Modeling of the solubility of different inorganic sodium salts in black liquor under varying conditions

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ABSTRACT: To create a model for predicting the solubility of burkeite and related sodium salts in the evaporation train of a kraft pulp mill, we conducted experiments covering the precipitation of burkeite ($Na_2CO_3 \cdot 2Na_2SO_4$) and dicarbonate ($2Na_2CO_3 \cdot Na_2SO_4$). Results from the experiments were implemented in a chemical model that used the Pitzer ion-interaction theory to describe the activity factors of the constituting ions in solution at high ionic strength.

Application: The predictive model can be useful in avoiding problems related to the scaling of burkeite and dicarbonate in evaporation trains of kraft pulp mills.

Burkeite, a sodium salt ($Na_2CO_3 \cdot 2Na_2SO_4$), is a mineral that precipitates during black liquor evaporation at a dry solid content of ~50% or more. It forms scaling on the heat transfer surfaces in black liquor evaporation units. This scale has to be removed by washing or by boiling it out with black liquor, which decreases the efficiency of the process equipment [1].

Recent research showed that the composition of the sodium salt that is precipitated during black liquor evaporation changes with the varying composition of the liquid phase. A high ratio of $[CO_3]/([CO_3] + [SO_4])$ in the black liquor results in a precipitate with a high content of carbonate [2–6]. When the carbonate fraction becomes high enough (above 0.8), another mineral, dicarbonate ($2\ Na_2CO_3 \cdot Na_2SO_4$), is formed. The research suggested that the negative effect of dicarbonate fouling is more pronounced than burkeite fouling, due to the higher affinity of dicarbonate for heat exchanger surfaces [7]. Therefore, the basis for our study was that the composition of the precipitating sodium salts is constantly changing with the composition of the black liquor.

The calcium ions in the black liquor interact with sodium salt in the evaporation train. The presence of calcium in a salt solution displaces the precipitation of sodium salts at a higher temperature than when calcium ions are not present [2]. An industrial sampling campaign of black liquors showed that the levels of dissolved calcium ions decrease during the simultaneous precipitation of sodium salts [8].

The fouling of sodium and calcium salts in black liquor evaporators must be minimized or at least controlled to mitigate their negative effects. Therefore, there is much interest in describing and predicting the precipitation of the fouling scales using computer modeling or simulations. Several previous studies suggested that there could be a simple equation for calculating the critical dry content of the liquor, based on the inorganic content of the liquor [9]. Another approach is the so-called NAELS model (Non-ideal Aqueous Electrolyte Simulator) [10]. More recently, Bialik [11] showed that the solubility of burkeite can be predicted by using the ion-interaction approach, as suggested by Pitzer [12]. We chose a similar approach for our study, in which we measured and modeled the solubility of burkeite and dicarbonate in pure solutions. Our aim was to formulate a chemical solubility model of the different sodium salts.

EXPERIMENTAL

Solubility experiments were carried out using a thermostat in a glycol bath at 105ºC, 115ºC, and 135 ºC in steel autoclaves. Sodium carbonate, sodium sulfate, and sodium hydroxide (p.a. grade) were added to water in varying amounts in order to cover the entire range of carbonate/sulfate ratios in a liquid phase.

Salts were dissolved with the molar ratios of $[CO_3]/([CO_3] + [SO_4])$ from 0.33 to 0.93 and in the initial concentrations displayed in **Table I**. Salt solutions that precipitate spontaneously at room temperature were not used. The total concentrations of salt ranged from 30%–34%, with the initial levels for each individual experiment being chosen empirically. When sodium hydroxide was present, the initial concentration of sodium hydroxide was ~1 mol/l H_2O.

We prepared 150 mL of the solution at room temperature, of which 80 mL were put in autoclaves. The autoclaves were then sealed and kept at the experimental temperature for 5 h under constant stirring. All the experiments resulted in a solid phase.

The autoclaves were then cooled for 1 min in cold water. The liquid phase was filtered off, using a G4 glass filter. The solid phase was collected from the interior of the autoclaves, rinsed with a small amount of water, and dried at 100ºC overnight. We analyzed the liquid and the solid phases for the content of carbonate and sulfate using a TOC instrument (Shimadzu model TOC-5000) and ionic chromatography (ISO Standard 9198, 2001), respectively.

Temp ° C	Na_2CO_3 mol/kg H_2O	Na_2SO_4 mol/kg H_2O	$CO_3/(CO_3+SO_4)$	NaOH mol/kg H_2O
105	1.099	2.198	0.333	
105	1.444	1.925	0.429	
105	2.778	1.388	0.667	
105	1.894	1.893	0.500	
105	1.450	1.932	0.429	
105	3.805	0.951	0.800	
105	4.005	0.801	0.833	
105	3.961	0.660	0.857	
105	4.071	0.581	0.875	
105	4.151	0.519	0.889	
105	4.288	0.429	0.909	
105	4.364	0.335	0.929	
105	1.974	1.973	0.500	
115	1.073	2.145	0.333	1.151
115	1.420	1.892	0.429	1.148
115	1.707	1.707	0.500	1.093
115	2.376	1.187	0.667	0.970
115	2.880	0.959	0.750	1.015
115	3.191	0.797	0.800	1.035
115	3.473	0.579	0.857	1.030
115	3.556	0.508	0.875	0.976
115	3.636	0.454	0.889	1.028
115	3.676	0.367	0.909	1.009
115	3.707	0.285	0.929	0.989
115	2.422	1.210	0.667	
115	3.481	0.870	0.800	
115	3.974	0.662	0.857	
115	4.080	0.583	0.875	
115	4.287	0.428	0.909	
115	1.099	2.197	0.333	
115	1.451	1.934	0.429	
115	1.728	1.728	0.500	
115	2.783	1.391	0.667	
115	3.512	1.170	0.750	
115	3.481	0.870	0.800	
115	3.974	0.662	0.857	
115	2.759	1.379	0.667	
115	3.867	0.552	0.875	
115	3.834	0.766	0.833	
115	4.164	0.520	0.889	
115	4.287	0.428	0.909	
115	4.407	0.339	0.929	
115	3.990	0.570	0.875	
115	1.450	1.932	0.429	
115	2.780	1.389	0.667	
115	3.974	0.662	0.857	
115	4.285	0.428	0.909	
135	1.098	2.195	0.333	
135	1.451	1.934	0.429	
135	1.811	1.810	0.500	
135	2.783	1.391	0.667	
135	3.210	1.069	0.750	
135	3.486	0.871	0.800	
135	3.661	0.732	0.833	
135	3.803	0.633	0.857	
135	1.451	1.934	0.429	
135	3.975	0.497	0.889	
135	4.103	0.410	0.909	
135	4.210	0.324	0.929	

I. Temperature of the solubility experiments and the initial concentration of salts.

The density of the final liquor samples was determined gravimetrically on 5 mL samples at a time.

RESULTS AND DISCUSSION

Experimental work

The carbonate ratio, defined as $[CO_3]/([CO_3]+[SO_4])$ in the liquid phase, was varied in the experiments. **Figure 1** shows the composition of the precipitated salt at different carbonate ratios in the liquid phase.

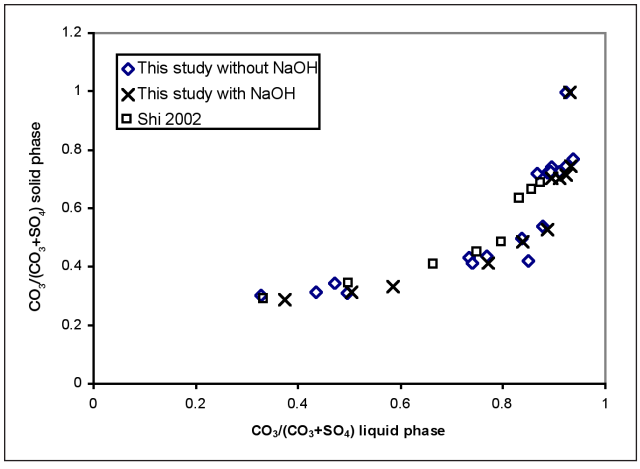
A comparison with the literature values shows that the chemical content of the solid phase, as measured, was similar to compositions in the work of Shi [13]. Higher carbonate ratios in the liquor led to the formation of a solid with a higher content of carbonate. The sudden increase in carbonate ratios in the solid phase, of ~0.8 in the liquid phase also agrees with Shi's data, which indicated that dicarbonate was formed during the experiments. Sodium salts may adsorb carbon dioxide from the ambient air. Other research suggested that an experimental procedure should be established to protect the salts formed from the ambient air [14]. The samples in our work were not protected from the ambient air to any great extent, which meant that carbon dioxide may have been absorbed by the samples. Salts from later experiments (data not shown), conducted under similar conditions but with restricted contact with the ambient air, showed compositions similar to those in Fig. 1. Thus, it was assumed that any absorption of carbon dioxide into the samples only had a minor effect on the results.

Adding NaOH to the solution did not influence the composition of the solid phase. The main parameter controlling the composition of the solid phase was the carbonate ratio in the liquid phase.

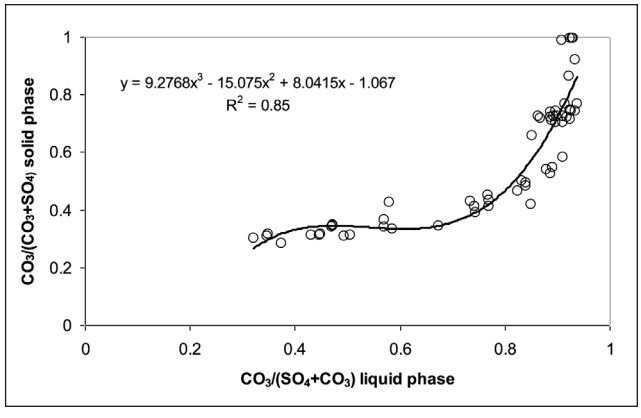
The agreement between the data in Fig. 1 and the data in [13] suggested that dicarbonate was formed at high carbonate ratios in the liquid phase. This was assumed during the rest of our study and no further analysis of the solid phase was done.

The composition of the solid phase varied with the composition of the liquid phase. Results from earlier work suggested three different regions [3]. However, according to the data we obtained, the composition of the solid phase was not absolute; both dicarbonate and burkeite may form in a mixture. In order to translate the composition of the salt into a form that could be used in a chemical model, we used the function shown in **Fig. 2**.

Figure 2 shows the composition of the solid phase, formed with or without added NaOH, at three different temperatures. The data ranged



1. Composition of the solid phase, formed at different compositions of the liquid phase at 115° C, with and without the addition of NaOH, compared with literature values [13].



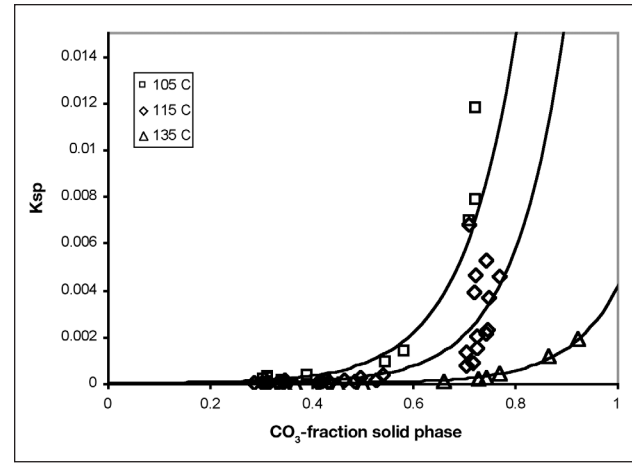
2. The relationship between the composition of the liquid and solid phases, formed at all the temperatures investigated, combined in one series (105°C, 115°C, and 135°C). Experimental points are compared with a regressed line used in the chemical model.

over the various compositions, so the fit with the function was considered high. The compositions could be divided into three different regions representing the solid salts formed: burkeite, dicarbonate, and carbonate. However, using the regressed line instead of three different regions resulted in a smoother transition within the compositional range. This result favored the use of the regressed line, shown in Fig. 2, instead of three previously discrete regions.

The solubility of sodium salt in the burkeite region can be described by using the Pitzer ion interaction theory [15]. We used a similar approach when the compositional range was extended to include the dicarbonate region.

Figure 2 presents the stoichiometric composition of the solid salt. Using the Pitzer interaction theory with parameters from the literature [15, 16], we calculated the solubility product for the solid phase. **Figure 3** shows the resulting solubility products.

The experimental points in Fig. 3 show that the solubility



3. The solubility product of the solid sodium salt, formed as a function of the carbonate ratio in the solid phase at three temperatures. (Magnification of the major part of the experimental results.) R^2 values: 0.90–0.99.

of the sodium salt was dependent on the temperature, which is in accordance with the behavior of the pure salts, i.e., sodium carbonate and sodium sulfate [17]. Deviations from the regressed exponential lines show that any variations in the experiments were quite small.

A parabolic function, with its minimum at the composition of ideal burkeite, was previously proposed [11]. The form of the function was explained by the sodium salt with the composition of ideal burkeite ($Na_2CO_3 \cdot 2Na_2SO_4$) being thermodynamically favored. In our study, the use of a parabolic function gave a poorer fit with the experimental data. This result implied that exponential functions should be used instead of parabolic functions, as shown in Fig. 3.

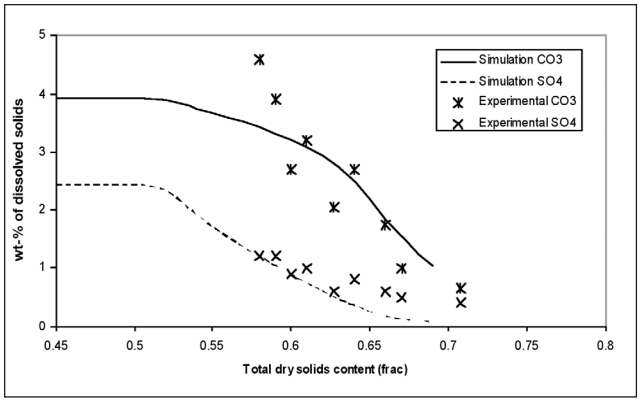
The absolute values of the solubility products were slightly lower than the previously modeled values for burkeite [11]. The reason for the different values was likely due to basing the experimental results on equilibrium periods of 5 h, while the previous model included data describing the conditions at the onset of crystallization.

Implementation of the model

The data in Fig. 2 and Fig. 3 were implemented in WinGEMS 5.0 (Pacific Simulation/Metso Automation), a commercial process simulator. This allows for direct use of the experimental results and makes the model directly applicable to mill cases, providing the composition of the black liquor is known. The temperature dependence was described by the linear interpolation of the experimental values.

Figure 4 shows an example of a result from the implementation, where the output from a simulation is compared with values from the literature [18]. Calculations were made to illustrate the soluble levels of carbonate and sulfate as a function of the increasing dry solids content in industrial black liquor.

Overall, agreement between the experimental literature data and the output from the simulations was high. The sim-



4. Dissolved levels of sulfate and carbonate ions in a black liquor, as a function of the increasing dry content. The output from simulations (lines), using a model based on results in Fig. 2 and Fig. 3 and the approach by [11], compared with experimental literature values (points) [18].

ulations showed that the concentration of the ions in the solution started to decrease at a dry solids content of ~51%. As the dry solids content increased, the concentrations continually decreased. The change in the form of the lines, primarily observed in the carbonate line, is a combination of the results in Fig. 2 and Fig. 3. The carbonate fraction of the remaining liquid phase and the solubility product of the corresponding solid phase changed continually with the increasing dry solids content.

Data from the literature were previously compared with output from simulations using the NAELS-simulator [18]. The main difference between the two simulation approaches is that the interaction between the organic and inorganic phases was not accounted for in the current model. Also, the solubility of sodium salt in the dicarbonate region was implemented in the current model.

SUMMARY AND CONCLUSIONS

We evaluated and formulated the temperature dependence of the solubility of sodium salts in pure solutions as a solubility model, based on the Pitzer ion-interaction theory. The solubility of sodium salts was described over a wide range of the composition of the precipitating salts, i.e., the model handles both salts in the burkeite region (lower CO_3/SO_4 ratios in the black liquor) and in the dicarbonate region (high CO_3/SO_4 ratios in the black liquor). Implementing the solubility model in commercial process-simulation software increased accessibility to the model. Finally, we evaluated the solubility model against experimental data for real black liquors available in the literature. To a large extent, the results from the solubility model were in agreement with the literature data. **TJ**

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INSIGHTS FROM THE AUTHORS

Our study was based on a need to understand and describe the scaling problem in kraft pulp mills. It supports and expands previous research performed by IPST and co-workers. Reproducing laboratory data was the most difficult aspect of our study, but it was encouraging to see that the results supported the work of previous researchers.

Kraft pulp mills can use the results to control and minimize the problems related to scaling of sodium salts in black liquor evaporation. The next step is to describe the solubility of calcium carbonate in kraft black liquors in order to avoid scaling of this salt.

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