Effects of chloride, potassium, and sulfate on the causticizing reaction in the kraft recovery process

SONA SAEIDI, HONGHI TRAN, AND VLADIMIRO G. PAPANGELAKIS

ABSTRACT: We studied the effects of chloride (Cl), potassium (K), and sulfate (SO_4) on the equilibrium of the causticizing reaction over a wide range of causticizing conditions, using OLI, an advanced thermodynamic program for equilibrium calculations in aqueous solutions of ionic salts. Cl, K, and SO_4 were shown to have little or no effect on the causticizing equilibrium. Under a given causticizing condition, coastal mills, due to their much higher NaCl concentration, are predicted to have a causticizing efficiency 1%–2% lower than that of inland mills.

Application: Mills do not have to worry about the effect of chlorine, potassium, and sulfate on their causticizing plant performance.

In the causticizing plant of the kraft recovery process, caustic (NaOH) is regenerated by reacting sodium carbonate (Na_2CO_3) in green liquor with slaked lime ($\text{Ca}(\text{OH})_2$) in the slaker, according to the reaction:

The causticizing reaction precipitates CaCO_3 (lime mud), which is dewatered, washed, dried, and calcined in a lime kiln to produce lime (CaO) for reuse in the slaker. The causticizing reaction is reversible so that the reaction rate decreases as more NaOH is produced. The reaction eventually stops when the system reaches equilibrium concentration of NaOH. For given liquor system, the conversion of Na_2CO_3 into NaOH is often referred to as the causticizing efficiency (CE), which is defined as:

$$\text{CE} = \frac{[\text{NaOH}]}{[\text{NaOH}] + [\text{Na}_2\text{CO}_3]} \times 100 \quad (2)$$

where $[\text{NaOH}]$ and $[\text{Na}_2\text{CO}_3]$ are concentrations of NaOH and Na_2CO_3 in the liquor system, expressed conventionally as g/L Na_2O .

Causticizing efficiency has a direct impact on the quality of the white liquor produced and on the lime mud load in the lime kiln. Much work has been done over several decades to determine the thermodynamics and kinetics of the causticizing reaction, particularly the effects of liquor characteristics, i.e., sulfidity, total titratable alkali (TTA) and temperature on the causticizing equilibrium [1–5]. The effects of lime characteristics (i.e., lime type, particle size, composition, and degree of calcining) and reaction time on CE are also known [6–10]. In general, CE decreases with an increase in TTA, sulfidity, lime particle size, and the amount of impurities in lime, but

increases with reaction temperature and time.

In addition to the main components, Na_2CO_3 , NaOH, and sodium sulfide (Na_2S), kraft liquor also contains minor components such as Na_2SO_4 , NaCl, and potassium salts. The concentrations of these water-soluble components vary greatly from mill to mill, and from boiler to boiler, depending on mill location, wood species, degree of mill closure, liquor sulfidity, types of makeup chemicals, as well as recovery boiler operating conditions [11]. **Table I** summarizes that, for inland softwood mills, the Cl and K concentrations in the green/white liquor are typically about 2.1 g/L Cl and 4.5 g/L K, respectively. For hardwood mills, the potassium concentration is higher, 14 g/L K, while for coastal mills, the Cl concentration is much higher, 12 g/L Cl. The concentration ranges for Cl and K in both g/L and mole% are also given.

The sulfate concentration in green and white liquors is typically 1.5–5 g/L Na_2SO_4 or 1–3.5 mole% $\text{SO}_4/(\text{Na}_2+\text{K}_2)$. Sulfate concentration can be as high as 12 g/L Na_2SO_4 or 8.5 mole% $\text{SO}_4/(\text{Na}_2+\text{K}_2)$ for high sulfidity mills when the recovery boiler reduction efficiency is below 80%.

Despite the presence of large amounts of Cl, K, and SO_4 in green liquor, little is known about the effects of these species on the causticizing reaction. We performed a systematic study to examine how Cl, K, and SO_4 may affect the causticizing equilibrium using a commercially available thermodynamic program. We describe the program and the simulation procedure, and discuss the key results obtained from the program predictions.

THE PROGRAM AND SIMULATION PROCEDURE

Modeling of the causticizing reaction [12, 13] focused generally on the kinetics of the reaction. For our study, we used an advanced thermodynamic program, OLI Stream Analyzer v. 2.0.31. The program is designed to calculate phase equilibri-

		Inland mills		Coastal mills	
		Typical	Range	Typical	Range
Softwood	Chloride, g/L as Cl	2.1	0.3 – 6.4	12	8 – 14
	Potassium, g/L as K	4.5	2 – 7	4.5	2 – 7
Hardwood	Chloride, g/L as Cl	2.1	0.3 – 6.4	12	8 – 14
	Potassium, g/L as K	14	11 – 19	14	11 – 19

		Inland mills		Coastal mills	
		Typical	Range	Typical	Range
Softwood	Chloride, mole% Cl/(Na+K)	1.4	0.2 – 4.2	8	5 – 10
	Potassium, mole% K/(Na+K)	2.8	1.3 – 4.5	2.8	1.3 – 4.5
Hardwood	Chloride, mole% Cl/(Na+K)	1.4	0.2 – 4.2	8	5 – 10
	Potassium, mole% K/(Na+K)	8.5	6 – 11	8.5	6 – 11

I. Concentrations of Cl and K in green and white kraft liquors.

um in aqueous solutions of ionic salts, and is mainly used to examine complex chemical and electrochemical phenomena in aqueous and mixed solvent solutions [14, 15]. The program's thermodynamic model is based on published experimental data. It uses data regression where applicable, estimation and extrapolation where required, and is capable of predicting composition and concentration for ionic salt mixtures in water over a wide range of temperature, total pressure, and ionic strength. The program has been successfully used to predict the solubility of recovery boiler precipitator ash in water under various conditions [16], and the solubility of PbSO₄-NiSO₄ mixtures in the metallurgical and mining industries [17].

In our study, the input parameters to the program were the amounts of different species, as well as temperature and pressure. The main species considered were water, Na₂CO₃, Ca(OH)₂, Na₂S, NaCl, KCl, K₂CO₃, Na₂SO₄, K₂SO₄ and KCl. In cases where simulated or predicted values were to be compared with experimental data, the input parameters also included the temperature and pressure of the liquor system and those under which experiments were carried out. The program outputs were the concentrations of Na⁺, K⁺, OH⁻, S²⁻, HS⁻, CO₃²⁻, SO₄²⁻, Cl⁻, etc. in the solution, and the amounts of precipitated CaCO₃ as well as un-reacted Ca(OH)₂. The concentrations were used to calculate the concentrations of the main species, causticizing efficiency (CE), according to Eq.1, total titratable alkali (TTA), and sulfidity of the liquor, which are defined in Eq. 3 and Eq. 4 as:

$$TTA = [NaOH] + [Na_2S] + [Na_2CO_3] \quad (3)$$

$$Sulfidity = \frac{[Na_2S]}{TTA} \times 100 \quad (4)$$

where [NaOH], [Na₂S] and [Na₂CO₃] are concentrations of NaOH, Na₂S and Na₂CO₃, in the solution, all expressed as g/L Na₂O.

To evaluate the suitability of the program in predicting CE, we used the program first to predict the causticizing equilibrium (or maximum CE) of pure systems that contain only Na₂CO₃, Na₂S, Ca(OH)₂, and water, as a function of TTA and sulfidity. We compared the predicted results with ex-

perimental data obtained from the literature and with the data obtained from selected experiments we performed. We then used the tested program to examine the effects of Cl, K, and SO₄ on CE.

PROGRAM EVALUATION

CE equilibrium for a pure Na₂CO₃ solution

Figure 1 shows the CE predicted by the program (solid curve) for the pure Na₂CO₃ system at 90°C, with a Na₂CO₃ to Ca(OH)₂ molar ratio of 1.25, as a function of TTA. The predicted CE is the maximum attainable CE for the system. The results are in reasonable agreement with experimental data obtained by various research groups that show the equilibrium CE decreases as TTA increases. We obtained the experimental data noted as open circles under well-controlled test conditions at 90°C for 1 h. The results were consistent with, but about 1%–3% lower than, the prediction results and literature data [1, 4, 5]. The lower experimental values we obtained suggest that the system may not have yet reached equilibrium.

CE of Na₂CO₃-Na₂S solutions

The program also simulated the CE of liquors containing both Na₂CO₃ and Na₂S. We performed the simulations at three sulfidity levels, 0%, 15%, and 30%, which have been frequently cited in textbooks [18, 19]. **Figure 2** shows the predicted results

1. Effect of TTA on the maximum attainable CE at 90°C for pure Na₂CO₃ solutions with a Na₂CO₃/Ca(OH)₂ molar ratio of 1.25.

2. Effect of Na_2S on equilibrium CE at 90°C and $\text{Na}_2\text{CO}_3/\text{Ca}(\text{OH})_2$ molar ratio of 1.25.

3. Effect of sulfidity on equilibrium CE at 90°C and $\text{Na}_2\text{CO}_3/\text{Ca}(\text{OH})_2$ molar ratio of 1.25.

(curves), along with literature data (data points) obtained at selected TTA levels. In all cases, there was good agreement between predicted values and literature data. At each sulfidity level, the equilibrium CE decreases with an increase in TTA, while at a given TTA, CE, decreases with an increase in sulfidity.

We also examined the effect of sulfidity on the equilibrium CE at three TTA values: 100, 120, and 140 g/L Na_2O . We chose these values because they cover the typical TTA range of $120 \text{ g/L Na}_2\text{O} \pm 20 \text{ g/L Na}_2\text{O}$. **Figure 3** shows these predictions. While increasing sulfidity results in a lower equilibrium CE, the effect is much smaller than that of TTA. At $\text{TTA}=120 \text{ g/L Na}_2\text{O}$, for example, increasing sulfidity from 25% to 40% will result in a decrease in the equilibrium CE of only about 1%.

EFFECT OF POTASSIUM

To test the accuracy of the program in predicting the equilibrium CE of systems that contain K, we performed simulations and experiments on solutions of Na_2CO_3 mixed with either 10 wt% K_2CO_3 , 10 wt% KCl, or 10 wt% K_2SO_4 . **Figure 4** shows these results. The predicted CE values were 2%–4% higher than the experimental values, presumably due to incomplete causticization during the 1-h experiments. The trend, however, was consistent in all cases, suggesting that the program can be applied to systems that contain K. Since

4. Effect of potassium on equilibrium CE at 90°C , 0% sulfidity, $120 \text{ g Na}_2\text{O/L TTA}$, $\text{Na}_2\text{CO}_3/\text{Ca}(\text{OH})_2$ molar ratio of 1.25.

5. Comparison between the effects of K_2CO_3 and K_2S on the predicted equilibrium CE, $\text{TTA}=120 \text{ g/L Na}_2\text{O}$, 30% sulfidity.

the potassium compounds in the green liquor before causticizing are mainly K_2CO_3 , K_2S , KCl, and K_2SO_4 , we examined the effect of these compounds on CE.

K_2CO_3 and K_2S

Since carbonate (CO_3^{2-}) and sulfide (S^{2-}) are the major anions in green liquor, the effects of K on CE were first studied by substituting Na_2CO_3 and Na_2S in the liquor with K_2CO_3 and K_2S , respectively. We then compared the effect of K_2CO_3 with that of Na_2CO_3 by replacing Na_2CO_3 with K_2CO_3 , while the effect of K_2S was compared with that of Na_2S by replacing Na_2S with K_2S .

Figure 5 presents the simulation results for both K_2CO_3 and K_2S for the typical liquor sulfidity of 30% and TTA of 120 g/L Na_2O . In both cases, the results are the same. As the K concentration in the liquor increases, CE increases slightly. We observed similar results at lower sulfidity levels, 0% and 15% (not shown). Since the potassium concentration in the liquor varies between 1.3 and 11 mole% $\text{K}/(\text{Na}+\text{K})$ (see Table 1), the results indicate that increasing the potassium concentration in the liquor will cause, at the most, a 0.5% increase in the equilibrium CE.

CHEMICAL RECOVERY

KCl and K₂SO₄

In the case of K₂CO₃ and K₂S shown in Fig. 5, it was possible to increase the K⁺ concentration and keep the concentrations of CO₃²⁻ and S²⁻ constant at the same time, by simply substituting Na₂CO₃ and Na₂S in the liquor with the same number of moles of K₂CO₃ and K₂S, respectively. However, this was not possible in the case of KCl and K₂SO₄, since there was no NaCl or Na₂SO₄ in the initial liquor (which contained only Na₂CO₃ and Na₂S) to substitute for. As a result, adding KCl and K₂SO₄ to the system would increase the K⁺ concentration and the Cl⁻ and SO₄²⁻ concentrations.

Figure 6 shows the effect of K on the predicted equilibrium CE obtained by adding KCl and K₂SO₄ to the liquor, as predicted by the program. Increasing K by adding K₂SO₄ does not appreciably change CE, while increasing K by adding KCl decreases it. Note that at a given mole% K/(Na+K), the K⁺ concentration in the system is the same for both K₂SO₄ and KCl. Therefore, the difference between the effects of these two potassium salts on CE is likely caused by the anions, either Cl⁻ or SO₄²⁻, and the effect of Cl⁻ is much greater than that of SO₄²⁻.

EFFECT OF CHLORIDE

The chloride compounds considered were KCl and NaCl. The simulation procedure for KCl was the same as that described in the previous section, since in this case the mole% K/(Na+K) is exactly the same as the mole% Cl/(Na+K). In the case of NaCl, the procedure was also the same, except that NaCl was used instead of KCl.

Figure 7 shows the effect of Cl on the predicted equilibrium CE of a liquor system with 120 g/L Na₂O TTA and 30% sulfidity. We observed a similar trend for both NaCl and KCl, suggesting that the presence of Cl lowers CE, and that NaCl has a slightly greater effect than KCl. This adverse effect of NaCl on causticizing has also been reported in the literature.

EFFECT OF SULFATE

Figure 8 shows the simulation results for Na₂SO₄ and K₂SO₄. In both cases, the predicted equilibrium CE remains relative-

6. Comparison of the effects of K₂SO₄ and KCl on the predicted equilibrium CE, TTA=120 g/L Na₂O, 30% sulfidity.

7. Comparison of the effect of KCl and NaCl on the predicted equilibrium CE, TTA=120 g/L Na₂O, 30% sulfidity.

8. Comparison of the effects of K₂SO₄ and Na₂SO₄ on the predicted equilibrium CE, TTA= 120 g/L Na₂O, 30% sulfidity.

ly constant as the SO₄ concentration increases. K₂SO₄ appears to have a slightly positive effect, while Na₂SO₄ appears to have a slightly negative effect. Since the SO₄ concentration in the green liquor is typically lower than 3.5 mole% SO₄/(Na₂+K₂), and would not exceed 9 mole% SO₄/(Na₂+K₂) even in the worst case scenario of high sulfidity (>40%) and low reduction efficiency (<75%), we can conclude that SO₄ does not have any practical effect on CE.

The above results clearly show that varying K⁺ and SO₄²⁻ concentrations would not cause appreciable change in the equilibrium CE, while increasing the Cl⁻ concentration would adversely affect the CE. The results are plausible since K⁺ and Na⁺ have the same charge (+1), while Cl⁻ has a different charge (-1), compared to SO₄²⁻ and CO₃²⁻ (-2).

CONCLUSIONS

The effects of chloride (Cl), potassium (K), and sulfate (SO₄) on the equilibrium of the causticizing reaction Na₂CO₃ + Ca(OH)₂ = 2NaOH + CaCO₃ were studied using an advanced thermodynamic program by OLI Systems. The simulation results suggest that:

- Although Cl has an adverse effect on CE, in any given kraft pulp mill, the variations in Cl concentration are not large enough to cause any practical effect on CE. However, since the Cl concentration in the green and white liquors in coastal mills are 2–4 times higher than those in inland mills, coastal mills are predicted to have a CE 1%–2% lower than that of inland mills.
- While K may cause a slight increase in CE, within the typical concentration range of K in the liquor system, the effect is insignificant.
- SO_4 has little or no practical effect on the equilibrium CE.

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INSIGHTS FROM THE AUTHORS

Although there has been much speculation about the effects of chloride, potassium, sulfate, and other non-process elements on causticizing equilibrium, the effects have not been systematically examined. Our work complements our research on chemical recovery, particularly our understanding of the effects of chloride, potassium, and sulfate in the causticizing plant.

Our most difficult challenge was to obtain sufficient experimental data on the causticizing reaction to validate our OLI base-thermodynamic model. We addressed it by performing numerous experiments in our laboratory and by conducting an extensive literature survey.

Our most interesting finding was that despite all the concerns, chloride, potassium, and sulfate have little effect on causticizing equilibrium. Mills no longer have to worry about the effect of the elements on their causticizing plant performance.

Tran

Papangelakis

Saeidi

Tran is Frank Dottori Professor of Pulp & Paper Engineering, Department of Chemical Engineering and Applied Chemistry, and Director, Pulp & Paper Center, University of Toronto, Toronto, ON, Canada. Papangelakis is a professor and Saeidi is a graduate student, University of Toronto, Toronto, ON, Canada. Email Tran at honghi.tran@utoronto.ca.