate scaling mechanism.

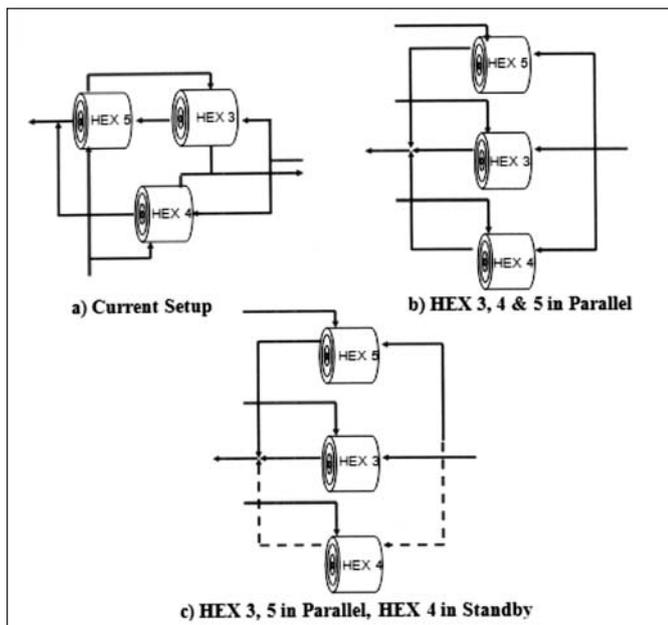


FIG. 23. Possible heat exchanger arrangements.

rate after cleaning. The fouling rate has also been faster since. The only difference the pulp mill could identify was switching from an external (high pressure) hose for cleaning to an in-house (lower pressure) hose, in order to reduce cost.

The lower maximum flow (~1200 L/min) after April 2005 could be explained by the failure of lower pressure cleaning to remove the deposits completely. So part of the heat exchanger was already blocked when the operation restarted. This however does not explain the cause of increased fouling rate.

Figure 22 shows the overlapping trend of flow rate through HEX 3 & 5 and temperature difference ((T) across the heat recovery system. It is apparent that since April, the temperature difference across the heat recovery system is higher. This could be the cause of the increased fouling rate because it has already been established that

$\Delta T$  ;Fouling Rate

However temperature difference in later dates (in August 2005) once again decreases to a low value. The fouling rate, however, remains fast. This could be due to the fact that the temperature difference is plotted around the entire heat recovery system and not around individual heat exchangers. The lack of data makes it difficult to accurately relate the temperature difference across HEX 3 and 5 to the flow rate trend through HEX

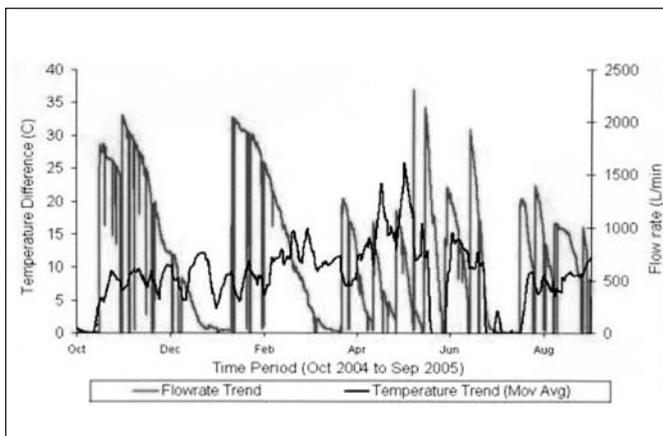


FIG. 22. Effect of temperature difference on overall flow trend through HEX 3 & 5.

TABLE IV. Summary of dissolved and suspended calcium oxalate content in effluent.

Temperature (Celcius)	Total Dissolved Ca-Ox per Liter (g/L)	Total Suspended Ca-Ox per Liter (g/L)	Ratio: Total Suspended/ Total Dissolved
75	0.013	0.90	72

TABLE V. Energy exchanged by individual heat exchangers in the current setup.

	Temp In (C)	Temp Out (C)	$\Delta T$ (C)	Flow (L/min)	Heat Exch. (kW)
Heat Exch 4	81	67	14	2100	2050
Heat Exch 3	81	75	6	2100	880
Heat Exch 5	75	59	16	2100	2340

3 and 5. Other reasons for the increased fouling rate could be a change in the bleaching chemistry or other process alterations not identified by the mill.

At this stage, there is insufficient information to conclude that the change in cleaning procedure has affected fouling rate. The maximum flow rate after cleaning is definitely lower when the cleaning operation is not performed efficiently. It is, however, possible to achieve higher maximum flow rate even with a lower pressure hose, because of evidence showing over 2000 L/min flow rate from two peaks achieved after April 2005, Fig. 12.

If indeed the reduction in plug up time from 53 days to 12 days, Table II, is due to reduced cleaning efficiency, then it implies that a low pressure cleaning has increased cleaning frequency by 4 times. The result confirms that a solution to the fouling problem would initially require the heat exchanger surface to be entirely clean. This reduces the nucleation sites available to facilitate calcium oxalate precipitation. Also if scale is already present when flow is started, then the suspended particles can settle and contribute to fouling right from the onset.

Effect of Heat Exchanger Arrangement

The final discussion is on heat exchanger arrangement, which affects both fouling and heat transfer rate. The pulp mill currently has 3 spiral heat exchangers with the same configuration. Figure 23 shows the different combinations of heat exchanger arrangement possible.

The existing setup, Fig. 23-a, is the first arrangement to be evaluated. Table V provides a snapshot of the energy exchanged in this setup. It is seen that for HEX 3,  $\Delta T$  is only 6°C. The low  $\Delta T$

means that the energy recovered from HEX 3 accounts for only 20% of the total energy exchanged. The low  $\Delta T$  combined with the frequent fouling problem means that the current setup is not operating efficiently. In the mill, fouling causes the actual flow rates to be lower than 2100L/min and the heat exchangers often have to be bypassed. Fouling thus creates frequent disruptions to operation and prevents energy recovery for a significant time periods.

If the three HEXs are operating in parallel, Fig. 23-b, the bulk volume of effluent is diverted through three HEXs instead of two. This reduces the flow rate through each heat exchanger. Spiral heat exchangers operate via countercurrent flow through a single long channel. The lower flow rate would mean that the mean effluent velocity is also low. Several researchers have shown that breaking rate for calcium oxalate crystals is proportional to average shear rate [13,14,15]. Average shear rate increases with velocity. Thus decreased velocity would result in a lower breaking rate and removal of fewer crystals. A low velocity also ensures that a higher percentage of precipitated particles have a chance to settle on the heat exchanger surface and form stable deposits. This setup possibly does not have heat transfer benefits because all three streams would have a  $\Delta T$  slightly higher than 16°C. The current setup has ~15°C change across the line with HEX 4 and ~22°C (16 +6) change across the line with HEX 3 & 5.

The final setup is shown in Fig. 23-c, with two HEXs operating in parallel and the third heat exchanger set in standby mode. When either operating HEX reaches an advanced stage of fouling, the standby HEX can be brought into operation while scale removal takes place. At maximum flow, the heat exchanged with this setup is comparable to all three units arranged in parallel. There is, however, a 20% reduction in heat transfer compared to the existing setup.

The final setup that could have been considered is all three HEXs in series. But this scenario is not evaluated based on the assumption that the HEXs would not be able to handle a single flow that is greater than 2100L/min. A detailed recommendation based on the effect of heat exchanger arrangement is provided in the next section.

## RECOMMENDATIONS

The above sections focused on determining the cause of heat exchanger fouling. The high fouling tendency has been attributed to several factors, such as temperature difference, high calcium oxalate content and inefficiency of scale removal. Recommendations based on the improved understanding of the heat recovery process are presented in this section.

The proposed recommendations are, however, based on limited knowledge of the pulp mill process and should be con-

sidered as preliminary. Detailed engineering studies/trials have to be conducted to determine specific economic benefits and the effectiveness of each recommendation. It is believed that the following suggestions would improve the robustness of the heat recovery operation and minimize problems associated with fouling. The main recommendations are presented initially followed by a summary of minor improvements.

### *Operating Heat Exchanger 3 as Backup*

The effects of different heat exchanger arrangements have been shown. The current setup has been deemed inefficient because  $\Delta T$  across HEX 3 is only 6°C and also because lack of standby heat exchangers offer insufficient flexibility in case of a blockage. The overall effect when heat exchangers are bypassed for cleaning is the flow of effluent with fluctuating temperature to the ASP plant and loss of heat transfer potential.

The recommended setup would be to use two heat exchangers in parallel and configure the third heat exchanger in standby, Fig. 23-c. The advantages would be

1. Increased operational stability and flexibility. Heat recovery system can be operational even when one heat exchanger is down for cleaning by diverting flow through the standby heat exchanger. This would also allow mill personnel more time to clean the heat exchangers.

2. Over a certain time period, the total heat exchanged would possibly be higher because heat exchangers do not often have to be bypassed.

The major disadvantage would be that, at maximum flow, the current setup recovers approximately 20% more energy due to a higher  $T$ . The following steps should be taken before proceeding with reconfiguring the heat exchanger arrangement.

1. Manual temperature readings should be taken for longer periods to validate claims made above.

2. Downstream effluent temperature requirements (in the ASP plant) must be checked for lowest temperature requirement. Lowest achievable temperature with suggested setup is higher than the existing setup.

3. Alfa Laval Inc. should be contacted to validate suggested changes to the process.

### *Converting Feed Storage Tank into a Clarifier*

The proposed mechanism suggests that the high amount of suspended particles (calcium oxalate, fiber, etc.) contribute to fouling after the scale has started to form. The suspended particles adhere to the scale surface and increase the rate of fouling. It is thus expected that reducing particle content would significantly reduce the fouling rate.

Different separation techniques (ex: filtration) could be employed to reduce the particle concentration. However, converting the feed storage tank into a clarifier

could be another engineering solution. The dimension of the storage tank is 8ft (height) by 10ft (diameter). In the existing setup, effluent is pumped only 2.5ft from the bottom. This arrangement inherently pumps a large quantity of fines, fibers and suspended particles to the heat exchangers.

Conversion to a clarifier and pumping the overflow from the top of the storage tank would drastically reduce the amount of suspended particles pumped through the heat recovery system. Detailed engineering (determining particle settling time, engineering cost) must be done for this project. This is expected to result in substantial reductions in the fouling rate within the system.

### *Partially Substituting NaOH with Mg(OH)<sub>2</sub> in Bleaching*

Another potentially effective solution would be removing the sources of calcium oxalate. It has been established by several researchers, as noted previously, that the main source of oxalate in BCTMP mills is alkaline peroxide bleaching. The pulp mill uses NaOH as the alkali. An investigation by Yu and Ni has shown that partial replacement of NaOH with Mg(OH)<sub>2</sub> significantly decreased calcium oxalate formation. Replacing between 30 to 50% NaOH with Mg(OH)<sub>2</sub> resulted in negligible calcium oxalate precipitation in laboratory experiments. A side benefit was also a gain in brightness of pulp [9].

The effectiveness of Mg(OH)<sub>2</sub> bleaching is based on the solubility chemistry. When a significant amount of magnesium is present in the system, the oxalate reacts preferentially with magnesium, rather than calcium, to form magnesium oxalate (MgC<sub>2</sub>O<sub>4</sub>). The lower solubility of magnesium oxalate means that this form of the oxalate would be dissolved in solution [9]. The solubility product (Ksp) for MgC<sub>2</sub>O<sub>4</sub> is  $7 \times 10^{-7}$ . The Ksp for CaC<sub>2</sub>O<sub>4</sub> is  $1.96 \times 10^{-8}$ . Therefore the Ksp for magnesium oxalate is approximately 35 times higher than calcium oxalate at 25°C. This indicates substantially higher solubility and lower tendency to form deposits.

The significant reduction of calcium oxalate would reduce the scale formation at other equipment downstream of the bleaching process. A detailed investigation must be performed to investigate this replacement solution before application. The results obtained by Yu and Ni are from experiments done on a laboratory scale. Trials must be conducted to verify the effectiveness in an industrial scenario.

### *Further Recommendations*

This section details the minor process adjustments that could further improve the system.

- Flow rate trends have shown that even with a lower pressure hose, scale can be removed sufficiently to achieve high flow

rate (>2000L/min). This is not done on a consistent basis, despite the best efforts of the mill personnel. The mill personnel responsible for cleaning must be suitably instructed to spend sufficient time to clean the heat exchangers in a manner that removes all visible deposits from the surface. The lack of deposits when the effluent flow starts significantly decreases the initial fouling rate and substantially reduces the time to foul up.

- A trial could be arranged to determine the effect of velocity on scale deposition. The loading of the feed pump could be ramped up (if possible) to increase flow rate prior to restarting the heat exchangers after cleaning. Spiral heat exchangers are designed to remove deposits with velocity increase. Researchers have also shown that increased velocity and shear strength disrupt agglomeration of calcium oxalate. It is thus possible that a high enough velocity could reduce residence time sufficiently to prevent scale from depositing. However, to prevent equipment malfunction, the heat exchanger design pressures must not be exceeded.

- The application of chemical scale inhibitors is another potential to reduce scale formation. Although limited study of inhibitors has been included in this thesis, there is a large body of literature that focuses on effective chemical anti-scalants. Different groups of chemicals inhibit scale formation by different mechanisms including chelation, dispersion and inhibition. Factors that affect selection of an inhibitor include water hardness, alkalinity, temperature and particulate amount [1]. Calcium oxalate scaling is also frequently experienced in sugar mill evaporators. Poly(acrylic acid) (PAA) and poly(maleic acid) are commonly used in sugar mills for scale inhibition. It has been shown that PAAs of molecular weight of 2000-4000 have optimum effectiveness [16]. Trials could be implemented in the pulp mill if these chemicals are available and have no adverse effect on pulp quality.

- All recommendations mentioned are based on theoretical studies and would require detailed engineering before application. The dirty nature of the effluent is such that it should not be expected that applying any combination of the above recommendations would completely solve the scaling problem. Scaling to some extent is thus inevitable. It is, however, expected that implementation of the above recommendations would substantially improve the current fouling problem and definitely increase the plug up time of the heat exchangers to more than 2 weeks.

## CONCLUSIONS

The objectives of this thesis were to determine the cause of fouling and recommend ways to delay or eliminate fouling in the spiral heat exchangers. The objectives have been successfully met and the

following conclusions reached.

1. Calcium oxalate has been identified as the main scaling component (> 85%).
2. The scaling mechanism that has been proposed begins with calcium and oxalate ions dissolving in the mill water. Decrease of temperature across the heat exchanger reduces the solubility of calcium oxalate, which results in supersaturation followed by precipitation. The precipitated calcium oxalate adheres to the heat exchanger surface and crystal growth begins. This leads to the formation of scales. Once the scale has formed, suspended particles settle directly on top of the scale and contribute to rapid fouling.
3. The effluent has been characterized as having 72 times more calcium oxalate in the suspended solids than in the solution, making it highly saturated with calcium oxalate and prone to fouling.
4. The precipitation rate due to temperature difference and the observed fouling rate across HEX 4 were 4.35 kg/day and 9.54 kg/day respectively. These rates are sufficiently close to imply that temperature difference affects scaling rate. A higher temperature difference would cause more frequent scale deposition in the heat exchangers.
5. The 15°C temperature difference and high calcium oxalate content means that scaling in the heat exchangers to some extent is inevitable.
6. It is recommended that decreasing calcium oxalate content would reduce the deposition rate. Partial replacement of NaOH with Mg(OH)<sub>2</sub> in the alkaline bleaching stage would form soluble magnesium oxalate instead of calcium oxalate.
7. Application of a separation technique, such as conversion of the feed storage tank into a clarifier, would also reduce calcium oxalate particle content passing through the HEXs.
8. A temperature difference of only 6°C across HEX 3 means that rearranging HEX 3 from continuous operation to standby mode will increase both operational flexibility and heat transfer efficiency.
9. Implementation of any or all of the men-

tioned recommendations might not completely eliminate the fouling problem. However, the modifications would significantly improve the existing process and increase stability and efficiency and reduce fouling.

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**Résumé:** La présente communication analyse la cause de l'encrassement par l'oxalate de calcium (CaC<sub>2</sub>O<sub>4</sub>) retrouvé dans les échangeurs spirales. La solubilité du CaC<sub>2</sub>O<sub>4</sub> diminue lorsque la température baisse. Le taux de précipitation prévu en raison de la différence de température correspondait au taux d'encrassement constaté. Cette observation suggère que l'effluent se sursature et forme un précipité (tartre) au contact de la surface froide de l'échangeur de chaleur. Les particules en suspension s'accumulent alors et entraînent un encrassement rapide. Nous recommandons d'utiliser des méthodes de séparation physiques et aussi de remplacer une partie du NaOH par du Mg(OH)<sub>2</sub> pendant le blanchiment alcalin afin de réduire la teneur en CaC<sub>2</sub>O<sub>4</sub> et l'encrassement.

**Reference:** HAQUE, M.R. Minimizing Fouling in Spiral Heat Exchangers at a BCTMP Mill. *Pulp & Paper Canada* 108(4):T71-80 (April, 2007). Paper presented at 92nd Annual Meeting in Montreal, QC, February 6-10, 2006. Not to be reproduced without permission of PAPTAC. Manuscript received on June 23, 2006. Revised manuscript approved for publication by the Review Panel on January 15, 2007.

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