Minimizing fouling in spiral heat exchangers at a BCTMP mill

By M.R. Haque

Abstract: This paper investigates the cause of calcium oxalate (CaC₂O₄) fouling in spiral heat exchangers. CaC₂O₄ 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 Mg(OH)₂ during alkaline bleaching to reduce CaC₂O₄ content and minimize fouling.

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 pumped through the three spiral heat exchangers) and cause fouling problems [3].

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.
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 thorough 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 (CaC₂O₄) 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...
other factors which are unknown as of yet that contribute to the rapid scale formation.

4) 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.

**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].

\[
\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O} \xrightarrow{\Delta} \text{CaC}_2\text{O}_4(s) \xrightarrow{\Delta} \text{CaO} \cdot \text{CO}_2(s) \xrightarrow{\Delta} \text{CaO} \cdot \text{CO}_2(s) \xrightarrow{\Delta} \text{CaO}(s)
\]

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-

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**Table I. Scale analysis results.**

<table>
<thead>
<tr>
<th>Element</th>
<th>% Ash</th>
</tr>
</thead>
<tbody>
<tr>
<td>Calcium</td>
<td>96.9</td>
</tr>
<tr>
<td>Silica</td>
<td>1.3</td>
</tr>
<tr>
<td>Magnesium</td>
<td>0.5</td>
</tr>
<tr>
<td>Aluminium</td>
<td>0.4</td>
</tr>
<tr>
<td>Iron</td>
<td>0.3</td>
</tr>
<tr>
<td>Manganese</td>
<td>0.2</td>
</tr>
<tr>
<td>Strontium</td>
<td>0.2</td>
</tr>
</tbody>
</table>

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

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**FIG. 5. Cross Sectional view of HEX5 before (left) and after (right) high pressure cleaning.**
um oxalate in the scale is estimated by the following calculation.

\[
CaC_2O_4(s) \rightarrow CaO(s) + CO_2(g) + CO(g)
\]

(Overall decomposition reaction)

Mol. Mass (g/mol) 128 56 44 28

Using a basis of 1 mole (128gm) of sample.

Theoretical mass loss % during total decomposition:

\[
\frac{\text{Mass of Gas Evaporated}}{\text{Total Mass of Sample}} \times 100\% = \frac{(44 + 28)\text{gm}}{128\text{gm}} \times 100\% = 56\%
\]

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 (\(CaC_2O_4\cdot H_2O\)) 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.](image1)

![FIG. 7. Pulp mill effluent.](image2)

![FIG. 8. Schematic of procedure to measure level of saturation of effluent solution.](image3)

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

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.
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 (H₂O₂) on oxalate precursors (OP) present with fiber in the pulp solution (Fiber-OP). Fiber-OP exists as Fiber-OP-H⁺, which is in equilibrium with Ca²⁺ ions to form Fiber-OP-Ca²⁺. Ca²⁺ ions enter the BCTMP process with hard water and wood. The oxidation of Fiber-OP with H₂O₂ 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 temperature 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.

\[ \text{Solubility (g/L)} = 0.0001 \times \text{Temp (°C)} + 0.0051 \]

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.

**Precipitation Rate = Δ Solubility × Flow rate**

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.

Fouling rate (kg/day) = Exposed Surface Area × Fouling Rate (mm/day) × Foulant Density Exposed Surface Area = 90.9 m² Fouling Rate = 0.07 mm/day, from Table II, HEX 4

Density is assumed to be 1500 kg/m³ based on the visible structure of deposits, which appears to have the same structure as clay. Typical clay density is 1500 kg/m³. 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
scaling

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.

**Undissolved Calcium Oxalate Particle Flow = Particle Density x 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-

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

<table>
<thead>
<tr>
<th>Data Analysis</th>
<th>Units</th>
<th>Before</th>
<th>After</th>
<th>Nov 04-Apr 05</th>
</tr>
</thead>
<tbody>
<tr>
<td>Flow after clean up (max)</td>
<td>l/hr</td>
<td>2100</td>
<td>1230</td>
<td>2100</td>
</tr>
<tr>
<td>Rate of flow decrease (L/hr)/day</td>
<td>40</td>
<td>90</td>
<td>20</td>
<td></td>
</tr>
<tr>
<td>Fouling Rate mm/day</td>
<td>0.14</td>
<td>0.3</td>
<td>0.07</td>
<td></td>
</tr>
<tr>
<td>Time to complete blockage # of days</td>
<td>53</td>
<td>12</td>
<td>105</td>
<td></td>
</tr>
</tbody>
</table>
significant. 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].

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 becomes 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 CaC₂O₄, 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
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 (\(\Delta T\)) 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

\[ \Delta T \text{ : Fouling Rate} \]

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

\[ \Delta T \]

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.

\[ \Delta T \text{ : Fouling Rate} \]

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 ΔT 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 counter-current 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 ΔT 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 a high velocity, the heat exchanger 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 considered 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 ΔT 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.

3. 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)₂ 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)₂ significantly decreased calcium oxalate formation. Replacing between 30 to 50% NaOH with Mg(OH)₂ 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)₂ 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 (MgC₂O₄). The lower solubility of magnesium oxalate means that this form of the oxalate would be dissolved in solution [9]. The solubility product (Ksp) for MgC₂O₄ is 1.96 x 10⁻⁸. The Ksp for CaC₂O₄ is 1.96 x 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
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)₂ 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. 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 mentioned 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.

**LITERATURE**


Résumé: La présente communication analyse la cause de l’encrassement par l’oxalate de calcium (CaC₂O₄) retrouvé dans les échangeurs spirales. La solubilité de CaC₂O₄ 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 saturerait 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)₂ pendant le blanchiment alcalin afin de réduire la teneur en CaC₂O₄ et l’encrassement.


**Keywords:** SCALING, FOULING, SPIRAL HEAT EXCHANGERS, CALCIUM OXALATE.