Predicting equilibrium causticizing efficiencies by a model based on ionic equilibrium

D. Mondal and A. Krishnagopalan

Graduate student and assistant professor, respectively, Dept. of Chemical Engineering, Auburn University, Auburn, Ala. 36849

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The variation in the conversion of sodium carbonate to sodium hydroxide during causticizing can be caused by an insufficient supply of lime or by variations in the chemical concentration of green liquor. A decrease in causticizing efficiency resulting from a shortage of lime can be corrected by increasing the lime feed rate. However, if the drop in efficiency is due to the increase in the chemical concentration of green liquor, the addition of excess lime serves no purpose. A model that could predict effectively the maximum attainable causticizing efficiency for a given chemical concentration of green liquor could prevent the addition of excess lime and economize the operation of the causticizing plant.

Our objective was to develop a working model for the causticizing reaction that could be used to quantify lime charge and carbonate conversion as a function of green liquor composition. Fundamental knowledge about the principles governing the causticizing reaction is valuable in understanding the factors that affect the extent of the reaction and could lead to better methods for control of the process.

Model development

The following chemical reactions represent the causticizing process in which the sodium carbonate in the green liquor is converted to sodium hydroxide by the addition of quicklime. The causticizing reaction proceeds in two stages, slaking and causticizing:

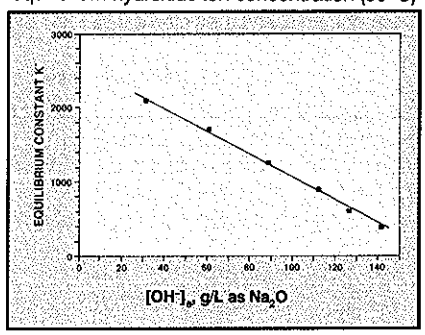
$$CaO_{(s)} + H_2O \rightleftharpoons Ca(OH)_{2(s)} \quad (1)$$

$$Na_2CO_{3(aq)} + Ca(OH)_{2(s)} \rightleftharpoons 2\,NaOH_{(aq)} + CaCO_{3(s)} \quad (2)$$

The slaking of CaO to calcium hydroxide is the first step in the causticizing process and is an exothermic reaction (ΔH = -65 kJ/mole at 100°C).* The causticizing reaction which follows the slaking reaction is slightly endothermic (ΔH = 6 kJ/mole at 100°C).* The two reactions are reversible and heterogeneous in nature. Since the rate of slaking is much higher than the rate of causticizing, the overall rate of the reaction is controlled by the causticizing reaction.

The thermodynamic equilibrium constant of the causticizing reaction can be expressed as:

1. Equilibrium constant K′ as a function of equilibrium hydroxide ion concentration (99°C)



$$K = [\hat{a}^2(NaOH) \cdot \hat{a}(CaCO_3)] / [\hat{a}(Na_2CO_3) \cdot \hat{a}(Ca(OH)_2)] \quad (3)$$

where

$\hat{a}$ = the activities of the respective species in the equilibrium mixture.

The activity of a substance in a mixture can be expressed as follows:

$$\hat{a}_i = (\gamma_i C_i f_i)/f^\circ_i$$

where

γ_i = activity coefficient of species i

C_i = concentration of species i

(f_i/f°_i) = ratio of the fugacity of species i to its standard state fugacity.

The ratio of fugacities can be assumed to be equal to unity for moderately low pressures. In the reaction mixture, $Ca(OH)_2$ and $CaCO_3$ are present as solid phases, and hence their activities can be taken as unity. With these simplifications, Eq. 3 can be written as

$$K = [\gamma^2(NaOH) \cdot [NaOH]_e^2] / [\gamma(Na_2CO_3) \cdot [Na_2CO_3]_e] \quad (4)$$

where the subscript e indicates the equilibrium for the concentration of species i. K can also be expressed as a product of two terms, A and the stoichiometric equilibrium constant K′ as follows:

$$K = (A)(K') \quad (5)$$

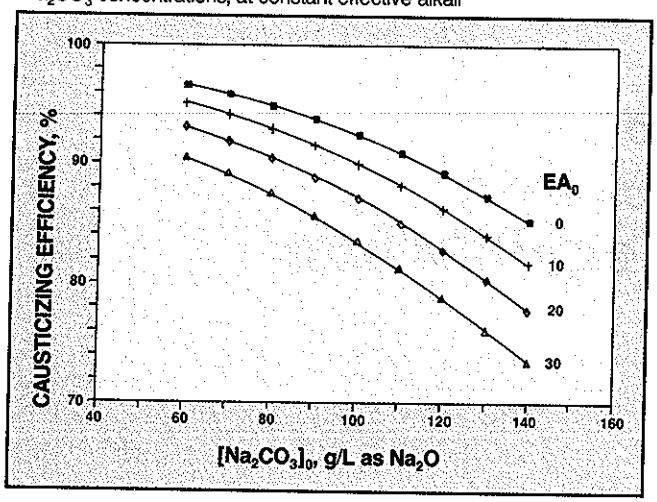
$$A = \gamma^2(NaOH) / \gamma(Na_2CO_3) \quad (6)$$

$$K' = [NaOH]_e^2 / [Na_2CO_3]_e \quad (7)$$

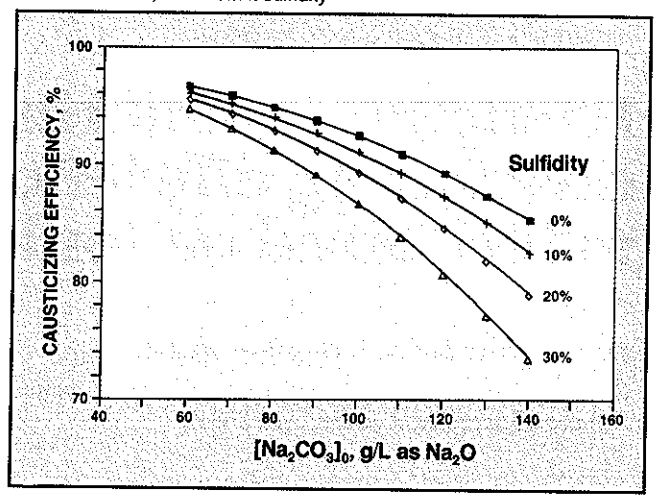
At a given temperature, the value of

*Lindberg, H. and Ulmgren, P., J. Pulp Paper Sci. 9(1):TR7(1983).

2. Causticizing efficiencies predicted by the model for different initial Na_2CO_3 concentrations, at constant effective alkali



3. Causticizing efficiencies predicted by the model for different Na_2CO_3 concentrations, at constant sulfidity



K is constant, and the value of K′ depends on the value of A. Thus, the value of K′ (referred to as the equilibrium constant) depends on the activity coefficients of these two species, which depend on the concentration of all the species in the equilibrium mixture.

The presence of inert electrolytes (like sulfate, thiosulfate, chloride, and hydrosulfide) and their interactions have been studied by Lindberg and Ulmgren*. They found that the presence of these inert anions had no appreciable effect on the value of K′. This absence of effect may be due to the fact that the hydroxide ion concentration in the equilibrium mixture is higher than that of all other anions. Therefore, the activity coefficients, γ (NaOH) and γ (Na_2CO_3), may be assumed to be strongly dependent on the hydroxide ion concentration of the reaction mixture. Thus, if

$$A = f([OH^-]_e)$$

then

$$K' = f([OH^-]_e)$$

The sodium sulfide concentration remains constant during the reaction. If the hydrolysis of Na_2S is assumed to proceed completely to the right, by

$$Na_2S + H_2O \longrightarrow NaHS + NaOH \quad (8)$$

then the initial hydroxide ion concentration can be taken as the effective alkali concentration, EA_0, of the liquor:

$$EA_0 = [NaOH]_0 + 1/2[Na_2S]_0 \quad (9)$$

1. Experimental and predicted causticizing efficiencies for different green liquor compositions

Experiment	Initial green liquor composition, g/L as Na_2O				Causticizing efficiency, %	
	Na_2CO_3	NaOH	Na_2S	EA	Measured	Predicted
1	31	0	0	0	98.5	98.6
2	62	0	0	0	96.6	96.5
3	93	0	0	0	93.1	93.3
4	124	0	0	0	88.8	88.5
5	130	0	0	0	87.5	87.3
6	155	0	0	0	81.9	81.8
7	186	0	0	0	73.7	74.1
8	100	10	0	10	89.8	90.0
9	100	15	0	15	88.3	88.6
10	100	20	0	20	86.5	87.1
11	100	25	0	25	85.1	85.4
12	100	0	10	5	91.5	91.3
13	100	0	20	10	90.1	90.0
14	100	0	30	15	88.3	88.6
15	100	0	40	20	86.7	87.1

The causticizing efficiency, E, at equilibrium can be expressed by the following equation:

$$E = ([Na_2CO_3]_0 - [Na_2CO_3]_e) / [Na_2CO_3]_0 \quad (10)$$

Therefore, the equilibrium concentration of NaOH becomes

$$[NaOH]_e = ([Na_2CO_3]_0 - [Na_2CO_3]_e) + EA_0 = [Na_2CO_3]_0 (E) + EA_0 \quad (11)$$

The equilibrium concentration of Na_2CO_3 becomes

$$[Na_2CO_3]_e = [Na_2CO_3]_0 \cdot (1 - E) \quad (12)$$

where both the initial concentration (subscript zero) and the equilibrium concentration are expressed in g/L, as Na_2O.

Now K′ can be expressed in terms of causticizing efficiency as follows:

$$K' = \frac{([Na_2CO_3]_0 \cdot (E) + EA_0)^2}{[Na_2CO_3]_0 \cdot (1 - E)} = f[OH^-]_e \quad (13)$$

Knowing the initial effective alkali concentration, the sodium carbonate concentration of green liquor, and the functional dependence of K′ on $[OH^-]_e$, the causticizing efficiency can be calculated from Eq. 13 by an iterative procedure.

Results

Based on the experimental results, the equilibrium constant K′ is a linear function of the equilibrium hydroxide ion concentration (**Fig. 1**). The constant can be represented by the following equation:

$$K' = 2600 - 16\,[OH^-]_e \qquad (14)$$

Combining Eqs. 13 and 14, the final form of the model can be expressed as:

$$([Na_2CO_3]_0 \cdot E + EA_0)^2 / [[Na_2CO_3]_0 \cdot (1\text{-}E)] = 2600 - 16\,[OH^-]_e \qquad (15)$$

where concentrations are expressed in g/L, as Na_2O.

The experiments were carried out at 99°C using green liquor prepared with reagent grade Na_2CO_3, Na_2S, and NaOH. Preliminary experiments have shown that excess lime had no effect either on the causticizing efficiency or on the equilibrium composition. The reaction reached a state of equilibrium after 2.5 h. The reactions were carried out for a period of 3 h, and the liquor samples were analyzed according to TAPPI T 624.

The experimental and predicted values of the causticizing efficiencies for different green liquor compositions are tabulated in **Table I**. The predicted values were found to be within the range of experimental error. The experimental data show that the causticizing efficiency decreases with increasing concentrations of Na_2CO_3, NaOH, and Na_2S in green liquor. An increase in the hydroxide ion concentration, due to the increase in effective alkali, suppresses the conversion of Na_2CO_3 to maintain the value of K.

Figure 2 shows the predicted equilibrium causticizing efficiency as a function of initial Na_2CO_3 concentration, at a constant concentration of effective alkali.

Figure 3 shows the effect of initial Na_2CO_3 on the predicted equilibrium causticizing efficiency, at constant green liquor sulfidity. For a given initial Na_2CO_3 concentration, the predicted causticizing efficiency decreases as the green liquor sulfidity increases. This decrease occurs because of the increase in the effective alkali concentration of green liquor, since at constant $[Na_2CO_3]_0$, the sulfidity can only be increased by increasing the concentration of Na_2S.

The curves illustrated refer to equilibrium conditions. No combination of excess lime or changes in operating conditions can result in a conversion greater than the equilibrium conversion. To avoid using too much lime, most mills operate at 5-10% below the equilibrium condition. However, when too little lime is added, the white liquor is produced at a lower active alkali concentration (NaOH+ Na_2S) than the target value. Conversely, if excess lime is added, poor settling and filtering conditions result because of the presence of unreacted $Ca(OH)_2$.

If the green liquor concentration varies from time to time, a fixed dosage of lime may cause too much liming or too little liming, depending on the composition of green liquor. Better causticizing control can be achieved with the on-line measurement of green liquor concentration in combination with a causticizing model.

Knowing the green liquor concentration, the equilibrium causticizing efficiency can be predicted with the help of the developed model. A feedforward control mechanism can be used to regulate the supply of lime, based on the quantity of lime required for equilibrium conversion. This control would result in operating conditions closer to the equilibrium level, which in turn would make the operation of the causticizing plant more stable and economical.

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