

## Solubility of Sodium Oxalate in Kraft Black Liquors Above 100 °C

Ahmed Naser Khafhafera,\* and Nikolai DeMartini

The solubility of sodium oxalate was measured in kraft black liquors at temperatures of 115 °C to 140 °C with dry solid contents of 45% to 70%. The composition of black liquors studied were varied with respect to sodium concentration by addition of sodium salts. The solubility of sodium oxalate increased with increasing temperature and decreased with increasing liquor dry solid contents. The solubility data showed no dependence on the liquor composition at a constant concentration of sodium. A mathematical expression was derived and validated from the experimental data at the conditions investigated to predict the solubility of sodium oxalate as a function of temperature and sodium concentration. An application to assess the solubility and precipitation risk of sodium oxalate is demonstrated in seven evaporator bodies using the newly derived models.

DOI: 10.15376/biores.18.1.720-732

Keywords: Black liquor; Evaporation; Precipitation; Solubility; Sodium oxalate

Contact information: Department of Chemical Engineering and Applied Chemistry, University of Toronto, 200 College St, Toronto, ON, M5S 3E5, Canada;

\* Corresponding author: [anm.khafhafera@mail.utoronto.ca](mailto:anm.khafhafera@mail.utoronto.ca)

### INTRODUCTION

Wood chips are digested in white liquor, an aqueous solution of sodium hydroxide and sodium sulfide, to dissolve lignin and other organic components from fibers during the kraft pulping process. Weak black liquor is a by-product of kraft pulping, composed of dissolved organics and the inorganic chemicals used in pulping. Black liquor initially contains about 85% to 88% water after the dissolved organics and inorganics are washed from the pulp.

Water is evaporated from black liquor in multi-effect evaporators, with the solids increased to the range 65% to 85% level prior to combustion in a recovery boiler. The inorganics, which are predominantly sodium sulfide and sodium carbonate after combustion, are recovered as molten smelt in the boiler. The smelt is dissolved in water, which is then processed to produce sodium hydroxide from sodium carbonate, regenerating white liquor for pulping (Hough 1985; Tikka 2008; Frederick and DeMartini 2019).

Black liquor solids are approximately one-third of the spent pulping chemicals, and the remaining two-thirds are the organic substances extracted from the wood (Hough 1985). The typical ranges for black liquor composition are given in Table 1. Sodium oxalate scaling during black liquor evaporation has been previously reported, and good solubility models are needed to help mills understand if and where scaling can occur (Schmidl and Frederick 1998).

**Table 1.** Typical Ranges for Black Liquor Composition

Element	Mean	Range
Na (wt%)	18.4	14.0 to 20.3
Na <sub>2</sub> CO <sub>3</sub> (wt%)	10.0	4.8 to 14.5
Na <sub>2</sub> SO <sub>4</sub> (wt%)	6.0	1.9 to 16.1
Residual active alkali (wt%)	5.7	0.06 to 12.9
Organic carbon (wt%)	33.5	30.2 to 39.7
C <sub>2</sub> O <sub>4</sub> (wt%)	0.52	0.20 to 1.34

Oxalate exists in wood primarily as oxalic acid, CaC<sub>2</sub>O<sub>4</sub>, and K<sub>2</sub>C<sub>2</sub>O<sub>4</sub>. In plants, oxalate balances the charge of excess cations by forming crystals; calcium oxalate is the most prevalent (Franceschi and Loewus 1995; Serdar and Demiray 2012). The concentration of oxalic acid/oxalate ion in North American hardwood and softwood is 0.1 to 0.3 g/kg, 0.1 to 0.4 g/kg, respectively (Krasowski and Marton 1983). In another study, the concentration of oxalic acid/oxalate in acacia and pine was determined as 0.80 g/kg and 0.13 g/kg, respectively based on 2 mol/L HCl solution at 70 °C (Li *et al.* 2012). The content of oxalate ion in the bark of North American hardwood and pine is found in the range of 9 to 15 and 4 to 10 g/kg, respectively (Krasowski and Marton 1983). The oxalate concentration in four Finnish wood species ranges between 0.035 to 0.38 g/kg, while the concentration in the bark ranges from 7.74 to 16.72 g/kg (Werkelin *et al.* 2010). The oxalate concentration in black liquor can be increased by improper debarking of the wood used in pulping. Oxalate is also formed during pulping, oxygen delignification, and bleaching (Fiskari and Gullichsen 1999; Elsander and Gellerstedt 2000; Ulmgren and Radestrom 2000; Li *et al.* 2012) and its formation appears to be at least partially species dependent.

As the black liquor is concentrated, the multi-effect evaporators suffer mostly from Na<sub>2</sub>CO<sub>3</sub> and Na<sub>2</sub>SO<sub>4</sub> double salts scaling, leading to fouling of the heat transfer surface. Table 2 shows the results of two industrial surveys of scaling in black liquor evaporators that have been published in the literature (Grace 1975; Schmidl and Frederick 1998). The responses of the surveys were provided primarily from North American pulp mills. Sodium oxalate, because of its normal solubility at room temperature, is found to cause scaling in lower temperature effects (Khafhafera *et al.* 2022). It is also found to co-precipitate with the sodium carbonate-sulfate double salts in high solids tanks, forming layered scales (DeMartini and Verrill 2005).

**Table 2.** Scale Types in Black Liquor Evaporators Based on Industrial Surveys

Scale Type	Number of Mills Reported	
	Survey No. 1	Survey No. 2
Sodium Sulfate Carbonate	19	17
Sodium Oxalate	-	1
Calcium Carbonate	20	11
Organics	6	9
Aluminosilicates	9	4
Pirssonite	-	1
Other Inorganics	-	1
No Scale	10	2
No Information	3	3
Total	67	49

Ulmgren and Rådeström (2002) measured the solubility of sodium oxalate in black liquor from 90 to 150 °C as a function of sodium concentration by adding sodium salts (sodium acetate and sodium chloride). They developed two empirical models for the apparent solubility product based on the experimental data, one at 90 °C and the other for temperatures from 110 to 150 °C. The dependence of the solubility product on sodium concentration was different in the two temperature ranges. However, the solubility of sodium oxalate has been studied in different systems other than black liquor as a function of temperature and sodium concentration. In a study by Fowler (1980), the solubility of sodium oxalate has been determined in a series of solutions of NaOH and NaNO<sub>3</sub> at temperatures of 20 to 49 °C. Similarly, Hefter and co-workers (2018) have investigated the solubility of sodium oxalate in concentrated electrolyte solutions containing NaCl, NaClO<sub>4</sub>, NaOH, LiCl, KCl, Me<sub>4</sub>NCl, and KOH at temperatures of 25 to 70 °C.

In a previous study, the authors measured the solubility of sodium oxalate in four kraft black liquors from different mills at temperatures ranging from 50 to 90 °C and dry solids ranging from 14 to 47 wt% d.s. to obtain necessary data for lower temperatures (Khafhafera *et al.* 2022). It was found that the solubility behaved similarly in all liquors. A single empirical equation for the apparent solubility product of sodium oxalate in black liquor was developed and validated for the temperature and solid ranges studied, as shown in Eq. 1:

$$\text{Log}(L_s) = 5.72 + (0.0047 \times [\text{Na}]) - (605/T) \quad (1)$$

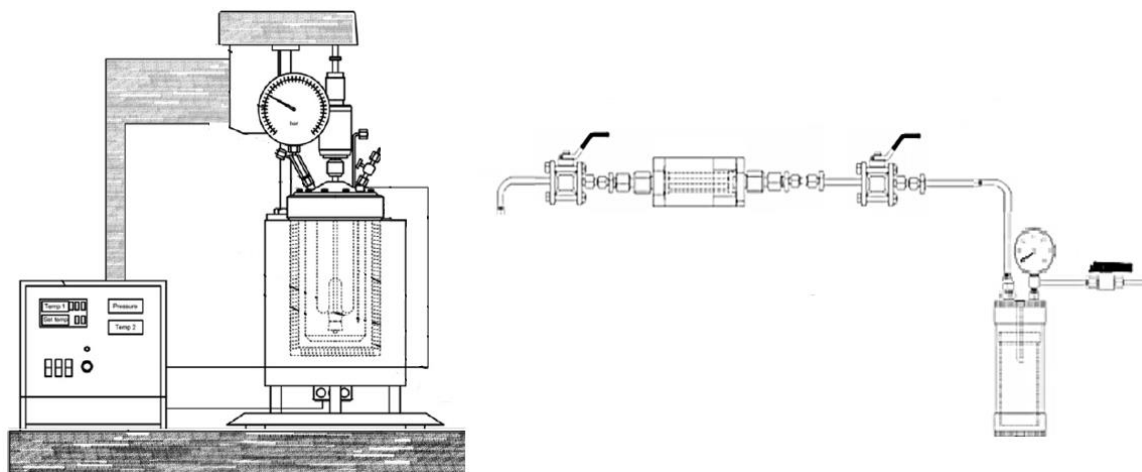
In this equation,  $L_s$  is the apparent solubility product of sodium oxalate. The concentration of sodium, [Na], is in g/kg H<sub>2</sub>O and the temperature,  $T$ , is given in degrees Kelvin.

The aim of this study was to determine the solubility of sodium oxalate in black liquors at temperatures ranging from 115 °C to 140 °C and dry solids ranging from 45% to 70%. This mostly represents the temperature range and solids from the 2<sup>nd</sup> effect through the concentrators. In this range, sodium carbonate and sulfate salts also precipitate and this is already accounted for. A model for the apparent solubility product was developed and compared with the solubility data obtained in this work as well as the existing models. The newly derived model was applied to an industrial evaporation set as an example. Evaporator suppliers and mill operators can use the model equations of this study and the authors' earlier study (Khafhafera *et al.* 2022) to identify where sodium oxalate might precipitate. For new installations, extra surface area can be added to account for lost heat transfer due to scaling. Additionally wash cycles can be planned to wash the scale.

## EXPERIMENTAL

The solubility of sodium oxalate in black liquors was determined simultaneously with that of sodium carbonate and sodium sulfate. The experiments were conducted in a mini-bench Parr reactor (Model: Parr4560, Parr Instrument Co., Moline, Illinois, USA; max volume: 300 mL, max temperature: 300 °C, max pressure: 200 bar). Figure 1 shows the components of the Parr reactor: reactor body, reactor head with various connections, stirring motor, programmable controller, and an integrated sampling line. The following are the key components of the sample line: stainless-steel filter with a larger surface area (13-mm diameter and 77-mm length) and nominal pore size of 2 µm (Norman Filter Co., Bridgeview, Illinois, USA, part number 4311GG-2XVN), a vessel for collecting samples, and a pressure gauge to monitor the pressure in the sampling line so that it can be kept

below the reactor pressure but above atmospheric pressure to avoid water flashing during withdrawing samples. Heating tape with an adjustable thermostat is used to warm up the filter to the same temperature as the black liquor to be filtered before pulling each sample. The rationale for heating the filter is that the temperature of the black liquor does not drop while sampling. The filter is then disassembled, soaked, and rinsed with de-ionized water, then air-dried for reuse.



**Fig. 1.** Schematic diagram of mini-bench Parr reactor with inline sampling apparatus

The solubility of sodium oxalate in a hardwood mix black liquor at temperature above 100 °C was determined simultaneously with sodium carbonate and sodium sulfate. The composition of black liquors used in this study is given in Table 3. Liquor A is referred to the liquor without salt addition, while liquors B and C are referred to the liquors with salt additions. The carbonate, sulfate, and sodium contents in liquors B and C were adjusted by adding sodium carbonate or sodium sulfate. In most cases, the solubility tests were conducted across a liquor dry solids (d.s.) range of 45% to 70%. Samples from the black liquors were first concentrated to increase the dry solids by evaporation at 70 °C and then the samples were put in the parr reactor and equilibrated at the desired temperature. The Parr reactor was loaded with 150 to 200 g of black liquor for each experiment, and an excess of sodium oxalate was then added to assure super-saturation of sodium oxalate to obtain solubility data for sodium oxalate. The reactor was assembled, the temperature and stirring were adjusted, and the liquor was allowed to equilibrate for 24 h. Upon sampling, the liquor sampling line was attached to the reactor, preheated, and then the sampling system was pressurized with air to above the vapor pressure of water for the given black liquor temperature and solids to prevent flashing across the filter. The reactor was then pressurized to about 10 to 20 bar above the water vapor pressure. The sampling valve was then opened, allowing the liquor to be pushed through the filter and into the collection vessel by the pressure difference. The sampling line was then disassembled, the filtered liquor sample was collected and weighted, and the sample was then diluted for Na, CO<sub>3</sub>, SO<sub>4</sub>, and C<sub>2</sub>O<sub>4</sub> analysis. Equilibrium was considered as having been reached when the concentrations of dissolved oxalate did not change in subsequent samples. An excess of solid was added and the dissolved concentration was always below the concentration that oxalate would have been at if all the solid was dissolved. It should be noted that the solid samples of sodium oxalate have not been quantified/analyzed in this work. The carbonate and sulfate results will be published separately.

**Table 3.** Black Liquor Composition Used in this Study

Liquor	Na (wt%)	CO <sub>3</sub> (wt%)	SO <sub>4</sub> (wt%)	C <sub>2</sub> O <sub>4</sub> (wt%)	Temperature (°C)	Dry Solids (%)
A*	18.1	5.3	2.5	0.22	115 to 140	50 to 70
B**	19.5	5.3	5.6	0.21	115	45 to 70
C**	20.9	8.9	2.5	0.20	115	45 to 70

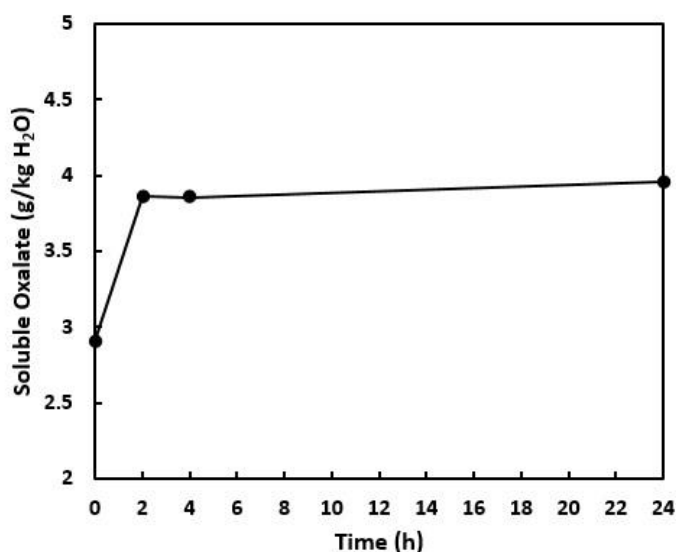
\*: represents the composition of black liquor without salt addition.

\*\* : represents the composition of black liquor after salt addition.

The dry solids measurements were performed overnight by drying in an oven, and the concentration of both sodium and oxalate ions in the black liquors were determined using ion chromatography (IC, Dionex Integion Rfic, Waltham, Massachusetts, USA). For anion determination, the eluent was potassium hydroxide at a concentration of 23 mM and the column used was Dionex IonPac AS18. For cation determination, the eluent was methanesulfonic acid at a concentration of 6 mM and the column was Dionex IonPac CS17.

## RESULTS AND DISCUSSION

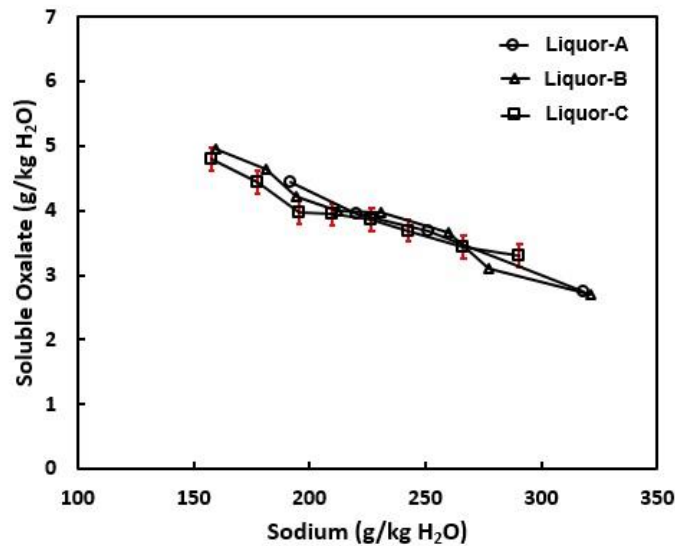
The equilibrium time for sodium oxalate was determined in liquor-A at a temperature of 115 °C and dry solids contents of 57%. Equilibrium was reached within 2 h for sodium oxalate in black liquor, (Fig. 2). At lower temperature, the equilibration time was 4 h (Khafhafera *et al.* 2022). Two samples were typically pulled between 4 and 24 h after the experimental temperature was reached, and the oxalate concentration obtained at these different times were averaged to obtain the equilibrium concentration.



**Fig. 2.** Equilibration time of sodium oxalate in liquor-A at temperature of 115 °C and dry solids of 57%

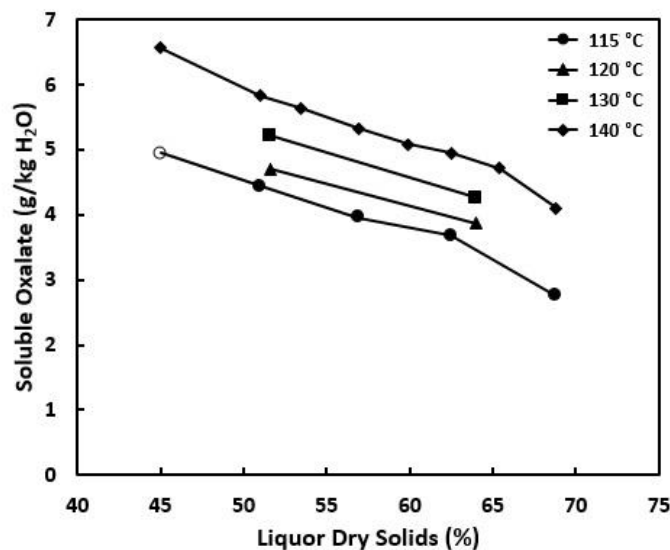
The solubility data for oxalate as a function of measured dissolved sodium concentration was plotted at 115 °C (Fig. 3). The solubility data obtained were highly

consistent at a given sodium concentration in liquors A, B, and C, as used in this study. Note that liquor A is referred to the liquor without salt addition, while liquors B and C are referred to the liquors with salt additions. It was observed that as the sodium concentration increases, the solubility of sodium oxalate decreases in black liquor.

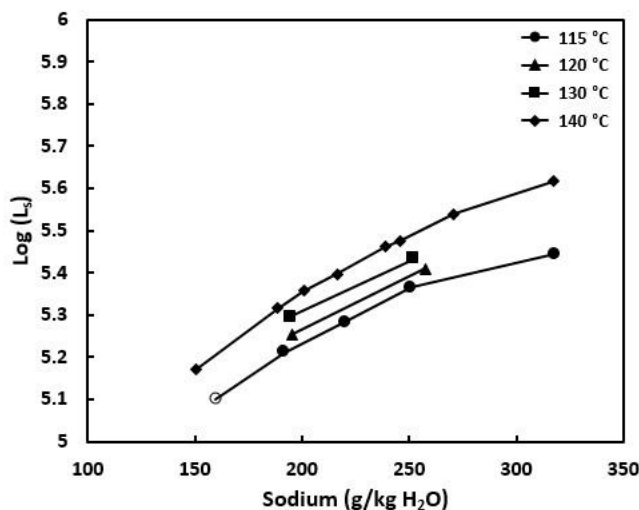


**Fig. 3.** Soluble oxalate as a function of measured dissolved sodium for all liquors at 115 °C ; The error bars represent the maximum and minimum from average of two samples, each analyzed twice by IC.

The solubility of sodium oxalate decreased with increasing liquor dry solids and increased as a function of temperature (Fig. 4). The log of the apparent solubility product,  $\log(L_s)$ , was calculated and plotted against the measured sodium concentration, (Fig. 5). A positive correlation with soluble sodium concentration was found, which was similar to the results at temperatures below 100 °C.



**Fig. 4.** Solubility of sodium oxalate in liquor-A as a function of liquor dry solids at 115 to 140 °C

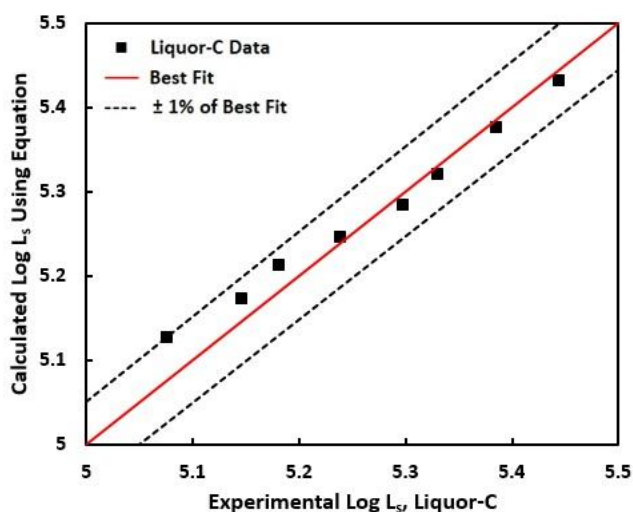


**Fig. 5.** The calculated apparent solubility product of sodium oxalate in liquor-A as a function of measured sodium at 115 to 140 °C

Using the solubility data obtained from liquors A and B, an empirical model was derived to predict the apparent solubility product as a function of sodium and temperature,

$$\text{Log}(L_s) = 6.93 + (0.0023 \times [\text{Na}]) - (841/T) \quad (2)$$

where  $L_s$  is the apparent solubility product, the concentration of sodium,  $[\text{Na}]$ , is in g/kg H<sub>2</sub>O, and the temperature,  $T$ , is given in degrees Kelvin. The measured solubility data for liquor-C at 115 °C was used to validate the newly derived model. The experimental apparent solubility product is plotted against the calculated values based on Eq. 2 (Fig. 6). The data fell within  $\pm 1\%$  of the best fit, indicating that the predictions of the model equation were reasonable and thus broadly applicable to estimate the solubility of sodium oxalate in black liquor at temperatures above 100 °C and dry solids above 50%.

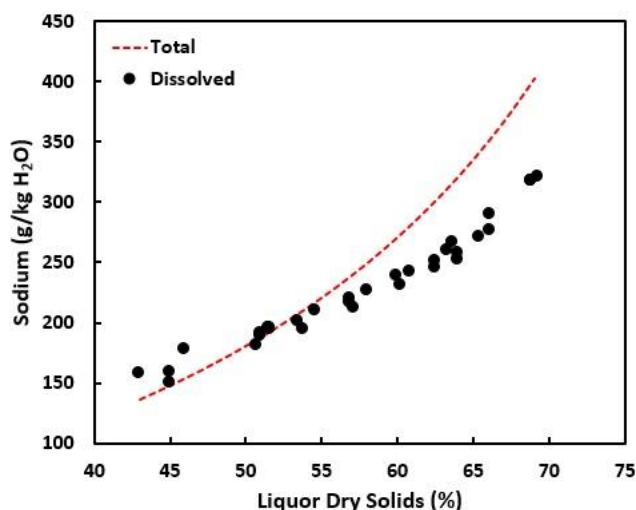


**Fig. 6.** The correlation between the experimental and calculated apparent solubility product in liquor-C at 115 °C

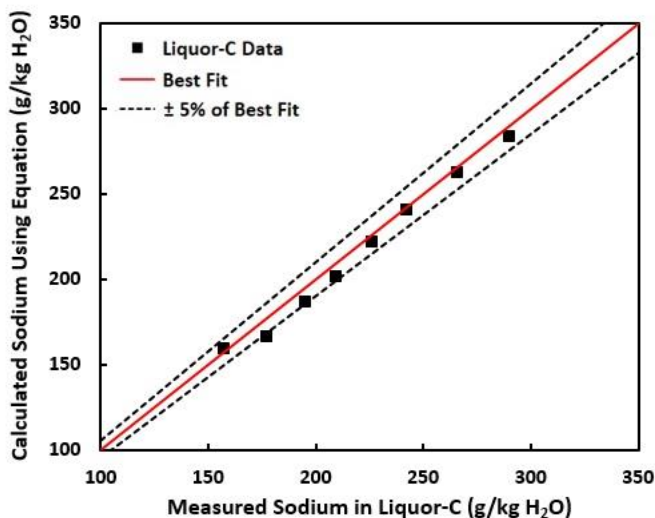
Because of the precipitation of sodium carbonate and sodium sulfate in black liquor at dry solids above 50%, not all sodium remains dissolved in black liquor. Figure 7 shows the dissolved and total sodium concentrations as a function of liquor dry solids. A higher amount of dry solids results in a higher amount of dissolved sodium in black liquor. A mathematical model was derived using experimental data from liquors A and B to estimate the dissolved sodium concentration as a function of liquor dry solids, Eq. 3,

$$Na_{\text{dissolved}} = 0.15DS^2 - 10.97DS + 353 \quad (3)$$

where the concentration of dissolved sodium,  $[Na]_{\text{dissolved}}$ , is in g/kg H<sub>2</sub>O and the total liquor dry solids, DS, is given as %.



**Fig. 7.** Correlation between black liquor dry solids and sodium concentration: The calculated line is interpolated assuming sodium is 18 wt% d.s. and no precipitation took place; the marks are for the measured sodium where precipitation of sodium double salts.

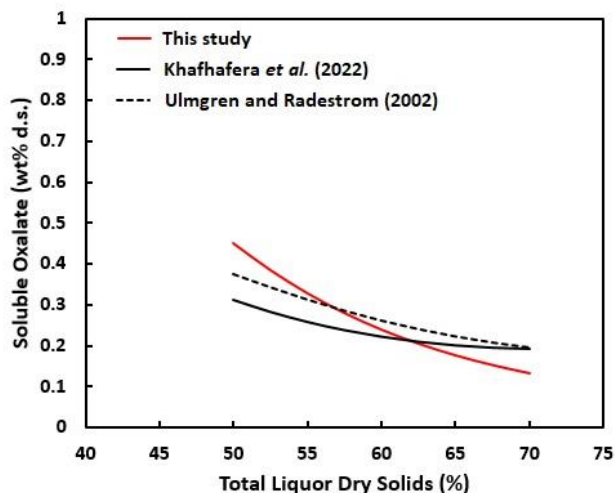


**Fig. 8.** The correlation between the measured and calculated dissolved sodium concentration in liquor-C at 115 °C

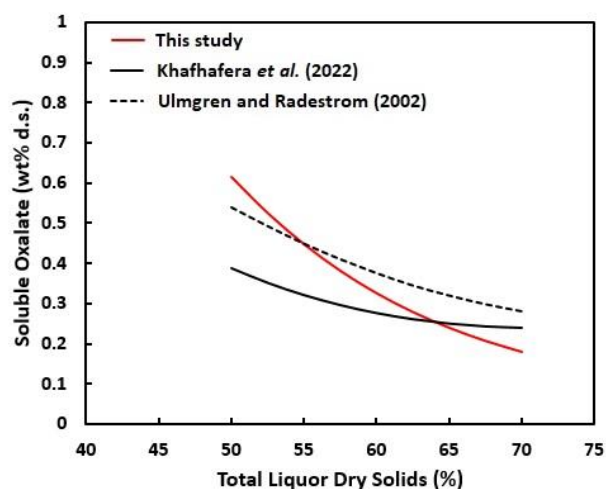


The measured concentration of dissolved sodium in liquor-C was excluded from deriving the model equation for soluble sodium and used for validation. Figure 8 shows the correlation between the measured and calculated concentrations; all values fell within  $\pm 5\%$  of the best fit. This observation indicates that Eq. 3 can reasonably predict the concentration of dissolved sodium at dry solids range investigated, taking into account the precipitation of sodium carbonate-sodium sulfate double salts.

The solubility predictions at 115 and 140 °C are different when comparing the models from this study and from previous studies (Figs. 9 and 10). At liquor temperature of 115 °C and dry solids of 50%, the predicted concentration of soluble oxalate using this work equation is 44% and 20% higher than those predicted using models generated in previous studies by Khafhafera *et al.* (2022) and Ulmgren and Radestrom (2002). Increasing the temperature further to 140 °C, the soluble oxalate at liquor dry solids of 50% is 56% and 13% higher compared to the predicted values from previous studies. This is likely due to the difference in activity of sodium in black liquor at different dry solid levels and temperature.



**Fig. 9.** The predicted solubility of sodium oxalate in black liquor at temperature of 115 °C



**Fig. 10.** The predicted solubility of sodium oxalate in black liquor at temperature of 140 °C

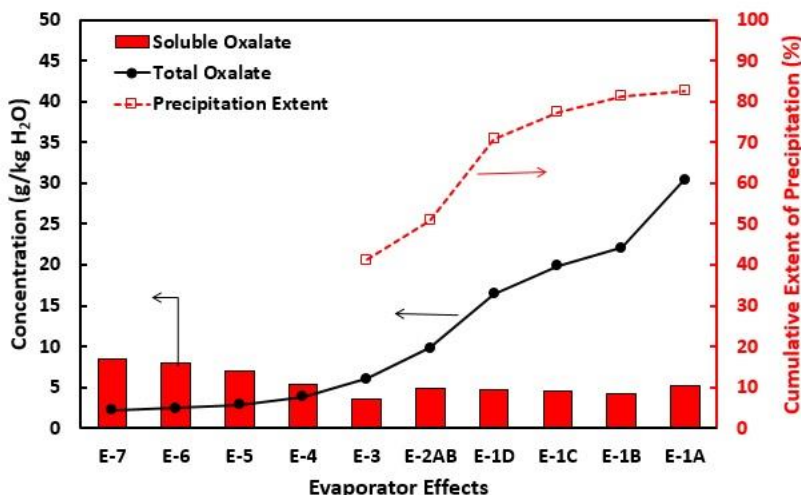
## INDUSTRIAL RELEVANCE

The authors used this work combined with their earlier study to evaluate the precipitation risk of sodium oxalate in a South American pulp mill's evaporation plant. The layout of the evaporation plant consists of seven effects with four bodies in the 1<sup>st</sup> effect. Table 4 shows the temperature and dry solids (d. s.) profile in the evaporators provided by the mill when it is considered to run under normal conditions. It should be noted that the mill is pulping *Eucalyptus* wood, in which the oxalate and sodium concentrations in black liquor were measured as 1.08 wt% d.s. and 18.1 wt% d.s., respectively. The equation model from the previous study (Khafhafera *et al.* 2022), Eq. 1, was used to calculate the solubility of sodium oxalate in the effects operate at temperatures below 100 °C, while the equation models from this study, Eqs. 2 and 3, were used for solubility calculation for effects operating at temperatures above 100 °C.

**Table 4.** Temperature and Dry Solids Profiles in a 7-effects Evaporation Train at a South American Pulp Mill

Evaporator Effect	Temperature (°C)	Dry Solids (%)
E-7	56	17
E-6	66	19
E-5	75	21
E-4	87	26
E-3	99	36
E-2AB	114	48
E-1D	139	60
E-1C	140	65
E-1B	137	67
E-1A	165	74

Using the operating conditions described above, the solubility of sodium oxalate in black liquor has been calculated in the temperature range 56 to 165 °C and dry solids range of 17% to 74% (Fig. 11). As water is evaporated, going from effect 7 to effect 1, the concentrations of sodium and oxalate increase but at the same time, the temperature of the black liquor increases, resulting in a higher solubility limit for a given black liquor dry solids. The solubility of oxalate is highest in effect 7 at a dry solids of 17% and temperature of 56 °C. The solubility behavior then exhibits a gradual decrease as the liquor dry solids increases from 19% to 36% in effect 6 to effect 3, respectively. Although the liquor temperature increases from 56 to 99 °C in effects 7 to 3, the solubility of oxalate decreases because the sodium concentration increases from 37 g/kg H<sub>2</sub>O to 102 g/kg H<sub>2</sub>O as a result of increasing liquor solids from 17% to 36%. The sodium oxalate becomes slightly more solubilized in effect 2 and the multiple body concentrator due to the increase in temperature and decrease in sodium concentration because of formation of sodium double salts. In (Fig. 11 and 12), the red bars represent the soluble oxalate concentration in g/kg H<sub>2</sub>O, the black line represents the total oxalate concentration in g/kg H<sub>2</sub>O, the red line represents the extent of precipitation in %.

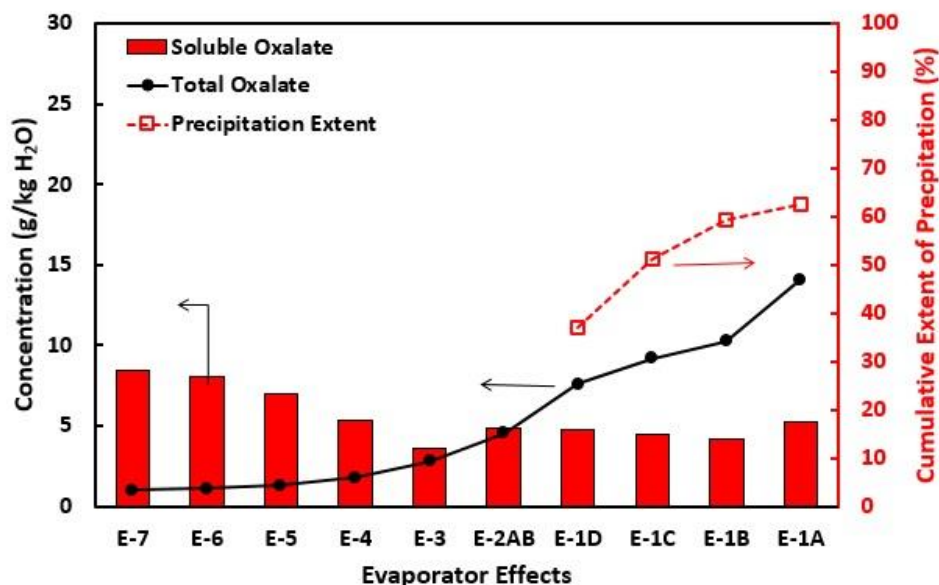


**Fig. 11.** Solubility of sodium oxalate in a South American mill's evaporation train and the assessment of precipitation risk when the initial oxalate concentration is 1.08 wt% d.s. The red bars represent the soluble oxalate concentration in g/kg H<sub>2</sub>O, the black line represents the total oxalate concentration in g/kg H<sub>2</sub>O, and the red line represents the extent of precipitation in %.

It should be noted that the total oxalate concentration in the black liquor on a molar basis increases as water is evaporated. The calculations indicate that sodium oxalate remains soluble within effects 4, 5, 6, and 7 under normal operating conditions. The precipitation of sodium oxalate starts in effect 3 and continues to precipitate out in effects 1 and 2. An earlier study by Khafhafera *et al.* (2022) shows that sodium oxalate precipitation can take place in the 7<sup>th</sup> effect when the effect operates at higher solids than normal. The cumulative extent of precipitation relative to the initial concentration in black liquor is calculated using Eq. 4. Over 80% of the sodium oxalate in black liquor precipitates out by the 1A body based on equilibrium solubility. The extent of precipitation can be calculated as shown in Eq. 4:

$$\text{Precipitation Extent} = (\text{Total oxalate} - \text{Soluble oxalate})/\text{Total oxalate} \quad (4)$$

Similar calculations can be performed to determine the initial oxalate concentration in black liquor before any sodium oxalate deposition occurs, assuming that the mill maintains the evaporation plant operational conditions given in Table 4. To avoid the sodium oxalate supersaturation in the effects 2 and 3, the initial oxalate concentration should not exceed 0.50 wt% d.s. as opposed to 1.08 wt% d.s. Despite lowering the initial oxalate concentration 50%, there is still precipitation of sodium oxalate in effect 1, which is expected to precipitate with Na-CO<sub>3</sub>-SO<sub>4</sub> salts, (Fig. 12). Approximately 60% of the sodium oxalate in black liquor precipitates out in effect 1 bodies based on equilibrium solubility. To completely eliminate the potential of sodium oxalate precipitation in the entire evaporator effects, the mill's initial oxalate concentration in black liquor must be reduced to 0.15 wt% d.s.



**Fig. 12.** Solubility of sodium oxalate in a South American mill's evaporation train and the assessment of precipitation risk when the initial oxalate concentration is 0.50 wt% d.s. The red bars represent the soluble oxalate concentration in g/kg H<sub>2</sub>O, the black line represents the total oxalate concentration in g/kg H<sub>2</sub>O, the red line represents the extent of precipitation in %

## CONCLUSIONS

1. As found by Ulmgren and Radestrom (2002), the solubility of sodium oxalate in evaporator effects operating below 100 °C and effects operating above 100 °C is best described by two different equations, presumably due to changes in the activity of sodium and oxalate salts with the changes in solids as well as temperature.
2. The equations developed in this study and an earlier study Khafhafera *et al.* (2002) can be used by kraft pulp mills to understand in which effects sodium oxalate will precipitate.

## ACKNOWLEDGMENTS

This work is part of the industrial research consortium project Effective Energy and Chemical Recovery in Pulp and Paper Mills - II at the University of Toronto supported by Andritz, Arauco, Babcock and Wilcox, Canadian Kraft Paper, Cenibra, Clyde Bergemann, CMPC, ERCO Worldwide, FITNIR, FPIInnovations, Georgia Pacific, International Paper, IRVING, KFS, Klabin, Mercer, NORAM, Rayonier, Sappi, Södra, Stora Enso, Suzano, Valmet, and WestRock. We would also like to acknowledge the support of the Natural Sciences and Engineering Research Council of Canada (NSERC), [IRCPJ 517715 -16]. Cette recherche a été financée par le Conseil de recherches en sciences naturelles et en génie du Canada (CRSNG), [IRCPJ 517715 -16].

## REFERENCES CITED

- DeMartini, N., and Verrill, C. (2005). "Evaporator fouling mitigation-case studies," in: *Engineering, Pulping, and Environmental Conference*, Philadelphia, PA, USA, pp. 1-10.
- Elsander, A., Ek, M., and Gellerstedt, G. (2000). "Oxalic acid formation during ECF and TCF bleaching of kraft pulp," *TAPPI Journal* 83(2), 73-77.
- Fiskari, J., and Gullichsen, J. (1999). "Laboratory experiments on oxalic acid formation in hardwood pulp TFF bleaching," in: *10<sup>th</sup> International Symposium on Wood and Pulping Chemistry*, Yokohama, Japan, pp. 324-328.
- Fowler, J. R. (1980). "Effect of temperature on sodium oxalate solubility," *Technical Division Savannah River Laboratory*. 1-6. DOI:10.2172/1475289.
- Franceschi, V. R., and Loewus, F. A. (1995). "Oxalate biosynthesis and function in plants and fungi," in: *Calcium Oxalate in Biological Systems*, CRC Press, Boca Raton, FL, USA, pp. 113-130.
- Frederick, J., and DeMartini, N. (2019). "Kraft pulp and black liquor production worldwide," in: *Black Liquor Evaporation*, 1<sup>st</sup> Edition, TAPPI Press, Atlanta, GA, USA, pp. 5-9.
- Grace, T. (1975). "A survey of evaporator scaling in the alkaline pulp industry," in: *IPST Project Reports*, Atlanta, GA, USA, pp. 1-71.
- Hefter, G., Tromans, A., May, P. M., and Konigsverger, E. (2018). "Solubility of sodium oxalate in concentrated electrolyte solutions". *Journal of Chemical & Engineering Data*, 63(3), 542-552. DOI: 10.1021/acs.jced.7b00690.

- Hough, G. W. (1985). "Principles of chemical recovery," in: *Chemical Recovery in the Alkaline Pulping Processes*, TAPPI Press, 1<sup>st</sup> Ed., Atlanta, GA, USA, pp. 9-14.
- Khafhafera, A. N., Kung, J. W. J., and DeMartini, N. (2022). "Solubility of sodium oxalate in kraft black liquors below 100 °C," *The Canadian Journal of Chemical Engineering* (Online, Early View), 1-9. DOI: 10.1002/cjce.24424
- Krasowski, J. A., and Marton, J. (1983). "The formation of oxalic acid during bleaching of kraft pulp," *Journal of Wood Chemistry and Technology* 3(4), 445-458. DOI: 10.1080/02773818308085175
- Li, H., Chai, X.-S., and DeMartini, N. (2012). "Oxalate release and formation during alkaline pulping," *Journal of Wood Chemistry and Technology* 32(3), 187-197. DOI: 10.1080/02773813.2011.633204
- Schmidl, W., and Frederick, J. (1998). "Current trends in evaporator fouling," in: *International Chemical Recovery Conference Proceedings*, Tampa, FL, USA, pp. 367-377.
- Serdar, B., and Demiray, H. (2012). "Calcium oxalate crystal types in three oak species (*Quercus* L.) in Turkey," *Turkish Journal of Biology* 36(4), 386-393. DOI: 10.3906/biy-1109-35
- Tikka, P. (2008). "Overview of kraft recovery," in: *Papermaking Science and Technology: Chemical Pulping. Part 2: Recovery of Chemicals and Energy*, 2<sup>nd</sup> edition, Paper Engineers' Association/Paperi Ja Puu Oy, Helsinki, Finland, pp. 10-15
- Ulmgren, P., and Radestrom, R. (2000). "On the formation of oxalate in bleach plant filtrates on hot storage," *Nordic Pulp & Paper Research Journal* 15(2), 128-132. DOI: 10.3183/npprj-2000-15-02-p128-132
- Ulmgren, P., and Radestrom, R. (2002). "Deposition of sodium oxalate in the black liquor evaporation plant," *Nordic Pulp & Paper Research Journal* 17(3), 275-279. DOI: 10.3183/npprj-2002-17-03-p275-279
- Werkelin, J., Skrifvars, B. J., Zevenhoven, M., Holmbom, B., and Hupa, M. (2010). "Chemical forms of ash-forming elements in woody biomass fuels," *Fuel* 89(2), 481-493. DOI: 10.1016/j.fuel.2009.09.005

Article submitted: September 6, 2022; Peer review completed: November 5, 2022;

Revised version received: November 17, 2022; Accepted: November 18, 2022;

Published: November 23, 2022.

DOI: 10.15376/biores.18.1.720-732