## Model for Solubility and Solid Phase Composition in High-Temperature Na<sub>2</sub>CO<sub>3</sub>-Na<sub>2</sub>SO<sub>4</sub> Solutions

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Scaling by the double salts of the Na<sub>2</sub>SO<sub>4</sub> and Na<sub>2</sub>CO<sub>3</sub> system has long been recognized as a problem in pulp and paper industry spent liquor evaporators [1-4]. The two double salts currently identified from this system in black liquor evaporators are burkeite and sodium sulfate dicarbonate. Burkeite is a sulfate-rich species with a nominal formula (Na<sub>2</sub>CO<sub>3</sub>·2Na<sub>2</sub>SO<sub>4</sub>) capable of forming solid solutions with a mole ratio of 1.4-2.2 SO<sub>4</sub>:CO<sub>3</sub> at 100 °C [5]. Sodium sulfate dicarbonate is a carbonate-rich species with a CO<sub>3</sub>:SO<sub>4</sub> mole ratio of 1.7-2.2 [6]. A limitation of traditional models based on the minimization of the Gibbs free energy is that the chemical composition of the solid species has to be defined so that the chemical potential of the solid species can be calculated. These models lack the flexibility to predict the composition of an equilibrium solid phase which precipitates as a solid solution. We have used a model for the burkeite system that is capable of predicting composition of both the precipitated salt and the solution using published solubility data. The model is based on a thermodynamic definition of a solubility constant with Pitzer ionic activity coefficients in the solution. This model has been fit to solubility data in the 100 to 115 °C range and also to data at 150 °C. Additional solubility data in the 115-150 °C range are being generated to increase the temperature range for which this model can be applied. We are also currently working to produce the solubility data necessary to apply the model to the solution composition range that produces the sodium sulfate dicarbonate phase.

## References

- Berry, L. (1966). "Black liquor scaling in multiple effect evaporators." <u>TAPPI J.</u> 49(4): 68A-71A.
- Grace, T. M. (1976). "Solubility limits in black liquors." <u>AIChE Symposium Series</u> 72(157): 73-82.
- Shi, B. Frederick, W. J., Jr., Rousseau, R. W. (2003). "Nucleation growth and composition of crystals obtained from solutions of Na<sub>2</sub>CO<sub>3</sub> and Na<sub>2</sub>SO<sub>4</sub>." <u>Ind. Eng. Chem. Res.</u> 42(25): 6343-6347.
- 4. Frederick, W. J., Jr., Shi, B., Euhus, D. D., Rousseau, R. W. (2004) "Crystallization and Control of Sodium Salt Scales in Black Liquor Concentrators," <u>Tappi J.</u> **3**(6):7-13.
- 5. Green, S. J., Frattali, F. J. (1946). "The system sodium carbonate-sodium sulfate-sodium hydroxide-water at 100°C." J. Am. Chem. Soc. **68**: 1789-1794.
- Shi, B., Rousseau, R. W. (2003). "Structure of burkeite and a new crystalline species obtained from solutions of sodium carbonate and sodium sulfate." <u>J. Phys. Chem. B</u> 107: 6932-6937.