A new method for calculating equilibrium solubility of burkeite and sodium carbonate in black liquor

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ABSTRACT

This work describes a new solubility model for black liquor using NAELS, a chemical equilibrium calculator. This model has use to determine the solubility of inorganic compounds in black liquor systems over a wide range of temperatures and concentrations. The model was developed by deriving thermodynamic data from solubility data for inorganic compounds of interest in black liquor. Addition of a hypothetical organic species that competes for sodium in solution was necessary to allow accurate predictions of solubility at high liquor solids levels. Several case studies show application of the model to calculate solubility of inorganic compounds in black liquor. Model results show that black liquor exhibits two critical solids points over the range of solids concentrations in typical concentrators. Burkeite begins precipitating at the first critical point, and sodium carbonate begins precipitating at the second point. Temperature and liquor chemistry influence the solubility of burkeite and sodium carbonate in black liquor.

Application:

The paper illustrates the usefulness of a robust solubility model to help understand the tendency to form soluble scales in black liquor concentrators.

RECENT YEARS HAVE BROUGHT an increased awareness of the impact of nonprocess elements (NPE) on operation of a kraft pulp mill. Efforts to reduce water consumption and increase the degree of closure for process systems have driven this awareness. The primary NPE of interest are Al, Si, Cl, K, and P; the transition elements Mn, Cu, and Fe; and the alkaline earth metals Ba, Ca, and Mg. Several studies have characterized typical concentrations and flows in a kraft mill (1-7). Subsequent modeling efforts have shown the need for more fundamental estimations of solubility leading to the development and application of equilibrium calculations for aqueous solutions (8-13). Interest in calculating the precipitation of Al and Si in evaporators had led to more research in aluminosilicate scales and the use of equilibrium codes (14-18).

The solubility of sodium carbonate and sodium sulfate in black liquor is of primary interest in kraft pulp mills because of the potential for scaling or deposit formation in evaporators and concentrators. Grace (19) did some pioneering work to apply the solubility data of Green and Frattali (20) for calculation of sodium carbonate, sodium sulfate, and burkeite solubility in black liquor. (Burkeite is a double salt, $2Na_2SO_4 \cdot Na_2CO_3$ that has a unique crystalline structure. It is not a simple mixture of Na_2SO_4 and Na_2CO_3.)

Frederick et al. (21) related the solubility of inorganic species to inflection points in boiling point elevation curves for black liquor. Rosier (22) applied Grace's method to develop a calculation model to predict precipitation of burkeite in evaporators or concentrators. Novak (23) examined sodium salt scaling during evaporation of black liquors and pure model solutions. Some experiments resulted in crystal formation with a different stoichiometric ratio of sodium carbonate to sodium sulfate than expected from burkeite precipitation.

The commercial development of falling-film crystallizers and forced circulation has allowed black liquor evaporation systems to reach more than 75% solids. Hedrick and Kent (24) described a method for estimating burkeite and sodium carbonate crystallization from black liquor and its application to black liquor concentrator design. Kaila (25) has reviewed the current technology for black liquor concentrators, and Rieke et al. (26) described results with a new crystallizer design. Balch and Moore (27) provided some hints on resolving evaporator and concentrator problems by applying a basic understanding of liquor chemistry. Smith and Hsieh (28) reported a solids deposition model for controlling "crashing" in falling film evaporators. All these developments use crystallization concepts to reduce the incidence of soluble scale formation during concentration of black liquor.

The discussion above applies primarily to prevention and elimination of water soluble scale. Some recent work relates to hard calcium scales—a type of water insoluble scale. Lyons and Bernard (29) described a device to eliminate hard calcium scale formation. Konopa (30) discussed additive chemistry to reduce hard calcium scales in evaporator systems. Uloth and Wong (31) provided some insight into the
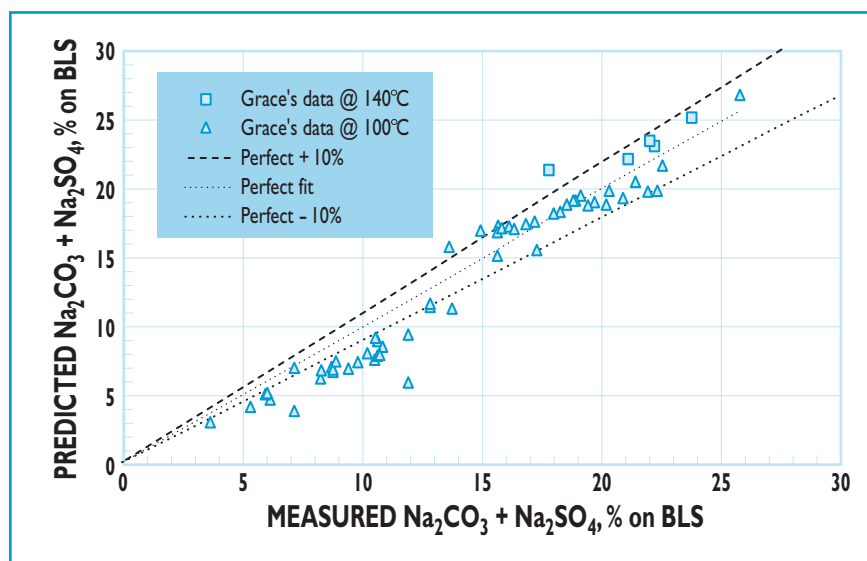
1. Comparison of black liquor solubility measurements by Grace (19) at 100°C and 140°C compared with predicted concentrations using the approach of ignoring organic to cation binding and balancing all Na+ with OH−

effects of soap content on burkeite scaling in evaporators. Harrison *(32)* indicated how operational strategies can reduce scale formation and decrease downtime in evaporation systems. Some interesting data on residual alkali effects *(33)* also are available. The data suggest ways to avoid lignin precipitation in falling film evaporators as contrasted to deposits of inorganic compounds.

The nature of scales or deposits in falling film concentrators consists primarily of soluble inorganic compounds such as burkeite, sodium sulfate, and sodium carbonate. Water or weak black liquor washing can remove this type of scale, but the concentrator must be off-line. Some systems have redundant bodies to help continuous washing. This approach requires additional concentrator bodies, extra piping, switching valves, and control equipment. Our interest in the soluble inorganic scales from black liquor concentrators can be contrasted to the water insoluble (hard) scales due to aluminosilicates or calcium carbonate. Historically, the hard scales have been removed from evaporator surfaces by periodic acid washing or high pressure water cleaning—hydroblasting. These cleaning meth-

ods require downtime and may include safety issues such as H_2S generation, acid handling, and handling high pressure cleaning systems.

Most previous research by Grace *(19)*, Rosier *(22)*, and Novak *(23)* to predict the solubility of inorganic compounds in black liquor ignored any organic binding of sodium, balanced Na^+ content with hydroxide ion, and disregarded the effect of temperature on solubility. Using this approach, one estimates the solubility of inorganic compounds in black liquor from the concentrations of SO_4^{-2}, CO_3^{-2}, and total sodium only. This approach has several limitations including the inability to predict solubility at higher total solids contents (greater than 55%), inability to account for temperature effects on solubility, and inability to predict solubility using actual liquor compositions. The work reported here uses the application of thermodynamic equilibrium calculations to describe the solubility of inorganic compounds in black liquor. We wanted to develop a model that corrects the inadequacies of previous approaches and provides better understanding about the effects of black liquor chemistry on precipitation of inorganic compounds. The

ultimate goal is to help solve soluble scaling issues in black liquor concentrators.

BACKGROUND

Grace *(19)* interpreted his black liquor solubility data at temperatures from 100°C–140°C using the phase diagram of the Na_2CO_3-Na_2SO_4-$NaOH$-H_2O system at 100°C *(20)*. After balancing the total sodium measured in the black liquor with OH^-, the inorganic solubility was determined from the phase diagram according to the measured concentrations of CO_3^{-2} and SO_4^{-2} ions and the adjusted OH^- concentration. The results in **Fig. 1** compare the equilibrium inorganic composition of black liquor measured by Grace *(19)* with that predicted from the available solubility data using Grace's computational method. The data are from experiments at 373K (100°C) and 413K (140°C). An ideal fit line has been inserted to indicate the deviation of the correlation from experimental data. Curves for ±10% change in the predicted value from the same measured value are also shown.

Grace's method *(19)* works very well to predict the solubility of inorganic compounds in black liquor over the concentration range of 16%–23% sodium carbonate plus sodium sulfate on black liquor solids. These values correspond to critical solids values of 45%–50% total solids. (Black liquor critical solids is the total solids concentration in percent at which precipitation of inorganic compounds in the liquor can begin. For typical liquors, critical solids values are 45%–55% total solids.)
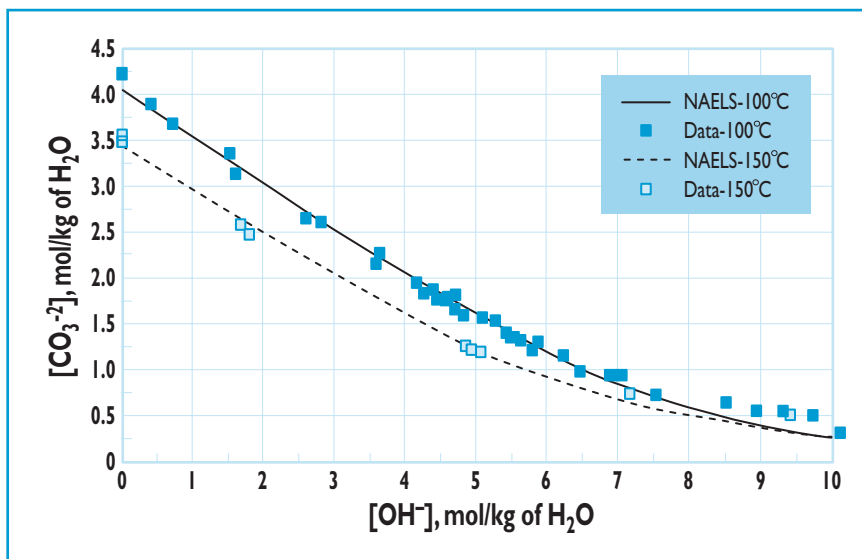
At low inorganic concentrations, the method predicts solubility poorly. At these low concentrations, Grace's method predicts the equilibrium solubility of the inorganic compounds on the low side. It predicts low critical solids values—low solubility—for liquors containing low

concentrations of sodium carbonate and sodium sulfate. This inaccuracy may be the result of the assumption that organic compounds do not influence solubility in black liquor. At the higher organic concentrations present at the critical solids point for liquors with low inorganic concentrations, the effects of the organic competition for Na$^+$ is more predominant and requires consideration.

The method of Grace *(19)* also predicted higher values than measured values at a higher temperature (413K). The results in Fig. 1 indicate that temperature does affect inorganic solubility in black liquor. Grace *(19)* hinted at this in the original analysis. Considering these difficulties and a need to predict solubility at higher liquor solids and temperatures, we began looking for a way to calculate inorganic solubility in black liquor. We wanted to expand Grace's approach to include all the pertinent solubility data at higher temperatures and account for organic binding of sodium. This would allow us to calculate a charge balance using a representative organic site and replace the OH$^-$ balance that appears to skew the solubility at higher solids levels.

DEVELOPMENT OF THE SOLUBILITY MODEL

The computation of multicomponent solubility in aqueous systems is a task that a chemical equilibrium approach can handle. Several programs are available *(8–11)*. Our approach used the nonideal aqueous electrolyte simulator (NAELS) code originally developed by Sinquefield *(8)*. NAELS uses the minimization of the total Gibbs free energy of a system to predict the solubility of inorganic salts in aqueous solutions. Solubility data for species of interest are available in the technical literature *(17–20, 23, 34–37)*. The key thermodynamic relationships for nonideal solutions are available in vari-

ous references *(14, 15, 36, 38–45)*. Several papers *(16–18, 45, 46)* outline their application to equilibrium modeling. The methods in this work parallel the path of Frederick and coworkers *(46)*. The solubility data are used to derive thermodynamic coefficients and chemical potentials for the species of interest. These values are then part of the database for the chemical equilibrium code and used by the NAELS code to calculate equilibrium concentrations and solid precipitants. The inorganic system of interest in black liquor evaporation

is NaOH-Na$_2$CO$_3$-Na$_2$SO$_4$-H$_2$O with the black liquor organic compounds. To illustrate the effectiveness of this approach, **Figs. 2–4** compare calculated solubility results with experimental data.

Figure 2 compares the predicted solubility of Na$_2$CO$_3$ in the NaOH-Na$_2$CO$_3$-H$_2$O system using NAELS with measured solubility data *(35)*. In this figure and Figs. 3 and 4, the soluble region lies below the lines at a given temperature. The line and data points represent saturated conditions where the first solid precipi-

2. Prediction of solubility for the NaOH-Na$_2$CO$_3$-H$_2$O system with NAELS using thermodynamic data developed from solubility data (35)
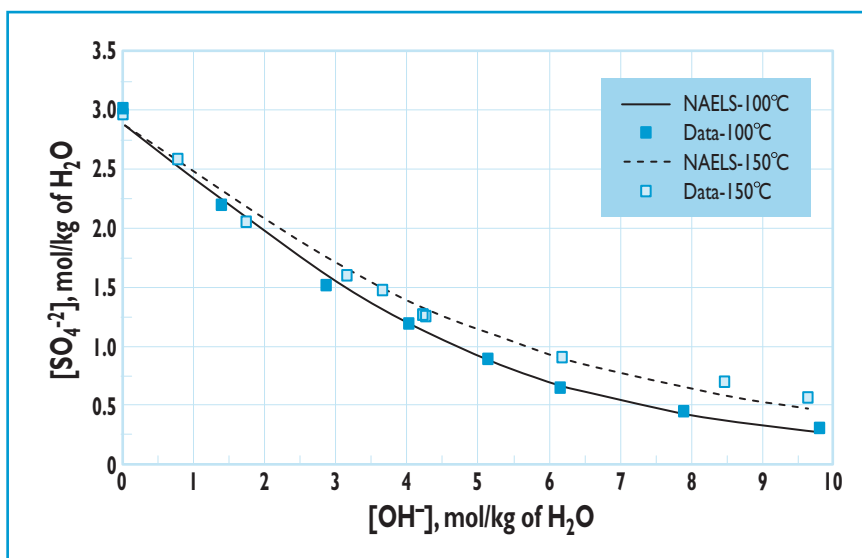
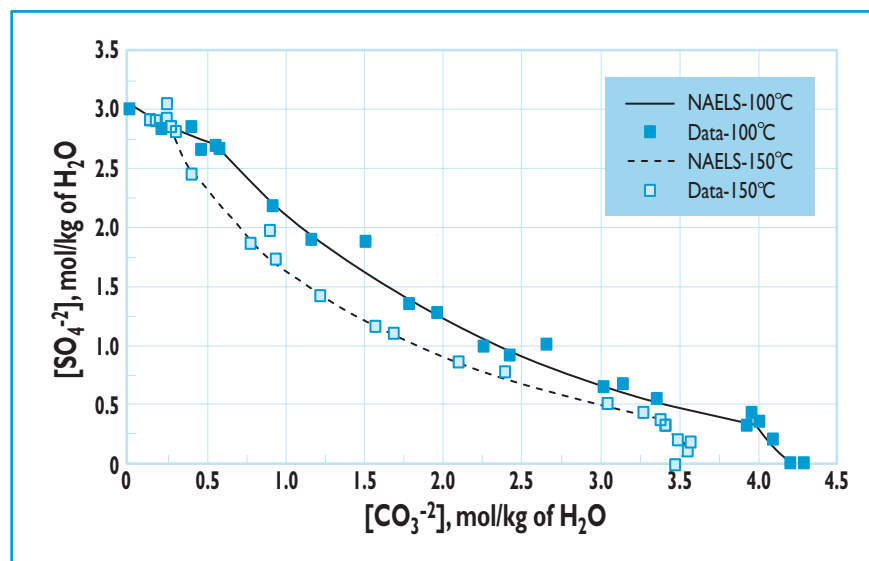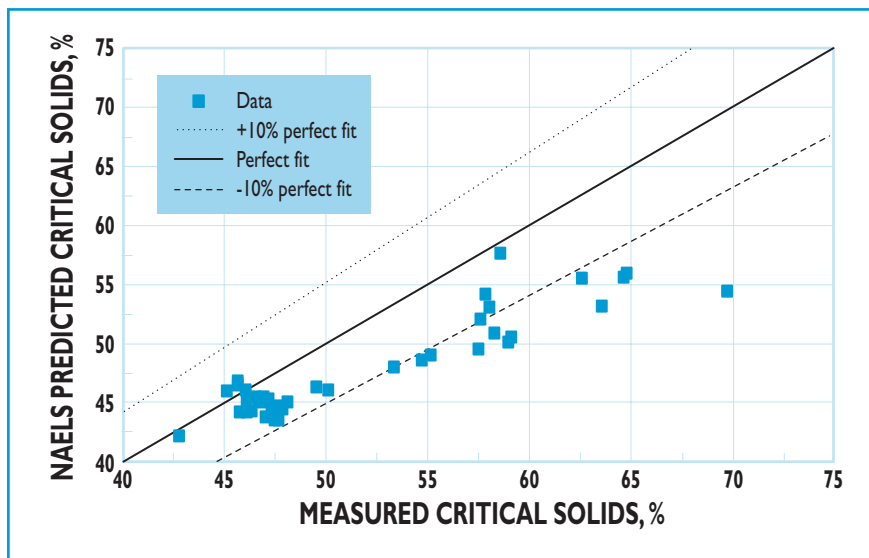**3. Prediction of solubility for the NaOH-Na$_2$SO$_4$-H$_2$O system with NAELS using thermodynamic data developed from solubility data (35)**

4. Prediction of solubility for the Na₂CO₃-Na₂SO₄-H₂O system with NAELS using thermodynamic data developed from solubility data (35)

5. NAELS prediction of critical solids for Grace's data (19) using new thermodynamic data and Grace's method to balance sodium

tates. The figure shows results for varying amounts of alkali and NaOH at 100°C and 150°C. Model calculations compare favorably up to NaOH concentrations of about 7 mol/kg of water. Typical white liquor concentrations of effective alkali are less than 4 mol/kg of water. Black liquor concentrations are about 1.5 mol/kg of water at 40% solids to approximately 6.5 mol/kg of water at 75% solids. Recognizing the effect of temperature on the solubility of sodium carbonate as Fig. 2 shows is also

important. Clearly, Na_2CO_3 has an inverse solubility relationship with temperature up to NaOH concentrations of about 7 mol/kg of water.

Figure 3 shows a similar comparison of the solubility of sodium sulfate in the NaOH-Na_2SO_4-H_2O system. The figure includes results at 100°C and 150°C. Throughout the range of concentrations in Fig. 3, sodium sulfate is the solid precipitant. The data indicates normal solubility relationships for sodium sulfate. Solubility is higher at higher

temperatures. Again, the model calculations agree well with experimental data.

Figure 4 compares solubility data for the system Na_2CO_3-Na_2SO_4-H_2O at 100°C and 150°C with calculated values using the chemical potential and ion activity coefficient parameters extracted from experimental data for this system. This system is of interest because it describes the precipitation of burkeite from aqueous sodium salt solutions. The system is also interesting because it contains two invariant points where the precipitant changes from one chemical species to another. At low carbonate concentrations, Na_2SO_4 is the solids species. Na_2CO_3 is the solid species at high carbonate concentrations greater than about 4 mol/kg of water at 100°C. Between these two extremes, burkeite precipitates. This is a good example illustrating the robustness of the NAELS model. The model can represent a system where different species precipitate at different compositions. Figure 4 also shows that burkeite like sodium carbonate exhibits inverse solubility behavior.

The extension of this system with NaOH has been used frequently to represent green and white liquor where the solubilities of minor species (NPE) are determined by the solubility of their carbonates, sulfates, or hydroxides. With extension to the Na_2CO_3-Na_2SO_4-NaOH-H_2O system, we again find good agreement between the calculated solubility and experimental data. With inclusion of all the thermodynamic parameters for the Na_2CO_3-Na_2SO_4-NaOH-H_2O system plus data for Cl⁻ and HS⁻, we have accounted for the key inorganic species in black liquor over the temperature range of interest, 25°C–150°C.

Using this data, we can now calculate the solubility of inorganic compounds in black liquor. **Figure 5** gives a comparison of the critical

solids predicted by the NAELS model with the measurements of Grace *(19)*. The calculations in Fig. 5 use all the new thermodynamic data derived from the solubility data shown above. The calculations still use OH⁻ as the anion to balance Na⁺ concentration. Note that the prediction is very good at a critical solids level of about 45%–50%. At higher critical solids levels with lower sodium carbonate and sodium sulfate concentrations, the prediction is much lower than the measured value. This is similar to the result of Fig. 1. Clearly, some additional effects are important at the higher solids levels. Our assumption was that the organic bonding of cations in black liquor could explain this deviation at higher solids.

We have now accounted for the primary inorganic species and temperature but have not addressed the effect of dissolved organics in the black liquor. To include the effect of an organic binding site that competes with the other electrolytes for Na⁺ in solution, a hypothetical black liquor organics species must be added to the model. This organic species would be completely soluble but would exhibit activity in solution. **Figure 6** shows the results of this addition. The prediction of critical solids by the NAELS model compared with the experimental data is much better than that in Fig. 5. The incorporation of an organic binding site in the model provides the capability to predict solubility better over the entire range of solids concentrations. Additional experimental data are necessary in this area to help account for lignin solubility *(33)* at low residual alkali levels and allow refinement of the method used here.

Some inaccuracy at the lower critical solids values remains. This may be due to compositional variability in the black liquors used by Grace *(19)*. His measurements
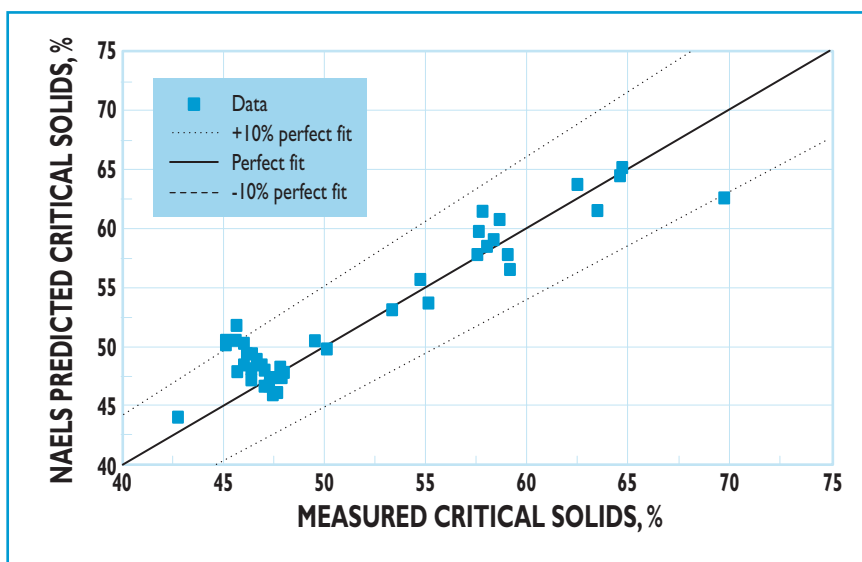
6. *NAELS prediction of critical solids predictions for Grace's data (19) using new thermodynamic data and a single organic binding site for Na⁺*

included sulfate, carbonate, total sodium, and residual alkali by titration. Other inorganic species in the black liquor may have influenced the solubility of the measured inorganic compounds in the black liquor. In addition, the NAELS model currently does not account for the impact of other soluble ions such as sulfite, thiosulfate, or potassium on solubility. Even with this limitation, the new model clearly provides the ability to calculate the solubility of inorganic compounds in black liquor over a wider range of liquor chemistries and process conditions than was previously possible.

APPLICATION OF THE SOLUBILITY MODEL

The model described above has practical application to solubility and scaling problems in black liquor concentration. Several case studies demonstrate the use of this new tool. These examples include calculation of critical solids for different liquor chemistries, calculation of black liquor solubility over the course of concentration, and demonstration of the temperature impact on solubility.
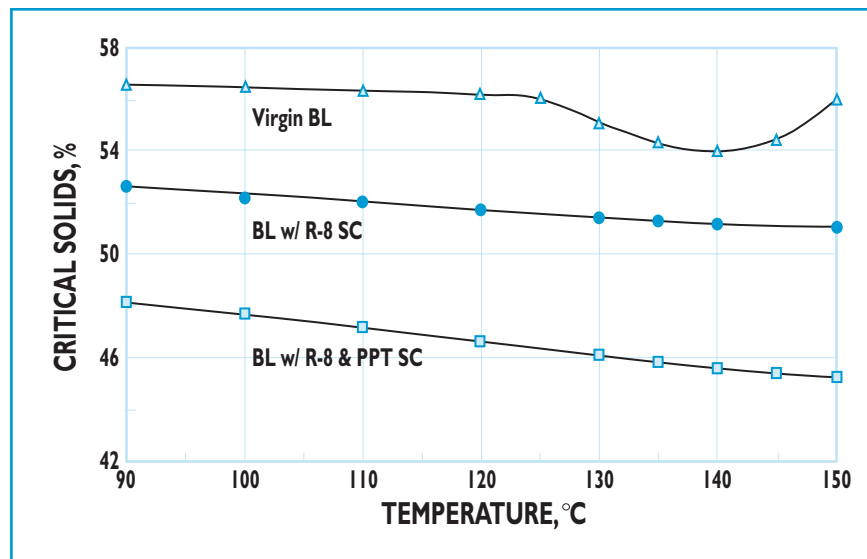
Critical solids calculations

Case 1. Mill A is evaluating changes to its liquor system. What are the implications of adding makeup saltcake (SC) from the R-8 generator and recycle saltcake from the recovery boiler precipitator (PPT) at different points in the liquor system? These saltcake streams could be added to weak liquor, to 50% liquor following the multiple effect evaporator (MEE), or to the firing liquor after the concentrator. For each combination, the MEE would see liquor with very different inorganic compositions. **Table I** shows liquor compositions resulting from the three possible combinations of makeup and PPT saltcake: virgin black liquor, black liquor with R-8 saltcake, and black liquor with R-8 saltcake and PPT saltcake.

Using NAELS, the critical solids of these three liquors were calculated as a function of temperature. **Figure 7** summarizes the results from these calculations. The plot shows clearly the effect of doubling and quadrupling the sodium sulfate concentration in black liquor. The critical solids at 120°C—a typical MEE first effect liquor temperature—ranges from 56% on virgin liquor to 52% with R-8 makeup saltcake added to 46.5% with R-8 saltcake and PPT ash. At this mill, the evaporator produces product solids consistently around 50%. Adding all the makeup and PPT ash to the weak liquor puts the evaporator at a high risk for soluble scale for-

Parameter	Virgin black liquor	Black liquor with R-8 SC	Black liquor with R-8 SC and PPT ash	Black liquor with R-8 SC and PPT ash @ higher residual
Na, % on BLS	18.3	18.6	19.2	20.1
SO_4^{-2}, % on BLS	1.3	2.7	5.7	5.7
CO_3^{-2}, % on BLS	4.6	4.5	4.5	4.1
S^{-2}, % on BLS	2.5	2.4	2.3	2.9
OH^-, % on BLS	2.4	2.4	2.2	2.7
Residual effective alkali, g/L as Na_2O in 15% black liquor	10.5	10.4	9.7	12.2

I. Composition of Mill A black liquors

7. Calculated critical solids using NAELS for Mill A black liquor as virgin liquor, with added R-8 saltcake, and with R-8 saltcake and PPT ash added to weak liquor

mation. Critical solids significantly below operating solids indicate that precipitation of inorganic compounds in the black liquor may occur. This can lead to formation of soluble scales in evaporator effects not designed to handle crystallization. A typical evaporator system design would target operations to achieve a black liquor solids value one to two points below the critical solids level. Figure 7 also shows that putting all the R-8 makeup in the firing liquor would not affect MEE operation since the critical solids of liquor with R-8 saltcake added is still well above current product solids.

The results in Fig. 7 give some insight into the characteristics of inorganic precipitation from black liquor. All the curves except virgin liquor show a consistent decrease in critical solids with temperature.

Burkeite is the precipitant predicted for black liquor with added saltcake over the entire temperature range shown. Burkeite shows inverse solubility. The virgin liquor with very low sulfate concentration shows the same trend up to 125°C where the initial solid changes from burkeite to sodium carbonate. The solubility characteristics of sodium carbonate are very different and lead to a rapid decrease in solubility or critical solids followed by an increase. This behavior needs verification with actual experimental data, but the behavior appears to indicate that sodium carbonate precipitation could be difficult to handle in black liquor evaporators.

Case 2. Mill A has modified the pulping operation and switched from conventional kraft batch cooking to extended modified cooking

with continuous digesters. The black liquor residual effective alkali has increased from about 10 g/L to approximately 12 g/L as Na_2O measured in weak liquor. Does this change in residual alkali affect the critical solids of the liquor? Table I shows the liquor compositions before and after the digester modification. During the modification, the mill was also putting R-8 makeup and PPT ash in the weak liquor.

Figure 8 shows critical solids as a function of temperature for the liquor before and after the digester modification. Clearly, the change in residual alkali has only a minor impact on critical solids. The critical solids drops only 0.5% at 120°C with the 2 g/L increase in residual alkali. By contrast, the addition of PPT ash to the weak liquor has a much larger effect on critical solids. It drops the critical solids 5.5% at the same temperature. This is very different from the result that would have been predicted without the ability to incorporate the effects of black liquor organic binding on solubility. Using OH^- as a balance for sodium and neglecting the effect of black liquor inorganic compounds, we would have calculated a 2% drop in critical solids with this residual alkali change. Our conclusions about the impact of the change would have been much different.

***Character of solid species precipitating from black liquor***

Case 3. Black liquor concentrators are normally designed to process black liquor from about 50% to approximately 75% total solids concentration. The feed concentration is

based on operation of the MEE. An ideal target is 1%–2% less than the critical solids for the black liquor stream. Typical high solids concentrators might have feed at 49% solids and 110°C, a second effect operating at 59% solids and 110°C, first effect operating at 72% solids and 135°C, and product liquor at 75% solids and 120°C. Knowing the solubility characteristics of the inorganic species is important to identify the appropriate operating conditions of the concentrator. This is particularly true if the concentrator is designed as a crystallizing concentrator. The unit should be able to handle the species precipitating from the liquor at specific operating conditions. Consider what happens according to the solubility model as Mill A liquor with R-8 saltcake is concentrated from 50% to 75% at 110°C. **Figure 9** shows the solubility curves for this liquor. The results are plotted as percent soluble material based on total black liquor solids vs. the total solids concentration. The three curves in Fig. 9 represent the amount of sodium sulfate, sodium carbonate, and the sum of the two that are still soluble in black liquor at a given solids content.

As the liquor is concentrated from 50% solids, the amount of sodium carbonate and sodium sulfate in solution remains constant at 8% and 4% on black liquor solids, respectively, until the total solids concentration reaches 52%. This is the critical solids for this temperature and liquor. At this point, the model predicts that burkeite, the double salt of sodium carbonate and sodium sulfate, will begin to precipitate. Further concentration of the liquor causes more burkeite to precipitate. Since burkeite contains two moles of sodium sulfate for every mole of sodium carbonate, the sulfate in solution is depleted rapidly until a second critical point occurs. At 60.5% total solids, the sulfate concentration is sufficiently low that
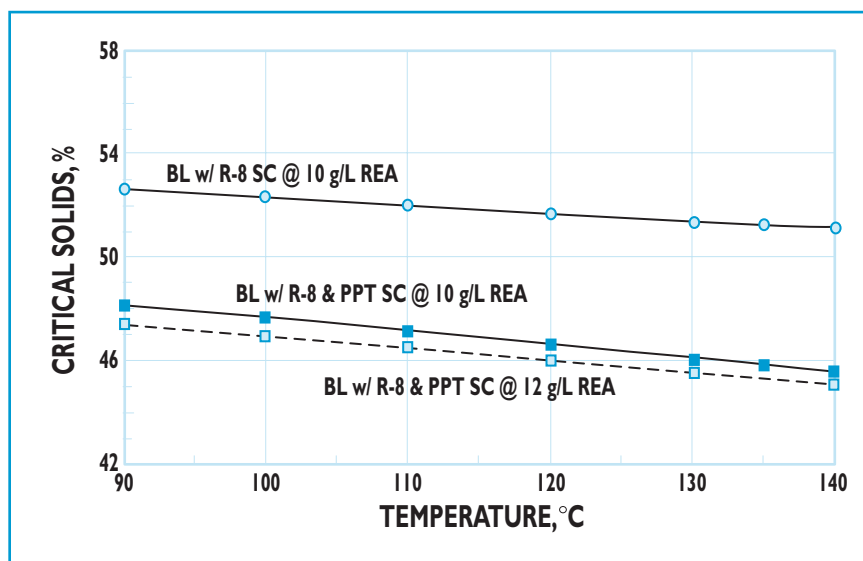
8. Calculated critical solids for Mill A black liquor at 10 g/L and 12 g/L residual effective alkali
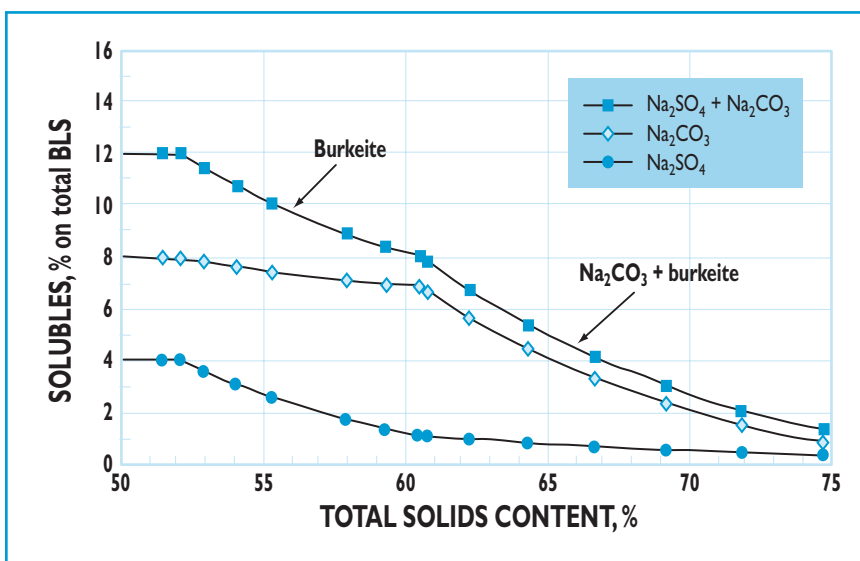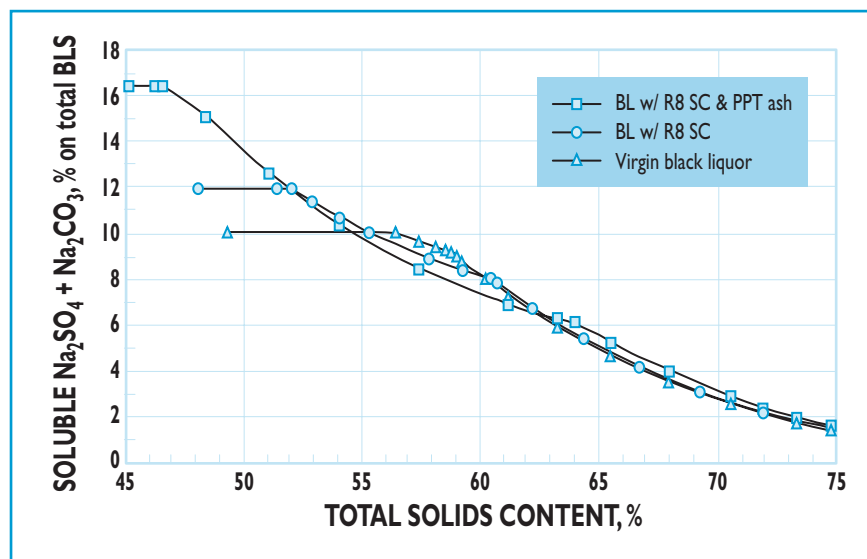

9. Solubility curve for Mill A black liquor at 110°C with R-8 saltcake added

sodium carbonate begins to precipitate. Beyond this second point, both sodium carbonate and burkeite precipitate. This is an important finding—two critical solids points exist rather than only one. Operation of evaporation equipment near these critical points or movement across them during upsets to the system or body-switching should be avoided.

Case 4. The results in Case 3 above prompt another question. How do these critical solids points change with liquor chemistry? The critical solids plots in Figs. 7 and 8

answer this question for the first critical solids point. Because a given liquor has two critical points, understanding if the second point is influenced by liquor composition is also important. The influence of liquor composition on the solubility curve for the Mill A liquors previously discussed is clear from the results in **Fig. 10**. The plot includes the total solubility curves—percent soluble Na_2CO_3 plus Na_2SO_4 on black liquor solids vs. total solids content—for Mill A virgin liquor, Mill A liquor with R-8 saltcake added, and Mill A black liquor with R-8 saltcake and PPT ash

10. Total solubility curves for Mill A virgin black liquor, Mill A black liquor with R-8 salt-cake added, and Mill A black liquor with R-8 saltcake and PPT ash added with results calculated at 110°C for all liquors
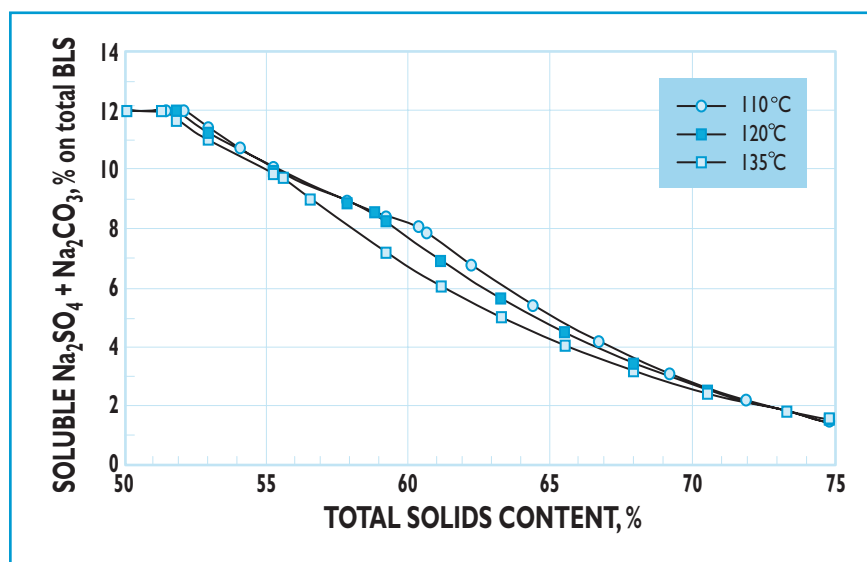
11. Total solubility curves for Mill A black liquor with R-8 saltcake added at 110°C, 120°C, and 135°C

added. As noted before, the first critical solids point drops from 56% to 52% and finally to 46.5% as the total sulfate concentration in the liquor increases. The results in Fig. 10 also show that the region of burkeite precipitation increases as sulfate is added to the liquor. The region increases because the upper and lower critical solids point both change. The second point where Na_2CO_3 begins precipitating changes from 59% for the virgin liquor to 60.5% for the virgin liquor with R-8

saltcake added to 64% for the liquor with both R-8 saltcake and PPT ash. This indicates that the addition point for salt makeup and recycle streams can influence more than just the MEE. The amount of crystallization that occurs in the various concentrator bodies changes with liquor chemistry as does the preferred solids targets for concentrator systems. For example, the second concentrator effect could operate very well at 59% solids on liquor with both makeup and recycle streams

added. Operation at this solids level would be very risky on virgin liquor. In that case, the operating solids level is exactly at the second critical solids point. The concentrator body would need to handle both burkeite and sodium carbonate crystallization.

Effect of temperature on solubility

Case 5. The temperature of the black liquor influences the solubility profiles and especially the critical solids point of the liquor. Figure 11 summarizes the effect of temperature on solubility for Mill A liquor with R-8 salt cake added. Three temperatures were chosen to approximate the feed temperature and operating temperature of the second concentrator effect (110°C), the first concentrator effect (135°C), and the concentrator product temperature (120°C). The results show that operating temperature has a small impact on the first critical solids point at which burkeite crystallization starts. Burkeite has a small inverse temperature effect. The first critical solids point is therefore lowest for the black liquor at 135°C and highest for the liquor at 110°C. The second critical point—the point where Na_2CO_3 begins precipitating—is strongly influenced by temperature. While the first critical solids point drops from 52% to about 51% with a temperature increase from 110°C to 135°C, the second critical point drops from 60.4% to 55.6% with the same temperature increase.

This difference in solubility with temperature strongly affects the crystallization load required of each effect. (Crystallization load is the amount of inorganic material that must be crystallized from the black liquor in a concentrator body under equilibrium conditions.) For the concentrator system with operating points noted under Case 3, the second effect would have a crystallization load of 3.5% on black liquor

solids (BLS) (12% minus 8.5%). By contrast, the first effect would have a crystallization load of almost 6.5% on BLS (8.5% minus 2%). This means that the concentrator body operating under the most difficult conditions carries 65% of the crystallization load for the entire concentrator system. A combination of the equilibrium calculations presented here with understanding of crystallization kinetics is necessary to determine whether this is a design prone to soluble scale formation.

The results in Fig. 11 also show danger areas for concentrator operation. Changes in concentrator operating points due to upsets in liquor feed rate, steam rate, inlet solids, or liquor chemistry may push the second effect close to the second critical point. Some evidence exists that the operation of each concentrator stage should avoid proximity to a critical point. For example, operation of the second stage concentrator at 110°C with 1%—2% higher solids may cause premature scaling of the concentrator. To avoid this possibility, operating temperature or solids could be shifted to move operation away from the critical solids point.

CONCLUSIONS

Using these results leads to the following conclusions:

- The NAELS-based solubility model using thermodynamic coefficients and chemical potentials derived from experimental data can predict the equilibrium solubility of inorganic compounds in black liquor over the concentration and temperature ranges of interest.
- The solubility of inorganic species in black liquor can be estimated by addition of a hypothetical black liquor organic species (Na^+ binding site) that is completely soluble but also exhibits activity in solution.
- Addition of the organic binding site for Na^+ allows the model to account for the effect of changes in liquor chemistry on solubility better. A 2 g/L change in residual active alkali has a negligible effect on the solubility of sodium carbonate and sodium sulfate in black liquor.
- Black liquor exhibits two critical solids points over the range of temperatures and solids concentrations used in high-solids concentrators. The first critical solids point occurs when burkeite begins precipitating at 45%–55% total solids. The second critical point occurs when sodium carbonate begins precipitating at 55%–65% total solids. The actual critical point depends strongly on liquor chemistry and liquor temperature.
- Solubility models of the type described in this paper are very useful to define the effect of operating conditions and liquor chemistry on black liquor solubility and to identify the tendency to form soluble scales in black liquor concentrators.
- More black liquor solubility data are necessary to define better the effect of temperature and liquor source on the organic and cation binding assumed in this model.
- The model reflects equilibrium conditions. The results shown here must be combined with crystallization rate data on black liquor. Understanding black liquor solubility is only the first step in eliminating soluble scales from black liquor concentrators. **TJ**

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