CHEMICAL ENGINEERING TRANSACTIONS
VOL. 39, 2014
A publication of AIDIC
The Italian Association of Chemical Engineering
www.aidic.it/cet
Guest Editors: Petar Sabev Varbanov, Jiří Jaromír Klemeš, Peng Yen Liew, Jun Yow Yong

ISBN 978-88-95608-30-3; **ISSN** 2283-9216 DOI: 10.3303/CET1439076

Study of Sodium Salts Solubility in Eucalyptus Black Liquor to Understand and Prevent Scale Formation in Evaporators

Brenno S. Leite*[a] , Melissa T. Andreuccetti[b], Sibele A. F. Leite[a], José V. H. d´Angelo[b]

[a] University Federal of Viçosa (UFV- Campus Florestal), Institute of Science and Technology, Rodovia LMG, 818 km 6 – CEP: 35.690-000, Florestal-MG, Brazil
[b] University of Campinas, Dept. of Chemical Systems Engineering, School of Chemical Engineering., Av. Albert Einstein, 500 – CEP: 13.083-852, Campinas-SP, Brazil.
brennoleite@ufv.br

Black liquor is a by-product of wood digestion process in pulp and paper mills and it is composed by organic and inorganic products. After this digestion process, black liquor has a solid content of 15 wt/% and to be used as fuel in the recovery boiler it is necessary to be concentrated above 75 wt/% of solids. This concentration process is performed in an evaporation plant using multiple effect evaporators. Some black liquor physical properties, such as density, solids content, viscosity and sodium salts content, are strongly dependent on the kind of wood processed (hardwood or softwood) and on operating conditions during the digestion process. Knowledge and comprehension of the relationship between these physical properties of black liquor are essential for studies aiming at a greater energetic performance of the black liquor evaporation unit. When black liquor reaches higher solids content (above 50 wt/%), scaling formation is observed on the heat transfer surfaces of evaporators and concentrators, due to the precipitation of sodium salts, reducing the overall efficiency of this equipment. The aim of this work is to investigate and comprehend the mechanism of formation and precipitation of sodium salts in eucalyptus black liquor evaporators, through the study of the relationship between some physical properties (density, viscosity, total solids content) and the solubility of sodium salts, evaluating the influence of these variables. In this study industrial samples of black liquor taken from different process streams of the evaporation plant were used. A greater comprehension of the mechanism which is responsible for the reduction of the solubility of these salts is very important for the development of alternative methods to avoid or reduce scaling formation. Experimental data were used to develop a model based on chemical equilibrium of salts dissociation reactions, considering also temperature and pH of the system, which is capable of estimating sodium sulphate solubility limit and comprehend the process that causes the formation of the first scaling and the behaviour of the salts in the system. This model may be used to establish some operating parameters, trying to avoid or control scaling formation in industrial evaporators.

1. Introduction

In pulp and paper mills the aqueous solution extracted from the pulping process in the wood digester is named black liquor, which consists of organic and inorganic compounds. The organics fractions are basically lignin, polysaccharides, carboxylic acid and extractive. Inorganic compounds present in black liquor consist mainly of sodium salts and small amounts of potassium, calcium, magnesium, silicon and iron salts. When leaving the digester sector black liquor has about 15 wt/% of solids and to be used as a fuel in the recovery boiler it is necessary to raise this solids content to 75 wt/%, removing water in a battery of multiple effect evaporators (Rosier, 1997).
Some black liquor physical properties, such as density solids content, viscosity and sodium salts content, are strongly dependent on the kind of wood processed (hardwood or softwood) and on operating conditions during the digestion process. Knowledge and comprehension of the relationship between these

Please cite this article as: Leite B.S., Andreuccetti M.T., Leite S.A.F., d´Angelo J.V.H., 2014, Study of sodium salts solubility in eucalyptus black liquor to understand and prevent scale formation in evaporators, Chemical Engineering Transactions, 39, 451-456 DOI:10.3303/CET1439076

physical properties of black liquor are essential for studies aiming at a greater energetic performance of the black liquor evaporation unit (Frederick et al., 2004).

When black liquor reaches higher solids content (above 50 wt/%), scaling formation is observed on the heat transfer surfaces of evaporators and concentrators, due to precipitation of sodium salts, reducing the overall efficiency of this equipment (Adams, 2001).

The aim of this work is to investigate and comprehend the mechanism of formation and precipitation of sodium salts in eucalyptus black liquor evaporators, through the study of the relationship between some physical proprieties (density, viscosity, total solids content) evaluating their influence over the solubility of sodium salts content in industrial black liquor samples.

A greater comprehension and knowledge of the mechanism which is responsible for the reduction of the solubility of these salts is very important for the development of alternative methods to avoid or reduce scaling formation. The results have shown that it is possible to use a model to estimate sodium sulphate solubility limit and comprehend the formation mechanism of the first scaling and the behaviour of the salts in the system.

2. Experimental

2.1 Characterization of eucalyptus black liquor

Data for solids and sodium sulphate content, density and viscosity of eucalyptus black liquor used in this working were presented by Andreuccetti et al. (2011). A detailed description of all techniques used may be found in the literature cited in Table 3 and in the work of Andreuccetti (2010). In this work, the industrial samples of eucalyptus black liquor were collected in three different process streams in the evaporation plant of a Brazilian Kraft mill. These process streams are identified as: evaporation plant input stream (EPI); 6th effect recirculation stream (6ER) and 2nd effect output stream (2EO). Industrial nominal values for solids content in each process stream are: 15 wt% for EPI, 30 wt% for 6ER and 45 wt% for 2EO.

2.2 Understanding the mechanism of the precipitation of the sodium sulphate

It is desirable that the salts contained in black liquor, in particular sodium salts should be completely dissolved, during black liquor concentration process. It is known that for black liquors with solids concentrations between 15 and 45 wt/% these salts are completely dissolved. At concentrations above 45 wt/% solids, the precipitation of sodium sulphate salts begins (Euhus et al., 2002).

Based in this information, this step has aimed to create a model for predicting the concentration of sodium sulphate salt from the following physical chemical properties: total solids content, sodium carbonate content, viscosity and density.

To understand the precipitation mechanism of sodium sulphate (Na_2SO_4), it is necessary to analyse the solubility of sodium salt and the relationship of the constant of the solubility product (Kps) as a function of the common-ion effect (total sodium present in black liquor), the competitor ion (sodium from sodium carbonate), density, solids content and viscosity of black liquor eucalyptus were analysed in this work. It important to mention that the parameters considered in this equation were determined experimentally except sodium carbonate content which was obtained from the literature.

3. Results and discussion

As mentioned before, industrial samples of eucalyptus black liquor were collected in three different process streams: evaporation plant inlet stream (EPI); 6th effect recirculation stream (6ER) and 2nd effect outlet stream (2EO). These samples were collected when the industrial process was operating at steady state conditions. Experimental data used in this work were taken from Andreuccetti et al. (2011). Table 1 shows the means and values of experimental values and their standard deviations for the physical properties of the selected black liquor samples.

Table 1: Experimental values of the physical properties in black liquor samples with their respective standard deviations

Process Stream	Solids Content (wt%)	Density (kg/m^3)	Viscosity* (mPa.s)	Sodium Sulphate Content (kg/m^3)
EPI	15.14 ± 0.76	1,084.55 ± 4.87	2.92 ± 0.13	2.59 ± 0.19
6ER	24.34 ± 1.05	1,144.83 ± 13.95	89.76 ± 9.35	4.56 ± 0.26
2EO	39.56 ± 1.56	1,233.69 ± 11.53	1,187.46 ± 167.09	3.17 ± 0.52

*for spindle rotation speed set in 60 rpm

To determine the solubility of sodium sulphate in the liquor, we used the concept of solubility product (Kps) of a salt. This concept is based on the molar ratio of a given salt concentration studied and its molar concentrations of cations and anions in the solution. The solubility product determines the maximum solubility of this salt and its disassociated ions in equilibrium conditions.
Eq(1) shows the dissociation of sodium sulphate to form 2 mol of sodium (cation) and 1 mol of the sulphate (anion). The solubility product of sodium sulphate is given by the ratio between molar concentrations of the dissociated ions, as shown in Eq(2).

$$Na_2SO_{4(S)} \leftrightarrow 2\mathrm{Na}^+ + SO_4^{2-} \tag{1}$$

$$Kps = \left[Na^+\right]^2 . \left[SO_4^{2-}\right]^1 \tag{2}$$

To determine the solubility of sodium sulphate in black liquor it was necessary to consider some specific characteristics of the reaction medium, which are responsible for significant modifications over salt solubility.
These characteristics are: the effect of common ion (sodium from other sources present in the black liquor) and competing anions (carbonate from dissociation of sodium carbonate); temperature; density; viscosity and solids content rising, caused by the evaporation of the solvent (Figure 1).

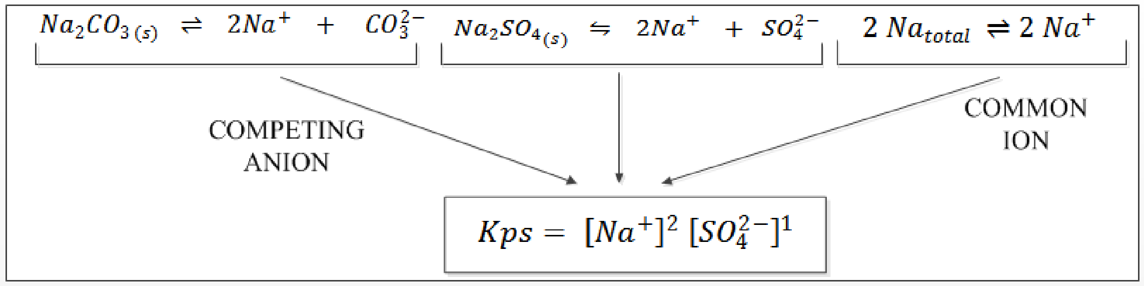

Figure 1: Reactions used in the development of the model

It is important to emphasize that initially all ions are dissociated and their concentration increases as black liquor is concentrated; to achieve a new equilibrium state where the precipitation of sodium sulphate occurs. This new equilibrium state was caused by the presence of a high concentration of common ions (sodium) which tends to decrease the concentration of sulphate in solution. The solubility product considering the boundary conditions is given by Eq(3).

$$Kps = \left[2C_{carbonate} + 2(0.17577T_{SS} + 6.4825\rho + 0.0006591\eta - 7.09) + Na_{OS}\right]^2 . \left[X_{Sulfate}\right] \tag{3}$$

where $C_{carbonate}$ is the total concentration of the sodium carbonate salt (mol/L); $X_{sulphate}$ is the total concentration of the sulphate anion (mol/L); Na_{OS} concentration sodium cation from other sources (mol/L); T_{SS} solids contents (wt%); ρ is the density (kg/m^3) and η is the viscosity (mPa.s).
Table 2 shows experimental data for sodium sulphate content and at the solubility limit values obtained with the model given by Eq(3).
Experimental data presented in Table 2 considers that the experimental procedure of acid degradation of organic matter reduces the complexation allowing the determination of the total mass of sodium sulphate present in the sample of black liquor. The column “Precipitate” represents the difference between sodium sulphate content in black liquor sample and the content at the solubility limit.
Thus negative values for precipitate indicates that the system did not reach sodium sulphate solubility limit and that at this concentration the salt is completely dissociated in the solution. On the other hand, the positive sign indicates that the solubility limit of the salt has been reached and that sodium sulphate has precipitated. This behaviour is consistent with the studies presented by Adams et al (1997) and Adams (2001) regarding to the inversion of sodium sulphate solubility limit in black liquor at concentrations near or above 50 wt/% and the ones presented by Mullin (2001) and Leite et al. (2012).

Table 2: Experimental sodium sulphate content and theoretical data for the solubility limit in black liquor samples

Samples	Solids Content (wt/%)	Sodium Sulphate Content (mol/L)		
		Experimental	Solubility Limit (model)	Precipitate
1	40.54	0.0522	0.0693	-0.0172
2	40.32	0.0505	0.0692	-0.0187
3	39.42	0.0489	0.0760	-0.0271
4	41.27	0.0611	0.0403	0.0208
5	37.97	0.0474	0.0783	-0.0309
6	37.52	0.0485	0.0809	-0.0324
7	39.05	0.0504	0.0744	-0.0240
8	49.27	0.0985	0.0580	0.0405
9	49.93	0.1044	0.0519	0.0525
10	49.12	0.0980	0.0533	0.0448

Scaling formation in evaporators is observed only at higher values of black liquor solids content (about 41 wt/%),and this phenomenon requires that sodium salts are dissociated no more in the solution. And while the system state constantly changes (solids concentration increases, temperature rises, salts precipitate) continuous changes occur in equilibrium conditions. The displacement of the equilibrium is based on the *Le Chatelier's* principle, the salts dissolved in the liquor assumed to have new equilibrium condition in order to minimize effects on the system and this new condition promotes the initiation of the precipitation process and scale formation. Mechanism and steps of the formation of the first scales (burkite) are shown in Figure 2. The mechanism was divided in three steps:

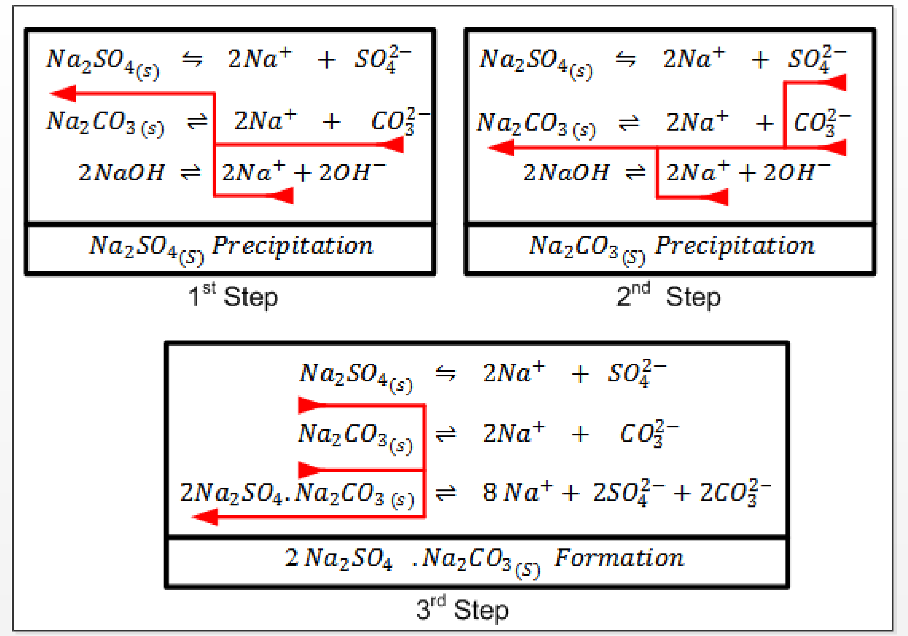

Figure 2: Step of the precipitation/incrustation formation

1st Step: Due to the presence of common and competing ion it happens the reduction of sodium sulphate solubility and then its precipitation;

2nd Step: the disturbance in the chemical equilibrium on the first step shifts the equilibrium state of the system. To balance this perturbation, the system performs a reduction of the anion sulphate dissolved (sodium sulphate salt precipitation) causing the sodium carbonate salt precipitation;

3rd Step: the Na_2CO_3 and Na_2SO_4 after precipitation combine to form the double salt burkite ($2Na_2SO_4.Na_2CO_3$) which consists in the scaling deposit found on the surface of the equipment walls. A continuous increasing of the production rate of pulp and paper mills also causes an increase of black liquor production and then the concentration process of this liquor may represent a bottlenecking problem when operating problems arise from scaling formation in evaporators.

Some studies were performed attempting to simulate and predict scale formation in evaporators. In 1998, Golike et al., have used NAELS (Non-ideal Aqueous ELectrolyte Simulator) to obtain the solubility of inorganic compounds in black liquor, particularly sodium sulphate and sodium carbonate). Schmidl et al. (2003) have presented solubility data for these same salts in aqueous solutions and in black liquor using batch evaporators, comparing these results to predicted solubility behaviour using a proprietary chemical equilibrium model. Soemardji et al. (2004) developed a study trying to understand crystallization process during black liquor evaporation, predicting crystal species transition in aqueous solution of Na_2CO_3 and Na_2SO_4 and in black liquor samples.

Bialik et al. (2007) have applied a thermodynamically-based model for predicting the solubility and solid-phase composition for burkeite precipitates and this model was also used in an attempt to represent the solubility behaviour in high-temperature Na_2CO_3-Na_2SO_4 solutions containing an additional anion.

These studies have contributed for a better understanding of scaling formation process at multiple evaporators in the recovery unit of pulp and paper mills.

4. Conclusion

This work is important to understand the process of scaling formation in black liquor evaporators. A model for predicting the solubility limit of sodium sulphate in black liquor eucalyptus was developed. The determination of solubility limit is fundamental to understand the process scaling formation, avoiding or reducing this operating problem. Another important contribution of this work is that there is still a lack in the literature involving studies that deal with eucalyptus black liquor. The great majority of works found in the literature deals with black liquors from pine wood.

Acknowledgment

The authors would like to thank the financial support from Fundação de Amparo à Pesquisa do Estado de São Paulo – FAPESP and Fundação de Amparo à Pesquisa do Estado de Minas Gerais – FAPEMIG.

References

Adams T., 2001, Sodium salt scaling in black liquor evaporators and concentrators. Tappi Journal Peer Reviewed Paper, 84, 1-18.

Adams T.N., Frederick W.J., Grace T.M., Hupa M., Lisa K., Jones A.K., Tran H., 1997, Kraft Recovery Boilers. Tappi Press, Atlanta, USA.

Andreuccetti M.T., 2010, Eucalyptus black liquor characterization in the evaporation process and correlation of its properties, 2010. MSc Dissertation, Chemical Engineering School, University of Campinas – Brazil.

Andreuccetti M.T., Leite B.S., d´Angelo J.V.H., 2011, Eucapyptus black liquor - density, viscosity, solids and sodium sulphate content revised, O Papel, 72, 52-57.

Bialik M.A., Theliander H., Sedin P., Verril C.L., DeMartini N., 2007, Solubility and solid phase composition in boiling-temperature Na2CO3-Na2SO4 solutions – A modeling approach, TAPPI Engineering, Pulping and Environmental Conference, 2, 1471-1498.

Euhus D.D., Shi B., Rousseau R.W., Frederick Jr W.J., 2002, Control of soluble scale in black liquor evaporators and concentrators: Part 1. Pilot plant studies, TAPPI Fall Technical Conference and Trade Fair, 1567-1574.

Frederick W.J., Shi B., Euhus D.D., Rousseau R.W., 2004, Crystallization and control of sodium salt scales in black liquor concentrators, Tappi Journal, 3, 7-13.

Golike G.P., Pu Q., Holman K.L., Carlson K.R., Wollwage P.C., Folster H.G., Rankin S.,1998, NAELS: A new method for calculation equilibrium solubility of burkeite and sodium carbonate in black liquor. International Chemical Recovery Conference. 1, 403-418.

Leite B.S., Andreuccetti M.T., Leite S.A.F., d´Angelo J.V.H., 2012, Investigation of thermal analysis techniques potential to determine solids content in eucalyptus black liquor samples, Chemical Engineering Transaction, 29.

Mullin J.W., 2001, Crystalization. Butterworth – Heinemann, 594, 153-155.

Rosier M.A., 1997, Model to predict the precipitation of burkeite in the multiple-effect evaporator and techniques for controlling scaling, Tappi Journal., 80, 203-209.

Schmidl W., Verril C.L., Frederick Jr. W.J., Ball A.W., DeMartini N., 2003, Experimental determination and modeling of sodium solubility in high solids kraft black liquor, TAPPI Fall Technical Conference, 1009-1022.

Soemardji A.P., Verril C.L., Frederick W.J., Theliander H., 2004, Prediction of crystal species transition in aqueous solutions of Na_2CO_3 and Na_2SO_4 and kraft black liquor, Tappi Journal, 3, 27-32.