

THERMAL STABILITY OF METAL-PITCH DEPOSITS FROM A SPRUCE THERMOMECHANICAL PULP BY USE OF A DIFFERENTIAL SCANNING CALORIMETER

Zhongguo Dai* and Yonghao Ni

Pitch-related deposition has been a significant issue in paper mills that produce wood-containing paper grades. A component analysis showed that a mill deposit sample was a mixture of wood resin, fiber, metal cations, and other inorganics. Based on the differential scanning calorimeter (DSC) method, some critical parameters, including pH, metal cations, and their interactions, on the thermal stability of pitch-related deposits were studied. The valency of metal cations determined the ability of capturing pitch the formation of deposits. Trivalent Al^{3+} or Fe^{3+} ions had much stronger effects than divalent Ca^{2+} , Mg^{2+} , or Mn^{2+} . It was also found that a higher pH and trivalent Al^{3+} or Fe^{3+} increased the thermal stability of deposits formed in colloidal pitch solutions.

Keywords: Pitch deposits; Extractives; Metal cations; Differential scanning calorimeter (DSC)

Contact information: Department of Chemical Engineering, University of New Brunswick, Fredericton, NB E3B 5A3, Canada; *Corresponding author: zhongguo.dai@unb.ca

INTRODUCTION

Wood itself contains a large variety of resinous substances, for instance, fatty acids, resin acids, triacylglycerols, sterols, etc. The wood resin (also called pitch) often causes serious deposit problems on papermaking equipment, especially under the conditions of using more thermomechanical pulp (TMP), higher machine speeds, higher shear rates, more system closure, and greater water recirculation (Hubbe et al. 2006; Laubach and Carol 1991). For a mechanical pulp based paper mill, the factors impacting pitch deposition may include the hardness, conductivity, and variability of process water, as well as the retention chemistry performance (Allen and Ouellet 2007). In a sulfite pulp mill, a lower pH, the presence of alum, and complex phosphates decreased the tendency of pitch to stick to process equipment surfaces, whereas calcium and hard water above pH 6 increased the chance of pitch deposition (Swanson and Cordingley 1956). Also during the manufacturing of non-wood fiber pulps, calcium, ferric, magnesium, aluminum, and other cations were identified as important sources of deposits (Gutierrez and Jose 2005).

Various metal ions, such as ferric (Fe^{3+}), aluminum (Al^{3+}), calcium (Ca^{2+}), manganese (Mn^{2+}), and magnesium (Mg^{2+}), can be present in a paper mill (Ni et al. 1997). They can originate from wood, and/or process water. Chemicals used in the process, for example magnesium hydroxide in the bleaching process (Li et al. 2005), may also increase the metal ion concentration in the mill processes. Their presence can bring about negative impacts on the product quality, for example, paper brightness (Hua and

Laleg 2008; Ghosh and Ni 1998; Peart and Ni 2001; Ni et al. 1999; Mao and Ni 2008), and on the operations, such as in the formation of pitch-related deposition.

In addition to metal ions and pH, temperature is another important factor in controlling the resin viscosity and pitch deposition (Back 1963). It was reported that fatty acid, resin acid, and triacylglycerols extracted from TMP had different responses in terms of deposition, and at a lower temperature, the amount of deposit from resin acid was actually higher, although that from fatty acid and triacylglycerols was independent of temperature (Stack et al. 1998). The deposition potential of an abietic acid-based pitch was minimal at neutral pH and low temperature, whereas a fatty acid-based pitch has its highest deposition potential under the same conditions (McLean et al. 2005). For a sulfite pulp production process a higher temperature decreased the pitch deposition (Gustafsson et al. 1952).

Recently we undertook a project aiming to decrease the pitch related deposit formation in a TMP-based speciality paper mill in Eastern Canada (Dai et al. 2010). It was found that wood extractives accounted for the majority of the mass in the deposit samples collected at the mill; also, various metal ions were present in all the collected deposit samples and some of them were quite high. The effects of process conditions, for example, the temperature profile of the supercalendering stacks, the amount of fresh water used, the dispersant versus fixation chemistry, on the pitch related deposit formation were reported; in addition the organics of the deposit samples were analyzed based on a gas chromatographic (GC) method (Dai et al. 2010). In the present study, our objective was to determine the effect of metal ions on the formation of pitch-related deposits, in particular, the thermal transitions of the deposits formed at various pH levels due to the presence of metal ions, such as Fe^{3+} , Al^{3+} , Ca^{2+} , Mn^{2+} , and Mg^{2+} . The results can provide further understanding of pitch-related deposit formation in the presence of these metal ions in the paper manufacturing processes.

MATERIALS AND METHODS

The deposit sample was obtained from the guide roll of the supercalender stack of a TMP-based paper mill (using a spruce TMP and small amount of softwood kraft pulp as the pulp furnish, with a pH of about 5 in its white water) in Eastern Canada and was dissolved in acetone. The solution was then centrifuged at 3000 rpm for 30 min to separate the suspended solids. The supernatant was put in a vacuum desiccator, and the dried sample was defined as acetone-dissolved resin. A vacuum desiccator was also used to dry the separated solids, which were then called acetone-dissolved residue.

Also, supernatant obtained from acetone dissolution and centrifugation was slowly added into deionized water with magnetic agitation. A colloidal pitch solution was prepared by dialysis in deionized water to remove acetone by following a procedure detailed in the literature (Sundberg et al. 1996a). The same deposit sample was subjected to combustion to determine the minerals content by following a TAPPI standard method T211 om-93. The metal ion contents were determined based on an atomic absorbance method by using a Perkin Elmer AAnalyst 100 model, and following the TAPPI standard method T266 om-94.

The metal ion solutions were prepared by dissolving their salts in de-ionized water. The concentrations for Ca^{2+} , Mn^{2+} , and Mg^{2+} , were all in 1mol/L and were in 0.1mol/L for Fe^{3+} and in 1g/L for Al^{3+} . For determining the interaction of metal ions and pitch, a total volume of 1 ml of these solutions was added to a 30 ml colloidal pitch solution that had 600 ppm, prepared by using the exact amount of extractives obtained from the mill deposit. Once the metal ions had been added into the pitch dispersion, sample vials were left on a shaker for 10 minutes to get a thorough mixing, and then centrifuged to separate the deposits. These deposits were then dried in a vacuum desiccator before the DSC analysis.

A differential scanning calorimeter (DSC), Model 2100, TA Instruments, was used to observe the thermal transitions of the deposit samples. The method consisted of an equilibration at 25°C for 5 minutes, a ramp of 2°C/min, and an equilibration at a final temperature 200°C for 2 minutes.

RESULTS AND DISCUSSION

Characterization of Pitch Deposit

Table 1 shows the chemical composition of a typical deposit sample. It can be found that the sample was composed of pitch, fillers, and fibers, among which pitch was the majority, accounting for about 56% of the mass. Detailed analyses of the pitch-related deposit samples for their organic compositions, based on a GC method, showed a high amount of resin acids and a trace amount of fatty acids (Dai et al. 2010). It is known that pitch-related deposit formation is a rheological phenomenon. Some pitch components became fluid under high temperature and moved to/out of the paper surface, which is due to the fact that pitch can exhibit tackiness when heated above its glass transition temperature (Hubbe et al. 2006). Subsequently, the tacky pitch peeled off fillers and fibers from the paper surface, and deposited onto the process equipment. It is noted that the sample was collected in April, and it is well known (Back and Allen 2000) that the organic composition of pitch may be affected by the harvesting season, for example, wood harvested in the summer months may contain more fatty acids, while that harvested in the winter may contain more triacylglycerols.

Table 1. Chemical Composition of Pitch-related Deposit (collected in April, 2007)

Components	Percentage (%)	Metal Ions	Content (ppm on deposit)
Acetone Extractable Substances	56.01	Calcium (Ca^{2+})	2720
		Ferric (Fe^{3+})	2870
Ash	28.87	Magnesium (Mg^{2+})	690
Fiber	15.12	Manganese (Mn^{2+})	84

It was also found that various metal ions were present in the deposit sample, among which Fe^{3+} and Ca^{2+} were in high concentrations. The reaction mechanism between multivalent metal ions and wood pitch, at a high pH, has been described as follows (Allen 1988):



At a low pH, multivalent metal ions can function as coagulants due to their cationic nature. By this means they could trap the anionic pitch by an electrostatic interaction.



Thermal Transition Behavior of Metal-pitch

Included in Fig. 1 are the DSC thermogram for three samples, the mill deposit, the acetone-extracted resin, and the acetone-dissolved residue of the deposit. The mill deposit, consisting of extractives, fibers and fillers, was absorbing heat during the entire heating process, which is indicated by the change of heat flow. For the acetone-dissolved residues, which essentially were fillers and fibers, there was almost no change of the heat flow, indicating that no thermal transition took place. However, the acetone-extracted resin started softening at the beginning of the heating period due to the presence of some low melting-point components; similar results have been reported in the literature. For example, Back and Allen (2000) reported that for some resin components such as oleic acid, linoleic acid and linolenic acid have melting points of 14, -5, and -11 °C, respectively. The pitch-related deposit is mainly formed at the guide roll of the supercalendering section, which has a typical temperature of 60 to 175 °C; therefore, the thermal transition behavior in the same temperature range would be most relevant to the deposit formation at the mill.

A study of the temperature dependence of deposition also showed that a 40% reduction in the deposit weight was observed for resin acid extracted from TMP when the temperature increased from 30°C to 40°C (Stack et al. 1998). It is interesting that an exothermic transition was observed until the temperature ramped to 125°C, which has been defined as an auto-polymerization process (Castro et al. 1996). Polymerized pitch was found to be the major component in the pitch deposit from a fine paper mill, and it was very sticky in nature because of its high molecular weight (Raymond et al. 1998). After auto-polymerization, the extracted resin went through a glass transition, and a sharp melting occurred around 185°C.

pH Effect

The pitch composition can be expected to be different at various pH levels. At low pH, resin and fatty acids were mainly insoluble “balls” that give a rise to the turbidity because of their hydrophobic nature. With an increase in pH by the addition of alkali, the acidic groups are saponified, and the insoluble resin components are converted to water-soluble salts, resulting in a decreased turbidity of pitch solution. A pitch-related study showed that at neutral pH and low temperature the deposition potential of an abietic acid pitch was minimal, whereas under the same conditions the deposition potential of a fatty acid sample was at its maximum (Dreisbach and Daniel 1989).

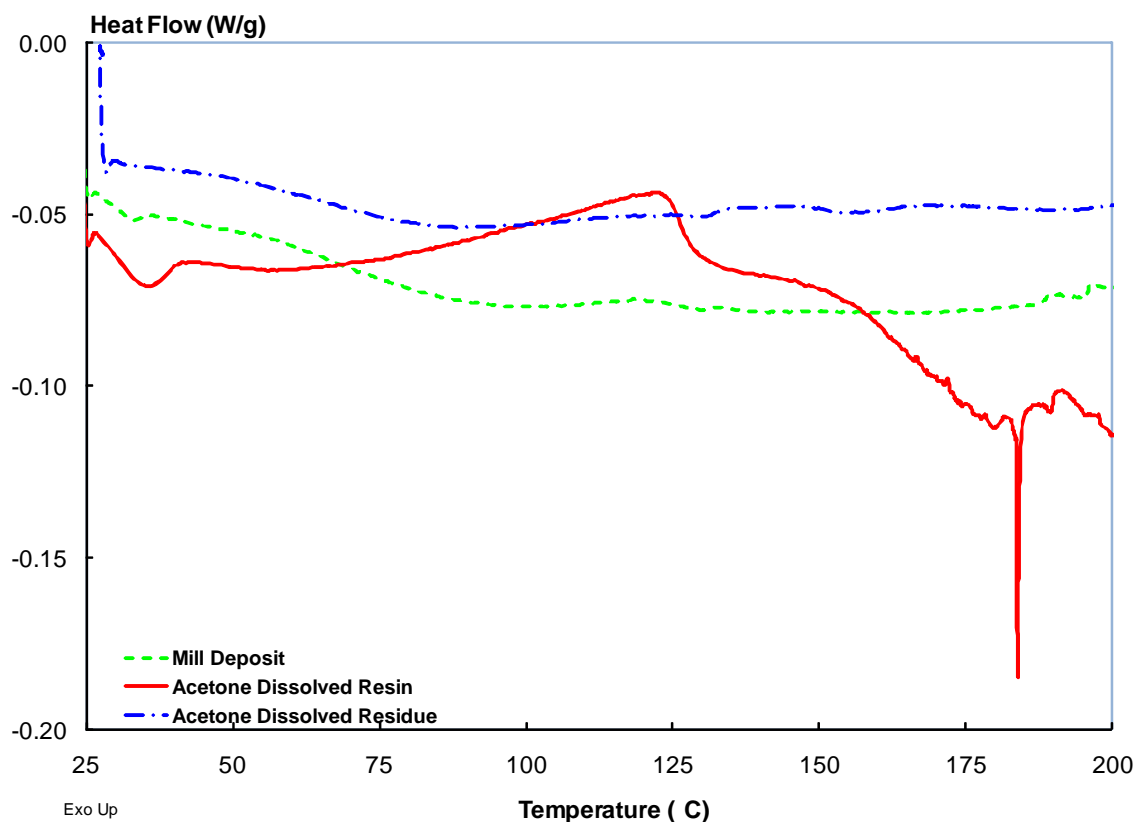


Fig. 1. DSC thermogram of the mill deposit, acetone extracted resin, and acetone dissolved residue

The mill under consideration uses clay as the filler to produce supercalendered paper grades, and the stock pH of bleached TMP is usually around 3.5 to 4.5. Therefore the pitch components are not in the form of their soluble salts, and mill testing results showed a typical turbidity of around 100NTU for bleached TMP; it is possible that pitch components could contribute to the observed turbidity, because the extractive content in the bleached TMP was about 1%.

As shown in Fig. 2, the original pH was 4.4 for the prepared pitch colloidal suspension. The turbidity increased significantly from 55 to 102 as the pH dropped to 2.6. With the addition of alkali, the turbidity decreased gradually, and the turbidity of the pitch suspension started dropping somewhat faster at pH above 9.5. These results are in agreement with those from a newsprint mill, where it was shown that the concentration of dissolved pitch anions increased rapidly at pH of about 10 in white water (Sundberg et al.1996a). Therefore, it follows that increasing the stock pH to neutral may help to control pitch-related deposition; however, such an approach may also increase the amount of the anionic trash, which leads to a high consumption of retention aids and an increase in the effluent load (He et al. 2004).

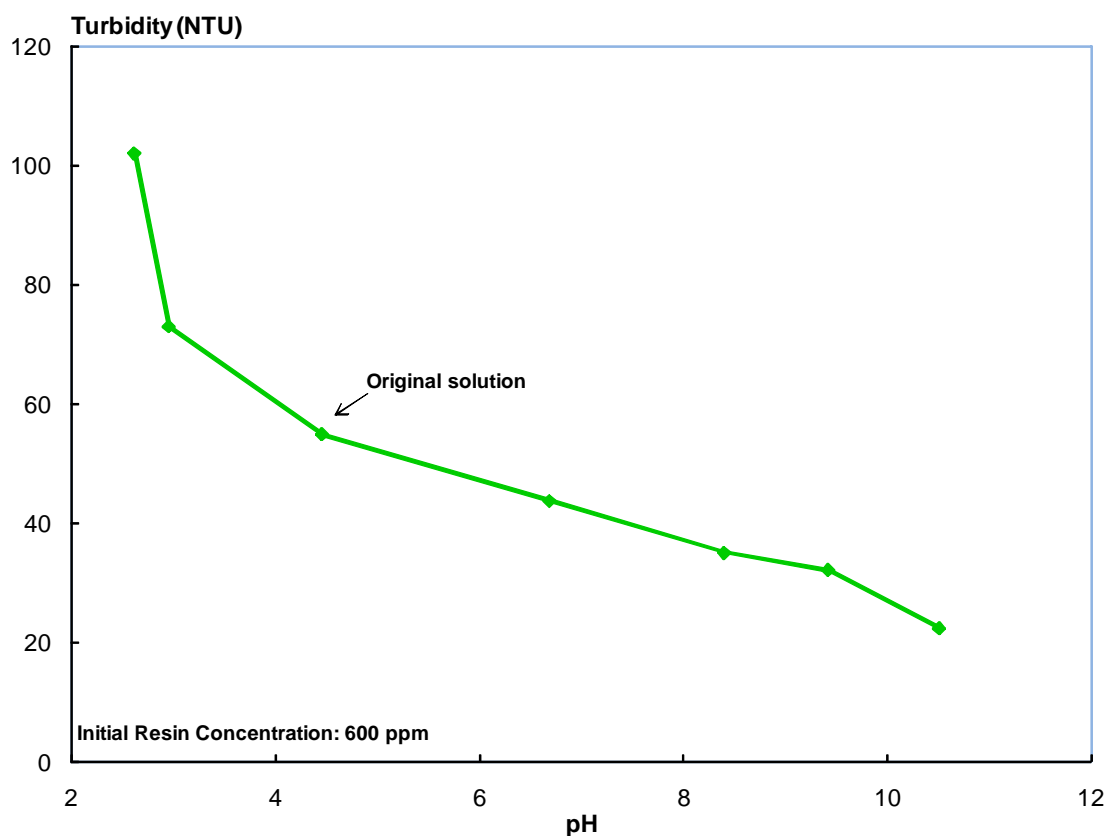


Fig. 2. pH effect on the turbidity of a pitch solution

Ionic Strength

Electrolytes have the ability to induce aggregation of colloidal pitch suspensions, and the amounts of different metal ions present in the suspension had a significant impact on the amount of deposit formed. As shown in Fig. 3, when calcium or magnesium salts were added to the prepared pitch dispersion, the turbidity increased dramatically with the increase in ionic strength up to 250 ppm for Ca^{2+} or Mg^{2+} , and with centrifugation, the turbidity didn't change much. However, when the amount of metal ions increased further, there was too much solid-like material suspended in the solution; thus a reasonable turbidity reading became difficult. The centrifugation removed the deposit formed, and the supernatant then had a low turbidity reading.

Figure 4 shows the deposit amount as a function of ionic strength for different metal cations. Obviously, with the increase in the concentration of metal ions in the acidic colloidal pitch solution (pH=4.5), the amount of pitch deposition also increased. However, different types of metal ions had various performances in terms of aggregating pitch out of the solution. For the same level of deposit formation, the amount of metal ions needed was much less for the trivalent metals, Al^{3+} and Fe^{3+} , in comparison to the divalent metal ions, Ca^{2+} , Mg^{2+} , and Mn^{2+} . Similar results have been reported previously that, at pH 5, resin formed aggregates when the concentration of NaCl , CaCl_2 , AlCl_3 exceeded about 200, 10, and 0.02 mmol/l respectively (Sundberg et al.1996b). These results confirmed that the deposit formed in an acidic solution was based on the electrostatic force, which is a function of metal ion valency.

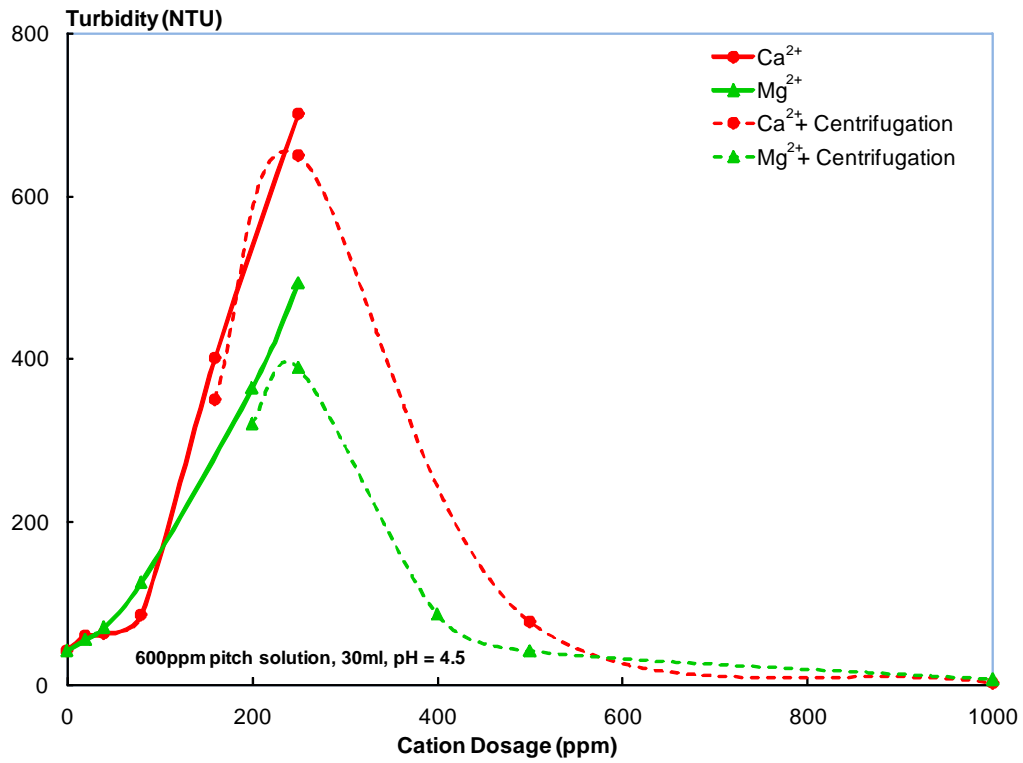


Fig. 3. Turbidity changes due to the increase in the ionic strength and the effect of centrifugation

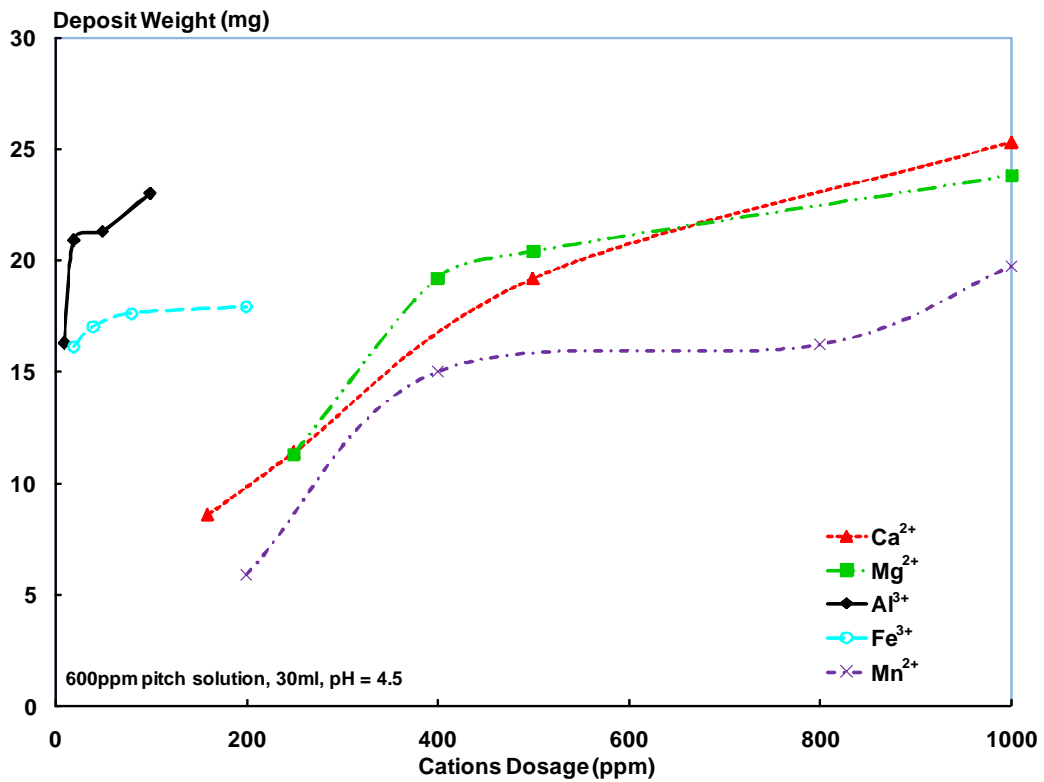


Fig. 4. Deposit formed at various metal ion concentrations

Mill data showed that the typical extractive concentration in the process water was in the range of 50~250 ppm, with metal ion concentrations of about 10 ppm Mn^{2+} and 1 ppm Fe^{3+} , although the exact concentrations will depend on the location and season. The metal ion concentrations in this study covered both the practical levels and those at much higher levels. The latter is needed in order to gain a good understanding of the metal ion-induced pitch-related deposit formation. Also, it is noted that in the mill operations, high local/occasional concentrations are possible, for instance during process start-up or when changing the process water streams.

Interaction of pH and Metal Cations

The pH not only affects the turbidity of pitch solution, but also has a great impact on the deposition of pitch in the presence of multivalent metal ions, Al^{3+} , Ca^{2+} , Fe^{3+} , and Mg^{2+} . The melting points of metal soaps of resin components are considerably higher than the original resin component (Back and Allen 2000). However, the deposits formed under acidic conditions may not be the same, because the deposit formed due to the electrostatic interaction can lead to the formation of much bigger agglomerates.

In Fig. 5, even below 50°C the Ca^{2+} -pitch deposits at various pH showed a very sharp valley, which indicated the presence of melting behaviors. Some metal soap that was formed from fatty acids, for instance, calcium oleate, could start changing states in the temperature range of 25 and 40°C (Kellar, et al. 1991).

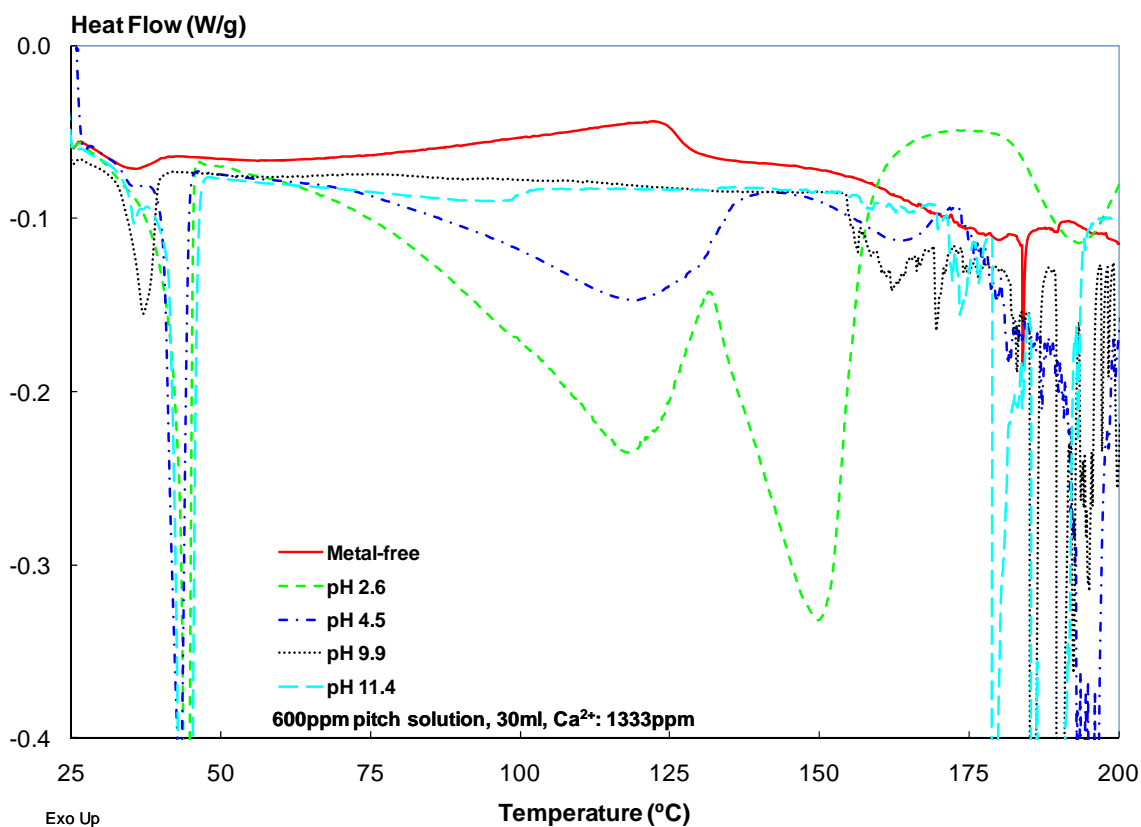


Fig.5. pH effect on softening the Ca-pitch deposit

In the temperature range of 50°C to 150°C, deposits formed under acidic conditions showed melting valleys, and those formed under alkaline conditions were stable. At the temperature of above 150°C, deposit formed at pH=2.6 was different from the other three samples that showed obvious melting behaviors. One explanation could be that some components had been melted at a lower temperature zone.

The effect of pH on the thermogram of Fe³⁺-pitch deposits is shown in Fig. 6. It can be seen that the deposits formed with ferric cations were stable under the conditions studied. At 175 °C or higher, some melting behavior can be seen at pH 2.6, while the deposits formed at other pH levels were stable.

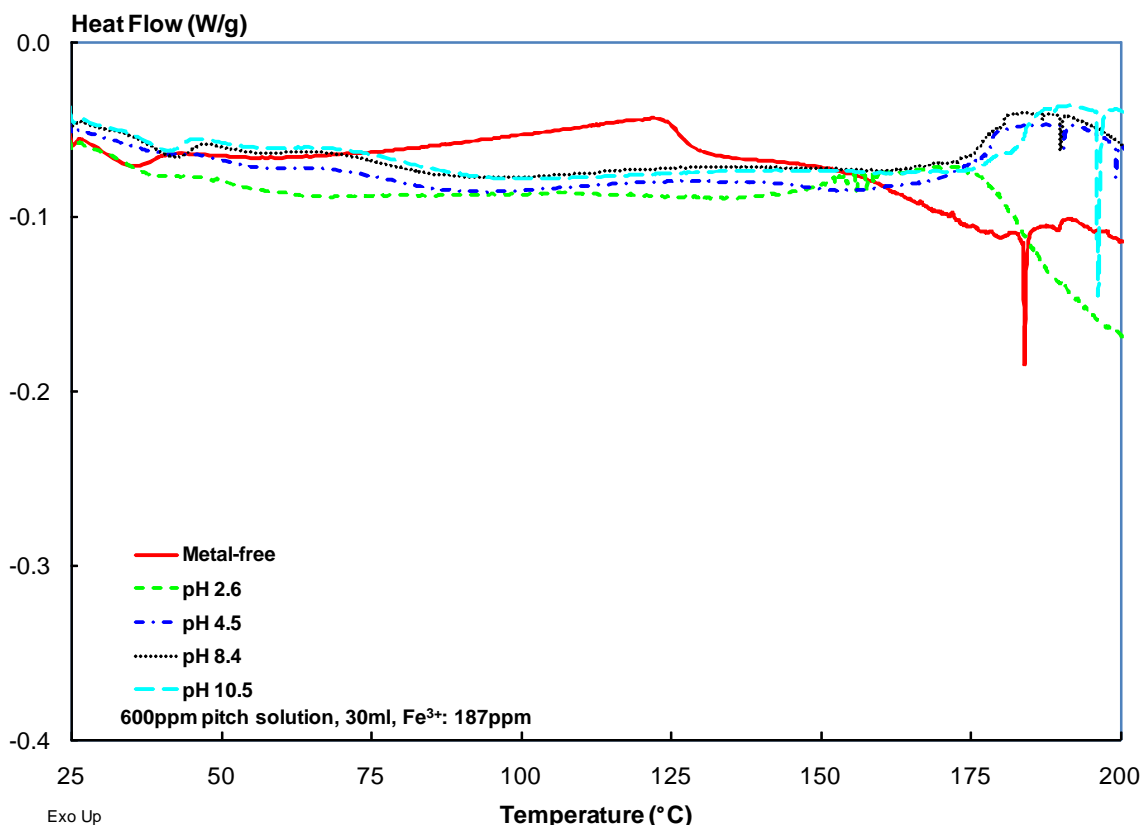


Fig. 6. pH effect on softening the Fe-pitch deposit

Magnesium ions were from the bleaching process, due to the fact that Mg(OH)₂ was used as the alkali source in the mill (Li et al. 2005). As shown in Fig. 7, some minor melting behavior can be seen in the range of 30°C to 50°C. The three deposits formed from acidic to neutral solutions (pH 2.9, 4.5, and 6.7) showed changes at 65-70°C, followed by the auto-polymerization process. The deposit formed at pH 9.4 was quite stable, supporting the conclusion that the presence of alkali stabilized the deposit formed with Mg²⁺.

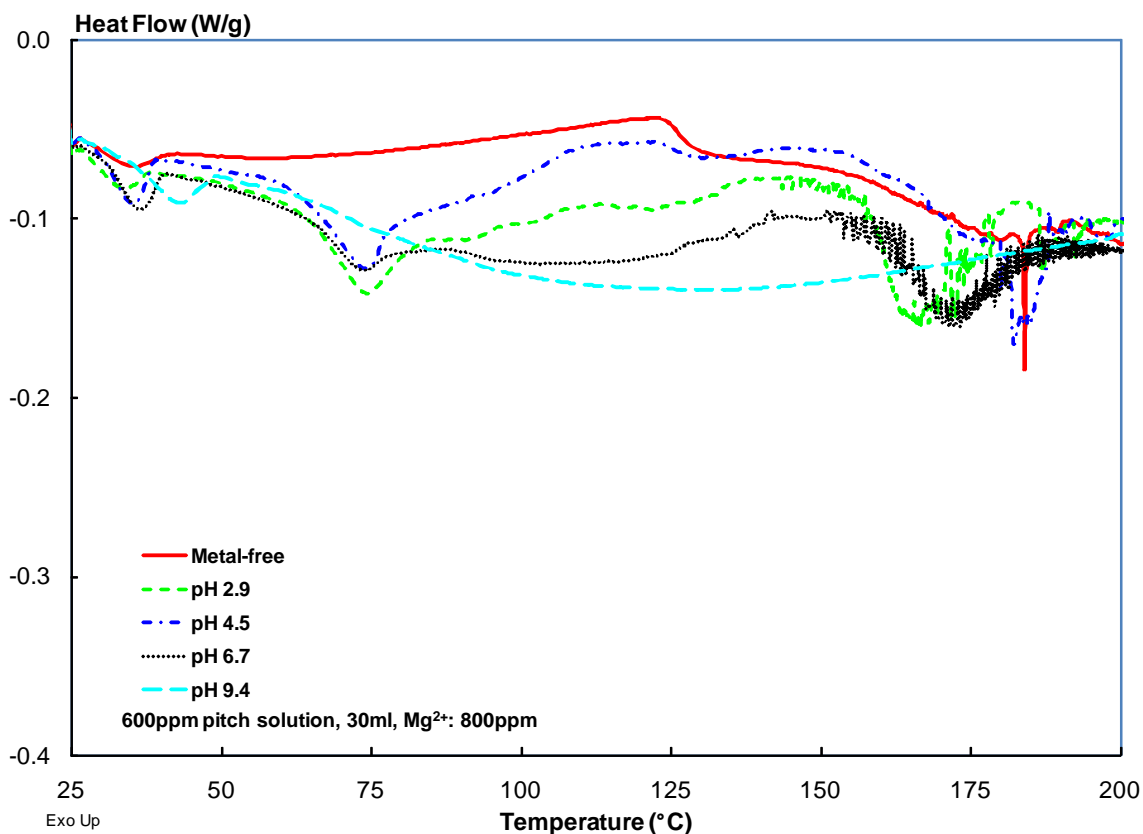


Fig. 7. pH effect on softening the Mg-pitch deposit

Although no appreciable amount of Al^{3+} was found in the mill deposit, wood resin deposits can also be formed when aluminum is present, as may be the case if certain clay is used as filler (Allen et al. 1997). As shown in Fig. 8, at a very low pH (pH 2.6) when alum was not in its cationic charge, which was reported at pH=4.2 (Strazdins 1989), the deposits went through thermal states such as glass polymerization and melting. With the increase in pH (pH 4.4, 8.4, and 11.6), there was almost no change of the thermal states for the deposit samples, probably because under these conditions aluminum can raise the softening temperature of pitch.

Generally there are two different papermaking processes based on the pH of the white water: acidic and, neutral processes. In the acidic process, clay usually is used as the filler, and the white water system is expected to contain more aluminum ions. As noted in Fig. 8, Al^{3+} -pitch deposits were usually stable in most of the pH ranges, except if it was too acidic. In the neutral papermaking process, calcium carbonate would usually be the filler. Evidently, as shown in Fig. 5, the presence of Ca^{2+} deteriorated the thermal stability of pitch-related deposits.

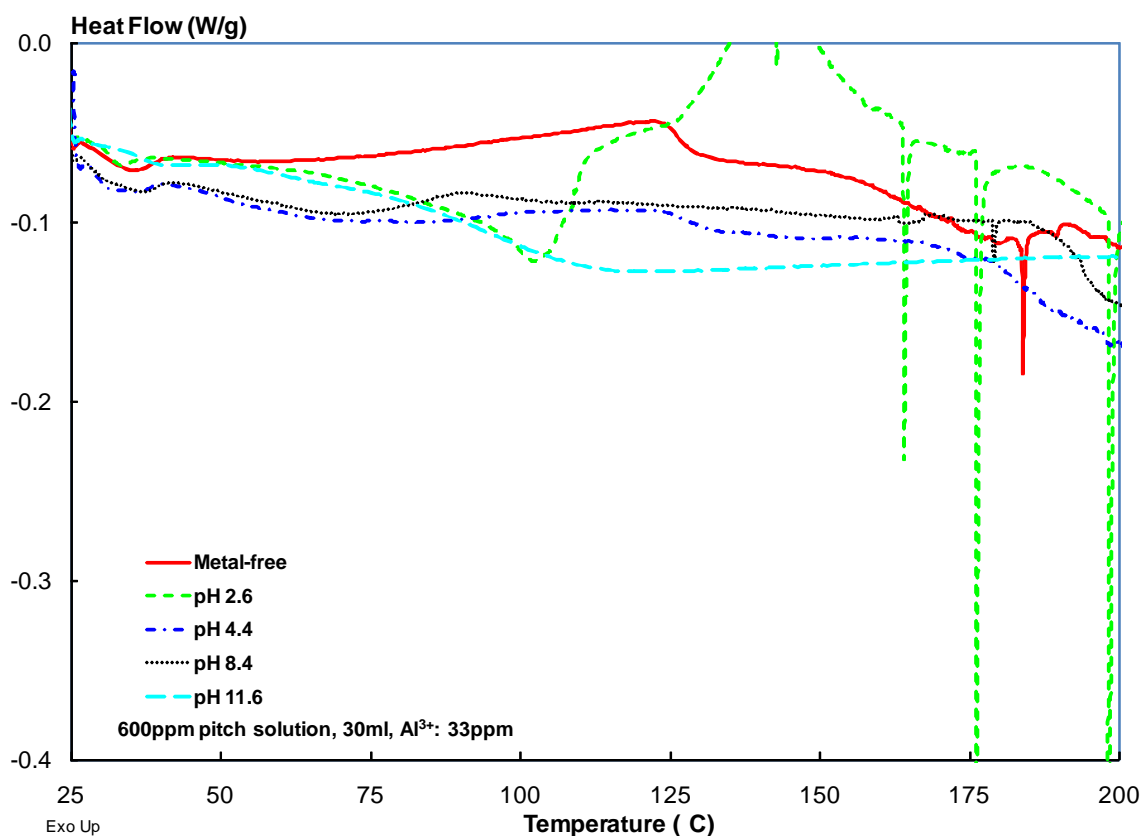


Fig. 8. pH effect on softening the Al-pitch deposit

SUMMARY

The pH and metal cations had significant impacts on the deposition caused by the resin from deposit collected in a supercalendered paper mill. Increasing pH improved not only the stability of pitch colloidal suspension, but also the thermal resistance of deposits due to the resin acids based extractives, when subjected to heating treatment.

Different metal metals showed various abilities in terms of forming pitch aggregates. Much lesser amounts of trivalent Al^{3+} or Fe^{3+} were required for the formation of same amount of pitch-related deposit than divalent metal ions, such as Ca^{2+} , Mg^{2+} , or Mn^{2+} . In the temperature range of 60-200°C, which is of practical interest to this TMP-based speciality paper mill, Ca^{2+} and Mg^{2+} can cause significant thermal instability of pitch deposits, whereas the thermal performances of deposits were more stable for Al^{3+} and Fe^{3+} , implying that the presence of Ca^{2+} or Mg^{2+} may cause more trouble in potentially forming pitch-related deposit than Al^{3+} or Fe^{3+} .

REFERENCES CITED

Allen, L. H. (1988). "The importance of pH in controlling metal-soap deposition," *TAPPI Journal* 71(1), 61-64.

- Allen, L. H., and Ouellet, S. (2007). "Deposit control: A team effort leading to improvements in a TMP/DIP newsprint mill," *Pulp & Paper Canada* 108(3), 45-50.
- Allen, L. H., Sithole, B. B., Lapointe, C. L., and Truitt, R. (1997). "Press roll pitch deposition problems associated with the use of certain clay products in newsprint manufacture," *Journal of Pulp and Paper Science* 23(4), 157-160.
- Back, E. (1963). "The mechanism of pulp resin accumulation at solid surfaces," *Svensk Papperstidning* (15), 556-564.
- Back, E. L., and Allen, L. H. (2000). *Pitch Control, Wood Resin and Deresination*. Altanda, Georgia: TAPPI Press.
- Castro, C., Daneault, C., and Dorris G. M. (1996). "Analysis of the accelerated thermal ageing of oil ink vehicles using thermogravimetry," *Journal of Pulp and Paper Science* 22(10), J365-J371.
- Dai, Z, Ni, Y., Court, G., and Li, Z.(2010). "Formation of pitch-related deposit in a TMP-based speciality paper mill," *Proceedings, 96th PAPTAC Annual Meeting*, 77-82.
- Dreisbach, D. D., and Michalopoulos, D. L. (1989). "Understanding the behavior of pitch in pulp and paper mills," *TAPPI Journal* 62(6), 129-134.
- Ghosh, A., and Ni, Y. (1998). "Metal ion complexes and their relationship to pulp brightness," *Journal of Pulp and Paper Science* 24(1), 26-31.
- Gustafsson, C., Kahila, S., and Lindh, T. (1952). "On pitch troubles caused by sulfite pulp" *Paperi ja Puu* 34, 121-128.
- Gutierrez, A., and Jose, C. R. (2005). "Chemical characterization of pitch deposits produced in the manufacturing of high-quality paper pulps from hemp fibers," *Bioresource Technology* 96, 1445-1450.
- He, Z., Wekesa, M., and Ni, Y. (2004). "Pulp properties and effluent characteristics from the Mg(OH)₂-based peroxide bleaching process," *TAPPI Journal* 3(12), 27-31.
- Hua, X., and Laleg, M. (2008). "Impact of machine whitewater on brightness of mechanical grades," *Proceedings, 94th PAPTAC Annual Meeting*, B417-B424.
- Hubbe, M. A., Rojas, O. J., and Venditti, R. A. (2006). "Control of tacky deposits on paper machines - A review," *Nordic Pulp and Paper Research Journal* 21(2), 154-171.
- Kellar, J. J., Young, C. A., Knutson, K., and Miller, J. D. (1991). "Thermotropic phase transition of adsorbed oleate species at a fluorite surface by in situ FT-IR/IRS spectroscopy," *Journal of Colloid and Interface Science* 144(2), 381-389.
- Laubach, G. D., and Greer, C. S.(1991). "Pitch deposit awareness and control," *TAPPI J.* 74(6), 249-252.
- Li, Z., Court, G., Belliveau, R., Crowell, M., Murphy, R., Gibson, A., Wajer, M., Branch, B., and Ni, Y. (2005). "Using magnesium hydroxide (Mg(OH)₂) as the alkali source in peroxide bleaching at Irving Paper," *Pulp & Paper Canada* 106(6), 24-28.
- Mao, C., and Ni, Y. (2008). "Effect of metal ion contamination in the process water on the brightness of peroxide- and hydrosulfite-bleached mechanical pulps," *Journal of Pulp and Paper Science* 34(2), 129-133.
- McLean, D. S., Stack, K. N., and Richardson, D. E. (2005). "The effect of wood extractives composition, pH and temperature on pitch deposition," *APPITA Journal* 58 (1), 52-55.

- Ni, Y., Li, Z., and van Heiningen, A. R. P. (1997). "Minimization of the brightness loss due to metal ions in process water for bleached mechanical pulps," *Pulp & Paper Canada* 98(10), 72-75.
- Ni, Y., Ng, A., and Mosher, M. (1999). "The formation of coloured metallic extractives complexes and its effect on the brightness of TMP pulp. Part I. Model compound study," *Journal of Wood Chemistry and Technology* 19(3), 213-223.
- Peart, C., and Ni, Y. (2001). "UV-Vis spectra of lignin model compounds in the presence of metal ions and chelants," *Journal of Wood Chemistry and Technology* 21(2), 113-125.
- Raymond, L., Gagne, A., Talbot, J., and Gratton, R. (1998). "Pitch deposition in a fine paper mill," *Pulp & Paper Canada* 99(2), 56-59.
- Stack, K. R., Stevens, E. A., Richardson, D. E., Parsons, T., Jenkins, S. (1998). "Factors affecting the deposition of pitch in process waters and model dispersions," 52nd *APPITA Annual General Conference*, 59-66.
- Strazdins, E. (1989). "Theoretical and practical aspects of alum use in papermaking," *Nordic Pulp and Paper Research Journal* 5(2), 128-134.
- Sundberg, K., Pettersson, C., Eckerman, C., and Holmbom, B. (1996a). "Preparation and properties of a model dispersion of colloidal wood resin from Norway spruce," *Journal of Pulp and Paper Science* 22(7), 248-251.
- Sundberg, K., Thornton, J., Holmbom, B., and Ekman, R. (1996b). "Effects of wood polysaccharides on the stability of colloidal wood resin," *Journal of Pulp and Paper Science* 22(7), 226-229.
- Swanson, W. J., and Cordingley, R. H. (1956). "Surface chemical studies on pitch I. A new approach to the pitch problem in papermaking," *TAPPI J.* 39(10), 684-689.

Article submitted: February 16, 2010; Peer review completed: March 13, 2010; Revised version received and accepted: July 27, 2010; Published: July 27, 2010.