Prediction of the solubility of recovery boiler precipitator ash

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ABSTRACT: The solubility of recovery boiler precipitator ash in water is important in the design and operation of ash treatment systems used to control chloride (Cl) and potassium (K) accumulation in the kraft recovery cycle. We determined the solubility of mixtures of alkali salts that constitute precipitator ash and several precipitator ash samples, through laboratory experiments and theoretical simulation using a commercially available thermodynamic program. The solubility of precipitator ash in water at 85°C varies widely, from 400–550 g/L H_2O, depending on ash composition. The composition of the liquid portion of an ash-water slurry changes significantly with an increase in ash concentration: the Cl concentration increases, the sulfate (SO_4) concentration decreases, and the K and carbonate (CO_3) concentration remain the same. Between 30°C–100°C, temperature has little effect on the solubility of precipitator ash and on the composition of the liquid portion of the slurry.

Application: Mills can improve control of chloride and potassium build-up in the recovery cycle by understanding the water solubility of recovery boiler precipitator ash under various conditions.

Chlorine (commonly referred to as chloride, Cl) and potassium (K) are known to have a negative impact on the operation of the kraft chemical recovery process. These elements, despite their small quantities in black liquor, can drastically lower the melting temperature of carryover particles/deposits, and contribute greatly to fouling and corrosion of heat transfer tubes in the superheater region of recovery boilers.

Due to the enrichment of Cl and K in recovery boiler precipitator ash, efforts to remove them from the recovery cycle have been directed at the precipitator ash. Many mills control their Cl and K levels by purging precipitator ash periodically through their sewage systems. Ash purging is easy and requires little capital investment, but it is not a viable solution due to environmental concerns and high costs associated with sodium (Na) and sulfur (S) lost with the purged ash.

Several commercially available ash treatment processes use different principles to selectively remove Cl and K from the recovery cycle [1]. These processes include ash leaching, evaporation-crystallization, freezing-crystallization and ion exchange, and a common feature is that they all need to mix the ash with water to produce either ash-water slurry or a nearly saturated aqueous solution of the ash. In the ash leaching process [2], precipitator ash is mixed with water to form slurry (a mixture of liquid and solids). In the evaporation-crystallization process [3], precipitator ash is completely dissolved in water to form a nearly saturated solution. The solution is then evaporated in a crystallizer to precipitate solids, which is separated from the solution and recovered. In the freezing-crystallization process [4], instead of being heated and concentrated, the nearly saturated solution is cooled below 15°C to precipitate sodium sulfate decahydrate (Na_2SO_4 $10H_2O$), which is then separated and recovered. In the ion exchange process, the solution is passed through a proprietary resin bed to selectively remove NaCl [5, 6]. These processes must all deal with the solubility of the precipitator ash in water.

The composition of precipitator ash varies widely from mill to mill and from boiler to boiler, depending on mill location, wood species, degree of mill closure, liquor sulfidity, and recovery boiler operating conditions [7–9]. For inland softwood mills, precipitator ash typically consists of mainly sodium (Na) and sulfate (SO_4), 2–3 wt% Cl, 3–4 wt% K, with small amounts of char (carbon) and inert materials. For inland hardwood mills, the potassium content is higher, 6–10 wt% K and for coastal mills, the Cl content is much higher, 10–15 wt% Cl. The carbonate (CO_3) content may vary widely from as low as 0 wt% CO_3 for boilers that operate at low bed temperatures and high or low sulfidity liquor, to as high as 20 wt% CO_3 for boilers that operate at high bed temperatures and low sulfidity liquor. This wide variation in ash composition is expected to have a great effect on the solubility of the ash.

Precipitator ash is essentially a mixture of ionic alkali salts (Na_2SO_4, Na_2CO_3, NaCl, K_2SO_4, K_2CO_3, and KCl). When dissolved in water, these salts dissociate into Na^+, K^+, SO_4^{2-}, CO_3^{2-}, and Cl^- ions. Thus, the solubility is determined mainly by ash composition and ash-water slurry temperature. Although the solubility of pure salts in water, and to some extent the solubility of salt mixtures, has been well documented [10], the solubility of precipitator ash is not well understood. Furthermore, the solubility of individual ions in the solution (e.g., the maximum concentration of Cl in the liquid portion of the ash-water slurry), and how may it be affected by slurry temperature and ash concentration are not known. Such information is critically important for designing and operating an ash treatment system to minimize Cl and K buildups in the chemical recovery cycle.

Our objective was to examine the solubility in water of various precipitator ash samples, as a function of ash composition, ash concentration, and solution temperature, both

through laboratory experiments and theoretical simulation using a thermodynamic computer program. We describe the program and its capability and discuss the key results we obtained from the program predictions and experiments and their implications.

THE PROGRAM

The advanced thermodynamic program we used is OLI Stream Analyzer v. 2.0.31, commercially available software designed for aqueous solution applications [11, 12]. The program is generally used for predicting complex chemical and electrochemical phenomena in aqueous and mixed solvent solutions. The program's predictive thermodynamic model is based on published experimental data. It uses data regression where applicable and estimation and extrapolation where required and can predict composition and concentration for ionic salt mixtures in water over a wide range of temperature, pressure, and ionic strength.

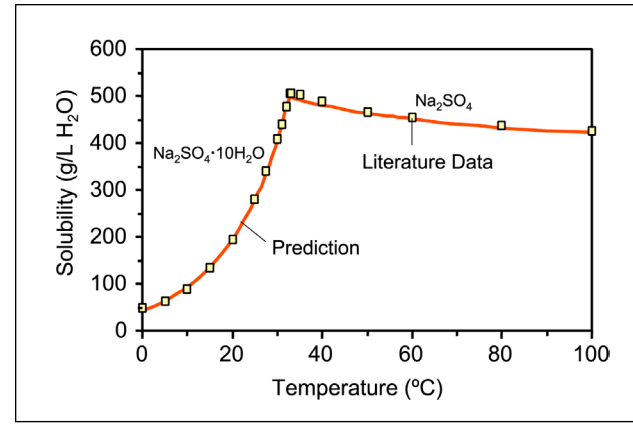
The input parameters are water and ash amounts (or individual salts), ash composition, and solution temperature. The output parameters are amounts and compositions of solids and liquid (solution), which can then be used to calculate the solubility of ash or salt mixtures.

We tested the program's suitability for use in predicting the solubility of precipitator ash in water by using it to predict the solubility of pure compounds. We compared the predicted results with data obtained from literature. The tested program was then used to predict the solubility of salt mixtures and precipitator ashes, and the predicted results were again compared with literature or experimental data.

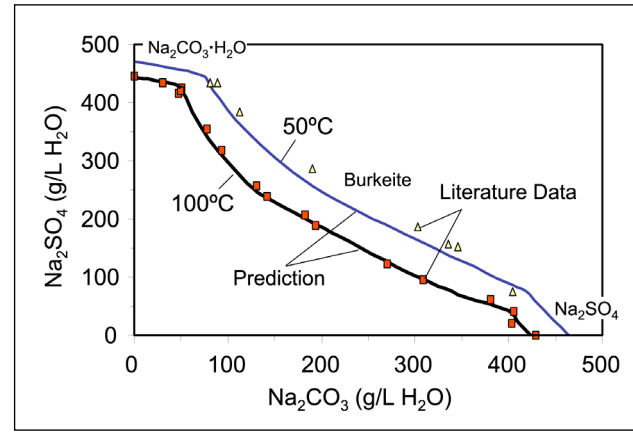
RESULTS AND DISCUSSION

Solubility of pure compounds

Figure 1 shows the solubility of Na_2SO_4 in water predicted by the program (solid line), together with literature data [13], as a function of temperature between 0–100°C. The results are in excellent agreement with each other, showing that the solubility of Na_2SO_4 increases from 90 g/kg H_2O at 0°C to about 500g/kg H_2O at 40°C, with sodium decahydrate ($Na_2SO_4 10H_2O$) as the equilibrium solid phase. Above 40°C, the solubility decreases slightly, with Na_2SO_4 as an equilibrium solid phase. Predictions were also performed on all other pure compounds (i.e., Na_2CO_3, NaCl, K_2SO_4, K_2CO_3, and KCl) and in all cases, the predicted results were very close to literature data.



1. Comparison between the solubility of Na_2SO_4 in water at different temperatures predicted by the program and literature data [13].



2. Comparison between the solubility of Na_2SO_4-Na_2CO_3 mixtures in water at 50 and 100°C predicted by the program and literature data [14].

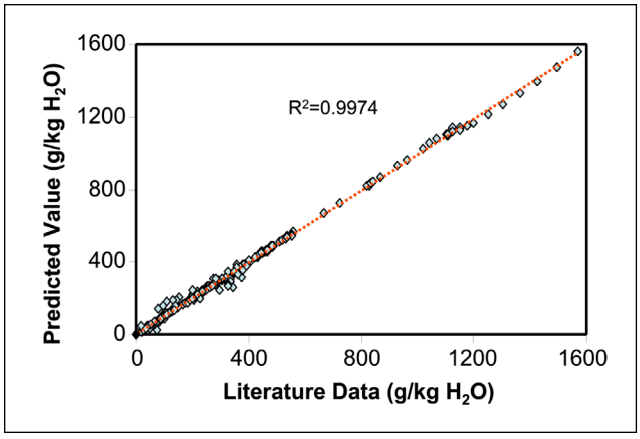
Solubility of mixtures of compounds

Figure 2 shows the solubility of a binary mixture Na_2SO_4-Na_2CO_3 in water predicted by the program (solid curves), together with literature data [14] at 50°C and 100°C. The predictions were again in good agreement with literature data. **Table I** shows similar results for various tertiary mixtures.

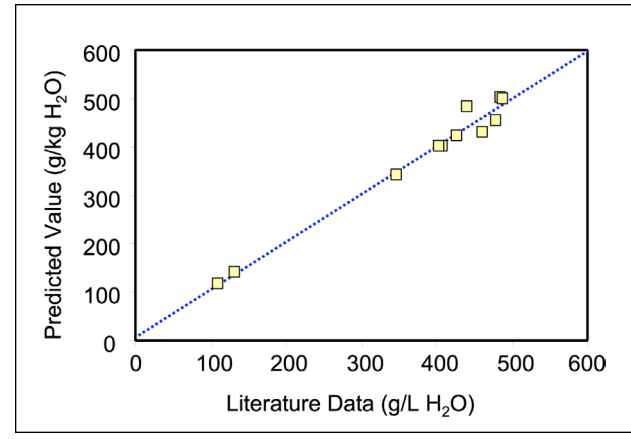
Over 180 predictions were performed using the program

Temp. (°C)	Composition (wt %) NaCl-Na_2SO_4-Na_2CO_3	Precipitated salt	Model prediction (g/kg H_2O)	Literature [10] (g/kg H_2O)
35	46 – 5 – 49	Burkeite/NaCl	528	501
35	70 – 11 – 19	NaCl/Na_2SO_4/Burkeite	444	441
100	10 – 13 – 77	Na_2CO_3*$H_2$0/Burkeite	477	481
100	40 – 8 – 52	Na_2CO_3*$H_2$0/Burkeite	466	473
100	57 – 5 – 38	Na_2CO_3*$H_2$0/Burkeite	466	473
100	26 – 66 – 8	Burkeite/NaCl	494	494
100	26- 69 – 5	Burkeite/NaCl	495	476
100	7 – 83 – 10	Burkeite/NaCl	451	441

I. Solubility data of NaCl-Na_2SO_4-Na_2CO_3 in water.



3. Comparison between model prediction and literature data (over 180 predictions).



4. Comparison between model predictions and experimental measurements of solubility in water for various precipitator ash samples at different temperatures obtained by Goncalves [14] and in this study.

on single compounds and various mixtures of compounds. **Figure 3** shows the predicted values agreed very well with literature data, which suggests that the program is capable of predicting the solubility of recovery boiler precipitator ash.

Solubility of precipitator ash

In her study of factors affecting Cl and K removal from recovery boiler precipitator ash using a leaching method [15], Goncalves determined the compositions of six ash samples collected from different recovery boilers (**Table II**), and the compositions (i.e., the concentrations of Na^+, K^+, SO_4^{2-}, CO_3^{2-}, and Cl^-) of the liquid and solids of each ash-water slurry prepared at 85°C and at an ash concentration of 800 g/kg H_2O. The experimental conditions were the same as those used in the ash-leaching process at a kraft pulp mill in Brazil [15, 16].

Using the test results, Goncalves determined the ash solubility (in g/kg H_2O) by subtracting the amount of solids (M_{Solids}, in g) in the slurry from the total amount of ash added (M_{Ash}, in kg), and dividing the difference by the total mass (or volume) of the water used (M_{Water}, kg), as in Eq. 1:

$$\text{Solubility} = \frac{M_{Ash} - M_{Solids}}{M_{Water}} \quad (1)$$

M_{Solids} is essentially the amount of the wet cake remaining on the filter paper after the ash-water slurry has been vacuum-filtered to remove the liquid, minus the amount of liquid in the wet cake. This liquid amount is equal to the amount of water in the cake (determined by evaporation), multiplied by the specific gravity of the liquid of the 0.8 kg/kg ash-water slurry that has been predetermined for each ash at 85°C.

Table III summarizes the experimental results, along with solubility values predicted by the program based on the ash composition in Table II. **Figure 4** plots the predicted and measured solubility values for these six precipitator ash samples and five additional other ash samples we investigated and shows they are in good agreement.

Ash	Composition (wt %)				
	Na	K	Cl	CO_3	SO_4
A	29.3	5.6	6.6	1.2	56.9
B	28.8	5.8	5.9	0.3	58.7
C	31.5	5.2	5.4	12.4	45.5
D	28.8	5.9	1.1	2.7	61.5
E	27.8	6.7	3.4	0.1	61.5
F	30.2	5.8	8.3	6.4	48.8

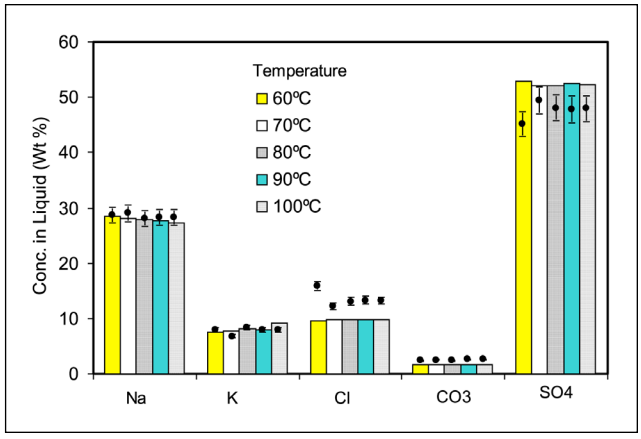
II. Composition of precipitator ash from six recovery boilers.

Ash	Solubility at 85°C (g/L H_2O)	
	Experiment [14]	Prediction
A	430	460
B	440	482
C	426	422
D	484	501
E	488	455
F	478	500
Ave.	458	470

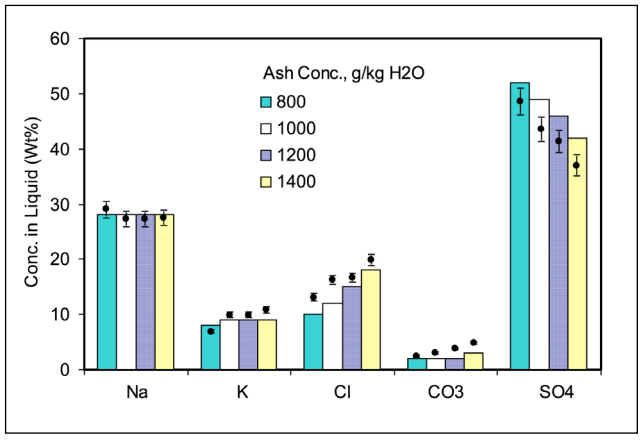
III. Solubility in water of precipitator ash from various boilers.

Effect of temperature and ash concentration

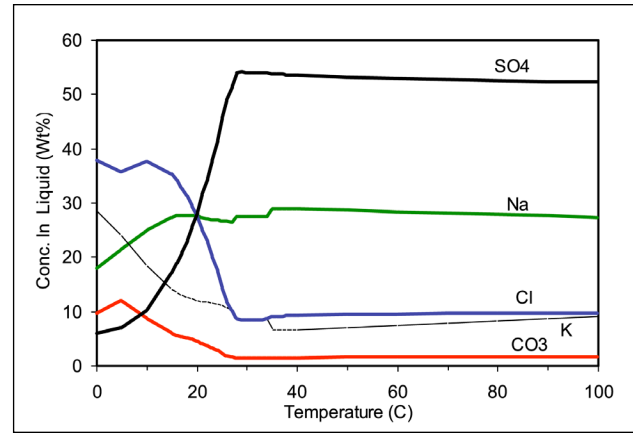
We used the program to examine the effect of temperature and ash concentration on Cl and K dissolution in ash leaching tests. **Figure 5** shows the effect of temperature on the composition of the liquid portion (the solution) of the slurry prepared from Ash "A" with an ash concentration of 800 g/kg H_2O. The predictions (bars) were consistent with experimental data (points with error bars) obtained by Goncalves [15], showing that temperature has little effect on the liquid composition, i.e., the concentration of each ash component in the liquid does not appreciably change between 60°C and 100°C. For example, the concentration of Na decreased only slightly from 28.4 wt% at 60°C (the leftmost bar) to 27.3 at 100°C (the rightmost bar), while the concentration of Cl increased from 9.6 wt% at 60°C to 9.7 wt% at 100°C. The predicted Cl concentration, however, was consistently lower than the experimen-



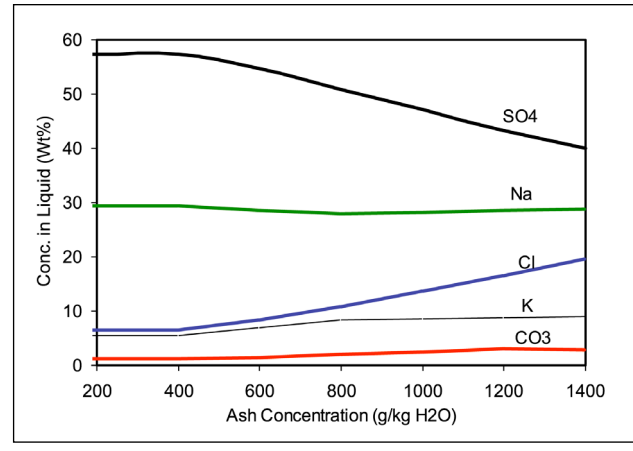
5. Composition of the liquid of Ash" A" slurry (800 g/L water) in a temperature range of 60–100°C. Bars are predicted values. Data points and error bars are experimental values.



6. Liquid composition of ash "A" slurry at 85ºC as a function of ash concentration. Bars are predicted values. Data points and error bars are experimental values.



7. Effect of temperature on liquid composition of Ash "A" slurry (800 g/L water), as predicted by the program.



8. Effect of ash concentrations on liquid composition of Ash "A" slurry at 85ºC, as predicted by the program.

tal data, whereas the predicted SO_4 concentration was consistently higher than the experimental data by the same amount that has been under-predicted for the Cl concentration. The cause of this discrepancy is not known, although it is likely due to the inaccuracy in the Cl and SO_4 analytical procedures.

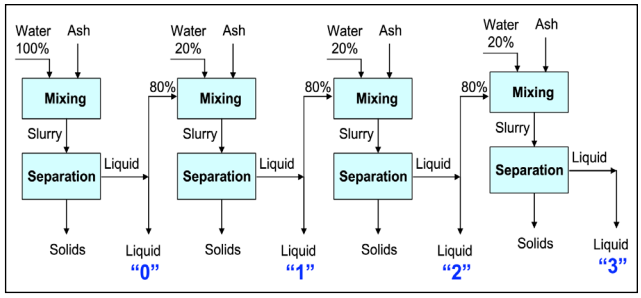
Figure 6 shows the effect of ash concentration on the composition of liquid of Ash "A" slurry prepared at 85°C. Again, the predictions were consistent with experimental data, showing little change in Na, K, CO_3 contents in the liquid with an increase in ash concentration, while the SO_4 content decreased and the Cl content increased markedly.

Because the program predicted well the liquid composition for all ash leaching tests, we performed further simulations to evaluate the effects of temperature from 0–100ºC and ash concentration from 200–1400 g/kg H_2O. **Figure 7** shows the simulation results at different temperatures for Ash "A" with ash concentration of 800 g/kg H_2O. Above 30°C, the liquid composition is not changed with temperature, as suggested in Fig. 5. Below 30°C, however, the composition changes dramatically; the SO_4 concentration in the liquid decreases from 55% at 30°C to less than 10% at 0°C and the Cl concentration increases from 10% to about 40%. **Figure 8** shows the liquid composition as a function of ash concentration in Ash "A" slurry at 85°C. The SO_4 concentration decreased and the Cl content increased as the ash concentration increased.

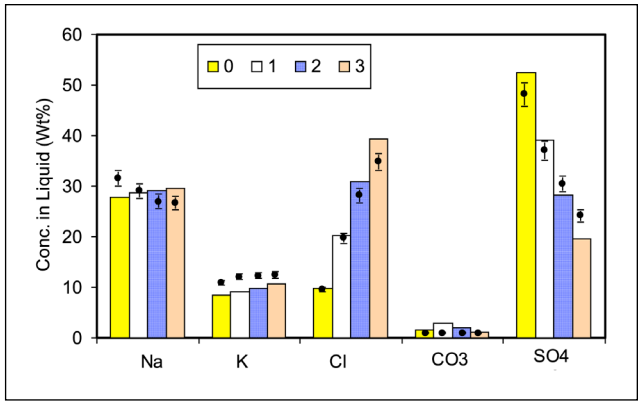
RECYCLING TESTS

Results shown in Fig. 8 also suggest that ash slurry with a higher Cl concentration would contain less SO_4. Thus, it may be possible to improve the Cl removal efficiency and the SO_4 recovery efficiency of an ash-leaching system by recycling the liquid back to the ash slurry tank. In order to verify this possibility, we conducted recycling tests along with simulations using the program.

The tests were performed on two ash samples, one with a low carbonate content, 0.3 wt% CO_3 (Ash "B") and the other with a high carbonate content, 12.4 wt% CO_3 (Ash "C"), as shown in Table II. **Figure 9** schematically shows the recycling test procedure for Ash "B". After each recycling test, 80% of the liquid, which has been separated from the slurry, was used along with 20% fresh water to dissolve the fresh ash in the subsequent test.



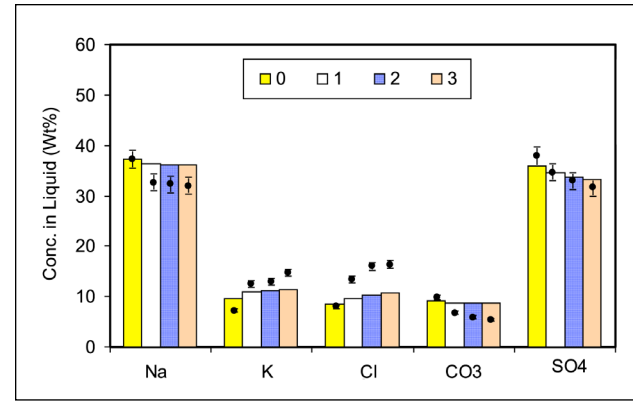
9. Recycling test procedure for Ash "B".



10. Change in liquid composition of Ash "B" (low carbonate) slurry at 85°C and ash concentration of 800 g/kg H_2O with number of recycles; 80% liquid recycling.

Figure 10 shows the change in liquid composition with each recycling test for Ash "B" at 85°C and at an ash concentration of 800 g/kg H_2O. Number 0 means without recycling and numbers 1, 2, and 3, respectively, represent the first, second, and third cycles. The bars represent the values calculated by the program and the dots and error bars are the experimental values. The results show clearly that for this ash, the Na and CO_3 concentrations in the liquid did not change much with the number of recycling tests. The potassium concentration increased only slightly, while the chloride concentration increased and the sulfate concentration decreased markedly. This is important, as it implies that the Cl removal efficiency and the SO_4 recovery efficiency of an ash-leaching system can be significantly improved by recycling a portion of the liquid back to the ash-water slurry tank.

Figure 11 shows results of the recycling test for Ash "C". In this case, the ash concentration in the slurry was 500 g/kg H_2O and only 50% of the liquid was recycled. The change in test conditions was necessary due to the high carbonate content of Ash "C" that makes it much more difficult to separate the liquid from the slurry, compared with Ash "B". The results were similar to those for Ash "B", although the increase in chloride concentration and the decrease in sulfate concentration in the liquid with increased number of recycling were much smaller. This is probably due to the lower concentration of Ash "C" in water and smaller volume of liquid used in the Ash "C" experiments.



11. Change in liquid composition of Ash "C" (high carbonate) slurry at 85°C and ash concentration of 500 g/kg H_2O with number of recycle; 50% liquid recycling.

SUMMARY AND CONCLUSIONS

We used an advanced thermodynamic-based computer program to examine the solubility of precipitator ash in water, as a function of ash composition, ash concentration, and solution temperature. The results show that:

- The predicted values by the program are in good agreement with literature and experimental data.
- The solubility of precipitator ash at 85°C is about 470 g/L H_2O. It varies widely from 400–550 g/L H_2O, depending on the carbonate content of the ash.
- In the ash concentration range of 0.8–1.4 kg/L, the composition of the liquid portion of an ash-water slurry changes significantly with an increase in ash concentration in the slurry: the Cl concentration increases, the sulfate concentration decreases, and the potassium and carbonate concentrations remain the same.
- Between 30°C and 100°C, temperature has little effect on the solubility of precipitator ash and on the composition of the liquid portion of the slurry. Below 30°C, it has a significant effect.
- For precipitator ash with low carbonate contents, the Cl removal efficiency and the SO_4 recovery efficiency may be improved by recycling a portion of the liquid back to the ash-water slurry tank.

ACKNOWLEDGEMENTS

This work was part of the research program Increasing Energy and Chemical Recovery Efficiency in the Kraft Process, jointly supported by the Natural Sciences and Engineering Research Council of Canada (NSERC) and a consortium of the following companies: Abitibi Bowater, Alstom Power, Andritz, Aracruz Celulose, Babcock & Wilcox, Boise Paper Solutions, Carter Holt Harvey, Celulose Nipo-Brasileira, Clyde-Bergemann, Diamond Power International, Domtar, DMI Peace River Pulp, Georgia Pacific, International Paper, Irving Pulp & Paper, MeadWestvaco, Metso Power, Stora Enso Research, Tembec, and Votorantim Celulose e Papel. **TJ**

Received: March 6, 2008
Accepted: August 10, 2008

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INSIGHTS FROM THE AUTHORS

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Tran

The solubility of recovery boiler precipitator ash in water is an important parameter in the design and operation of ash treatment systems. This study is a good complement to our research on chemical recovery, particularly the efficiency of ash treatment systems and the effect of Cl and K on recovery boiler fouling.

Our biggest challenge was to obtain sufficient experimental data to validate our OLI base-thermodynamic model. We addressed it by performing numerous experiments in our laboratory and by conducting an extensive literature survey on the water-solubility of relevant salts and their mixtures.

Interestingly, we found that the concentration of chloride in the liquid portion of an ash-water slurry increased, while that of sulfate decreased, with an increase in ash concentration in the slurry. Mills might use this information to increase their Cl removal efficiency and sulfur recovery efficiency by controlling the Cl and K concentrations in the liquor cycle.

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