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Kinetic studies on lime causticization using locally sourced soda ash and hydrated lime

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Abstract

Lime causticization was studied to develop the governing rate equation for the reaction. Under heterogeneous reaction conditions, the reaction was found to be limited by mass transfer. With thorough mixing (pseudo-homogeneous reaction) a rate equation was developed at optimized reaction time. The determining of initial rates method gave the order of reaction with respect to lime and soda ash to be 1.4 and 1.2 respectively. The overall rate equation was however found to follow a shift-order model; which indicates product inhibition characteristics of the reaction:

$$-r_A = \frac{k\triangle C_A}{1+K_M\triangle C_A}$$

Introduction

Lime causticization became an obsolete technology with the development of brine electrolytic processes, fueled by the high demand placed on chlorine after the First World War. However, the recent global environmental protection campaign against use of chlorine because of its strong interaction with the atmospheric ozone layer and the consequent global warming effect is already gathering a renewed interest in the old-lime process. It is imperative therefore, to examine the critical factors that placed the lime-soda processes disadvantaged in comparison with the electrolytic processes, with the aim of addressing them properly, if lime-soda process will be able to contribute meaningfully in this highly competitive age.

It is acceptable that the electrolytic processes forced the lime-soda processes to halt principally on comparative production cost value.

The electrolytic processes have the advantage of sharing the cost of production between caustic soda and chlorine, making it cheaper. In addition it offers better product quality.

From the relevant reviews, leading among the lime-soda process setbacks, are: low conversion at high reactant concentration, high dilution and poor product quality placing undue cost on product separation processes [1, 2]. Further to the above is the limited trona deposits across the globe, a problem already addressed by the development of Solvay Process, even though at additional production cost [1].

It is pertinent to note that to understudy the interrelationship of the above highlighted factors demand a rigorous empirical kinetic investigation of the process; hence it is the objective of the present report to present a developed rate equation from a study of lime-soda process. This will make possible

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the determination of necessary kinetic parameters for process analysis and provide data for subsequent design of the process reactor as opposed to the pre-World War era, where such designs were based on intuition and modelling methods using dimension analysis.

Experimental Procedure

Trona samples (Kanwa-Nguru) from Nguru, Yobe State of Nigeria and hydrated lime (powdered form) from the National Research Institute for Chemical Technology (NARICT), Zaria, Nigeria were used in this investigation.

The procured trona was beneficiated by soaking in water at about 105°C for a period ranging between 5 to 10 mins. This was allowed to cool to room temperature before filtering to remove all insolubles. The filtrate was concentrated by evaporation to facilitate the precipitation of the Na_2CO_3 and $NaHCO_3$. The precipitated carbonate and bicarbonate was dried at 60°C in an oven for 24hours, after which it was heated further to 160°C in the oven to decompose the bicarbonate according to Equation 1:

$2NaHCO_3(s)\rightarrow$
$Na_2CO_3(s)+H_2O(g)+CO_2(g)$ ....Equation 1

The prepared soda ash was reacted with lime in a laboratory batch reactor setup. Preliminary investigations reported in [3] showed that reaction time and conversion are optimized when complete off-bottom suspension of all solids was attained. This occurred when the stirrer speed was at least 660rpm. Based on this, 660rpm was chosen as stirrer speed for this investigation. A typical batch involves contacting 0.49mol/l of soda ash with 0.1176 mol/l of lime, under stirrer speed of 660rpm and reaction time of 0 – 10mins. The conversion of soda ash and yield of sodium hydroxide were monitored using acid/base titration method. The acid and indicator used were hydrochloric acid and methyl orange respectively. Initial rate and instantaneous curve differential techniques were employed in the analysis of the experimental data generated. The chemical equation for causticization is given as:

$Na_2CO_3(aq) + Ca(OH)_2(aq) \rightarrow$
$2NaOH(aq) + CaCO_3(s)$ ....Equation 2

Results

The results obtained from the experiments are presented in Figures 1 to 6 and Table 1. Figure 1 shows the result of lime-causticization at various soda ash initial concentrations under the following experimental conditions:
$T=70^\circ C$, $[Ca(OH)_2]_o= 120\%$ of stoichiometric equivalent and Stirrer speed = 660rpm.

Figure 2 in turn presents the result when initial concentration of hydrated lime was varied between 0.291M and 0.577M under similar temperature and stirring conditions while the initial concentration of the soda ash was kept constant (0.49M).

Treatment of these kinetic results by graphical differentiation of curves using the initial rates method detailed in [4] afforded the plots of initial rates (based on Na_2CO_3 consumption) versus $[Na_2CO_3]_0$ and $[Ca(OH)_2]_0$ respectively, as shown in Figures 3 and 4. Figure 5 gives a typical plot of instantaneous reaction rate against the analytical concentration while Figure 6 shows the consistency of the observed kinetics with the proposed model.

Table 1. The Values of *k* and K_M for the Causticization Reaction

Initial soda ash concentration, C_{Ao} (mol/lit)	*k* (min^{-1})	K_M(lit/mol)
1.960	7.170	3.112
0.980	7.166	6.449
0.490	6.860	10.450
0.245	7.693	35.575
0.098	7.010	99.900

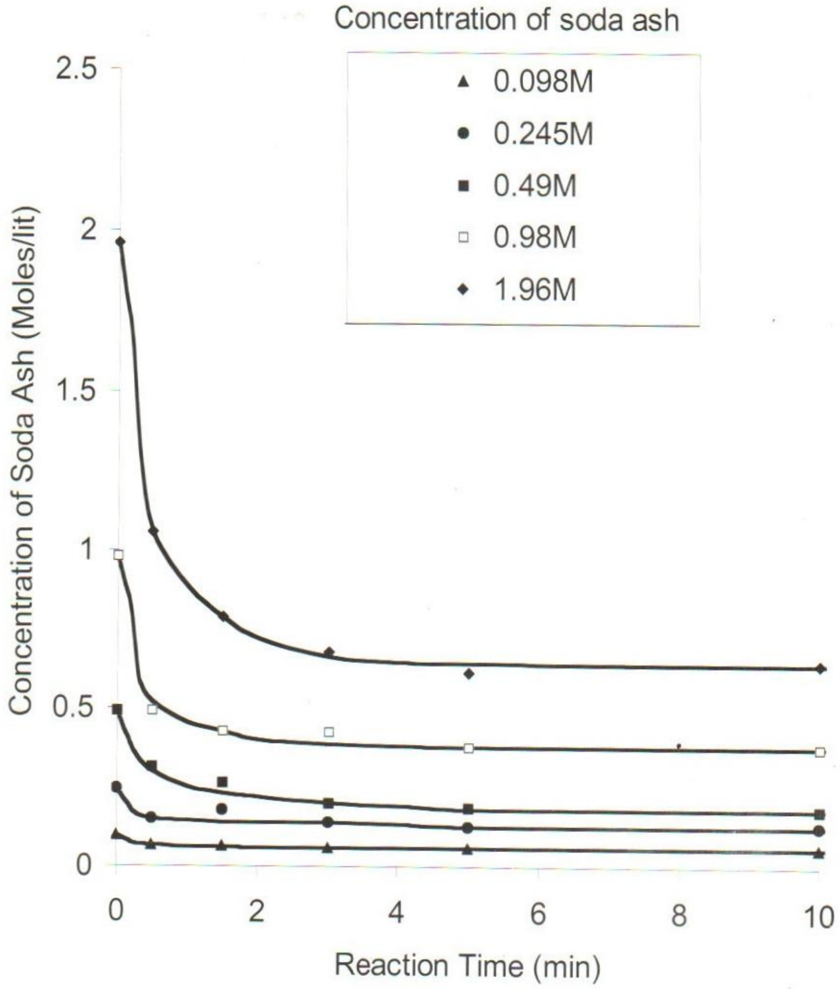

Figure 1: Effect of Initial Concentration of Soda Ash on Causticization

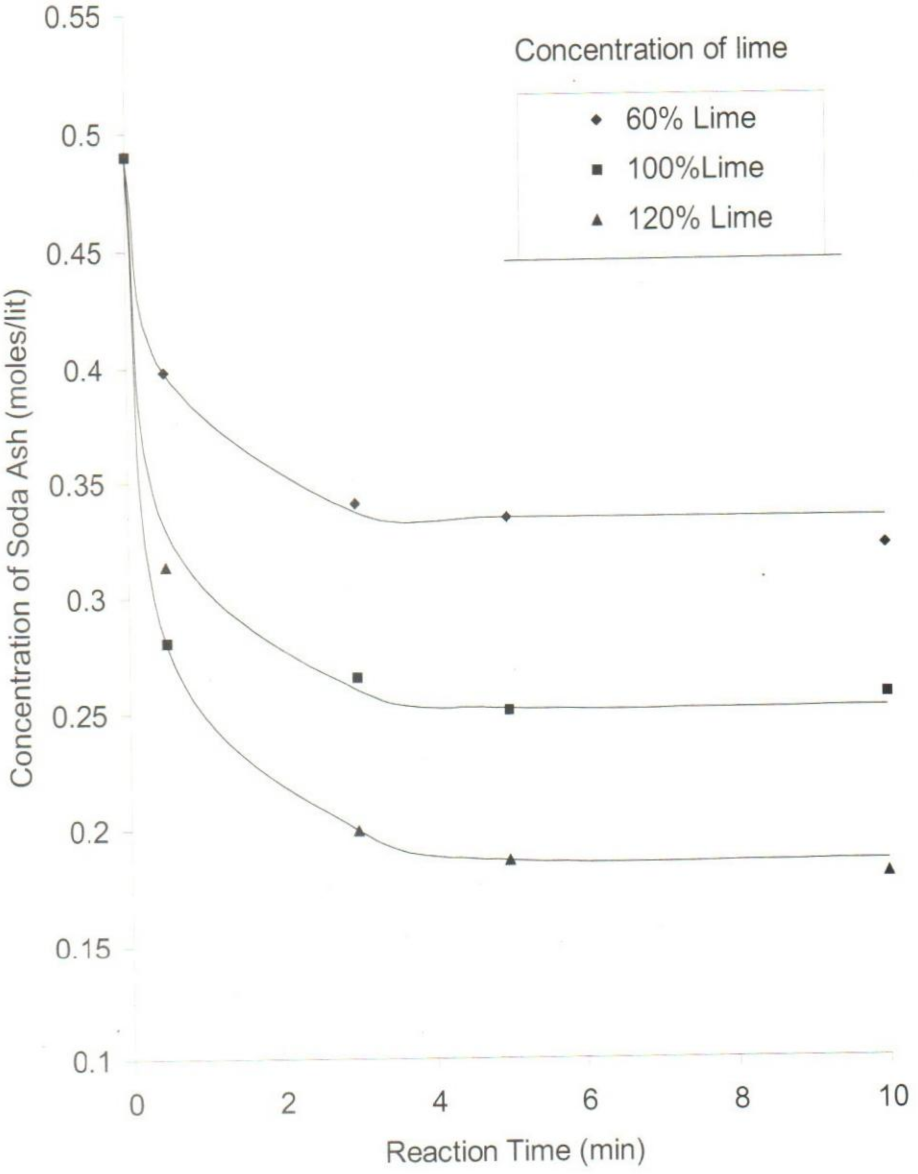

Figure 2: Effect of Lime Content on Causticization

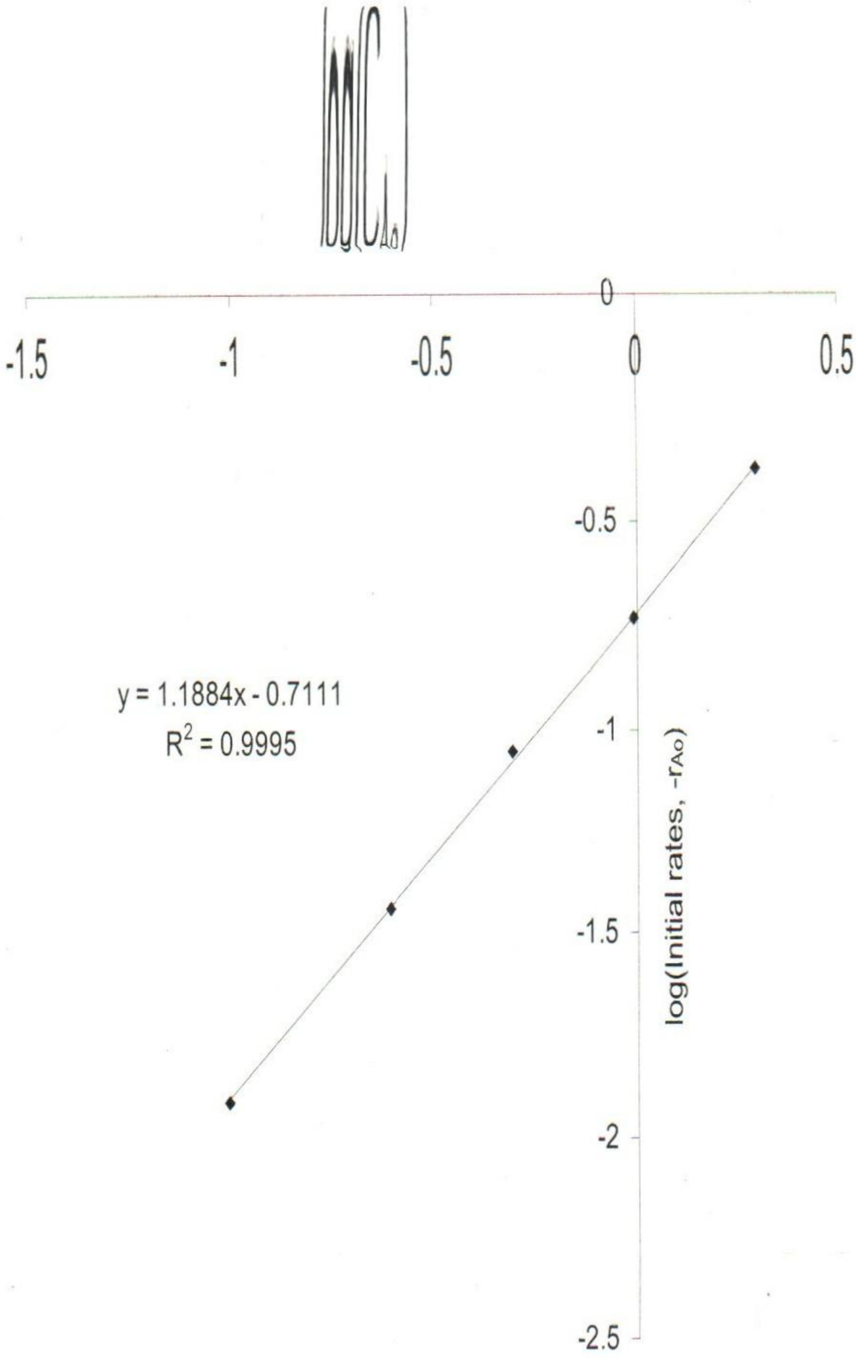

Figure 3: Initial-Rates-Evaluation of Order with Respect to Soda Ash

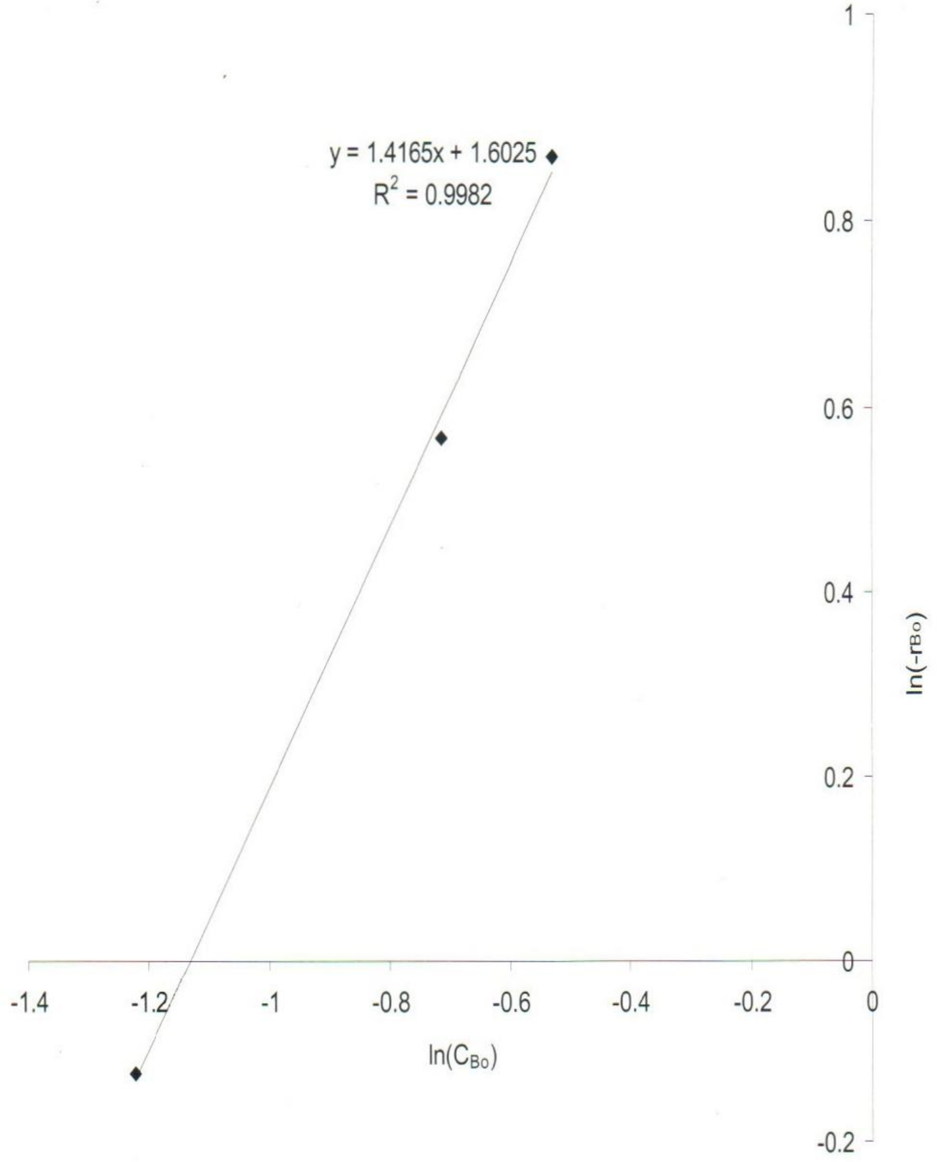

Figure 4: Order of Reaction with Respect to Lime Using Initial Rates

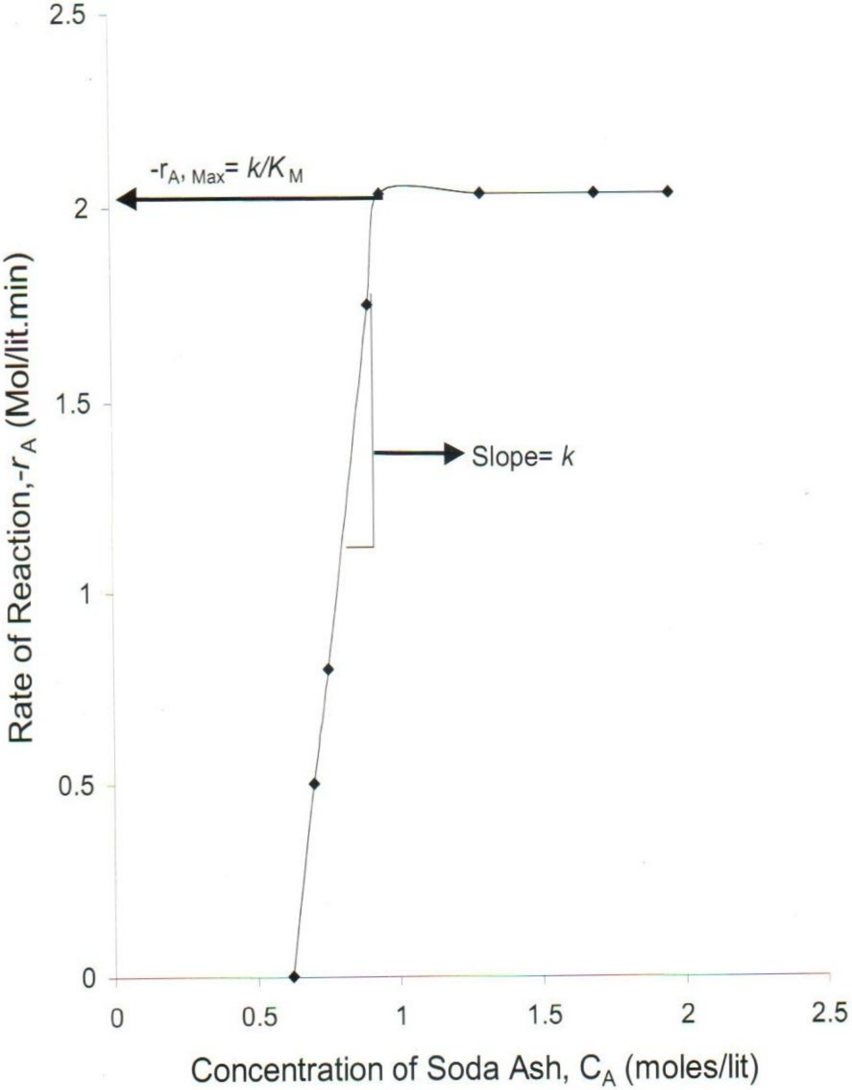

Figure 5: Typical Shift Order Behaviour of Causticization

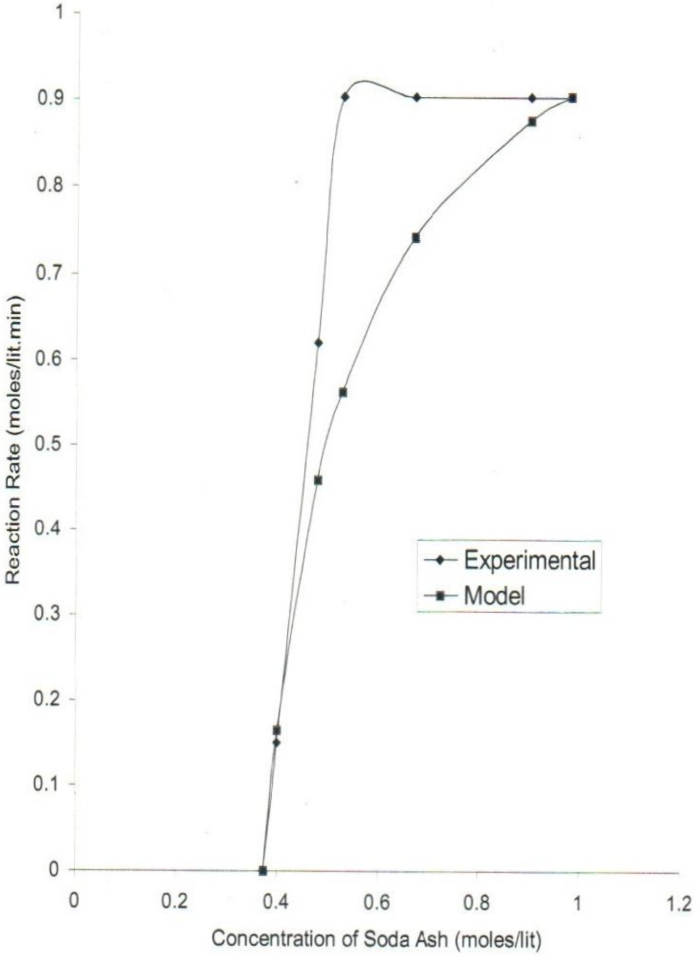

Figure 6: Typical Comparison Between Experimental Values and Predicted Values

Discussion

Analysis of the results of lime causticization presented in Figures 1 and 2 gave rise to Figures 3 and 4 and these plots showed that the dependence of reaction rate with respect to soda ash and lime is approximately 1.2 and 1.4 respectively. These fractional orders suggest a complex reaction mechanism similar to that reported in [5] for a dealumination process. However, in this case product (NaOH) inhibition on lime solubility is suspected.

Therefore, to confirm this inhibitory role of NaOH, the various curves in Figure 1 were differentiated at various analytical concentrations to obtain rates at these different points. A typical plot of instantaneous reaction rate against the analytical concentrations is shown in Figure 5. This plot readily suggests a change in order of reaction from zero at the onset to first order as the reaction progresses. The fact that the rate order obtained by method of initial rate differed significantly from that of instantaneous rate confirms a change in reaction mechanism in line with inhibition phenomena postulated [6].

This is in consonance with the often-postulated lime causticization mechanism presented by Equation 3 (made up of steps 1 and 2)[7,8].

$$Ca(OH)_2\,(s) \underset{k_2}{\overset{k_1}{\rightleftharpoons}} Ca^{2+}(aq) + 2OH^-(aq) \qquad \text{....Step1}$$

and

$$2Na^+(aq) + CO^{2-}_3(aq) + Ca^{2+}(aq) + 2OH^-(aq) \xrightarrow{k_3} 2Na^+ + 2OH^- + CaCO_3 . \qquad \text{.......Step 2}$$

... Equation 3

The reaction indicated by Step 2 of the Equation 3 is certainly limited by that in Step 1. Step 1 suggests that any factor that favours the forward reaction would favour the conversion of soda ash in Step 2 and vice versa.

Formation of $CaCO_3$ (s) in Step 2 literally suggests the possibility of the mud to cast a blanket on the lime, inhibiting further dissociation. Nevertheless, this factor has been taken care of in the experimental design through creation of sufficient turbulence (off-bottom suspension of all particles) to prevent such blanketing effect.

However, the effect of similar ions that is OH^- group in lime ($Ca(OH)_2$)and the product (NaOH) is expected to adversely affect further solubility of lime [7]. This possibly accounts for termination of the reactions within the first few minutes of operation.

Further considerations of Figure 5 in consonance with [6 and 8] shows the form of behaviour commonly described mathematically as:

$$-r_A = \frac{k\triangle C_A}{1+K_M\triangle C_A} \qquad \text{....Equation 4}$$

Where $k=k_3$ is the specific rate constant, $K_M= k_2/k_3$ = equilibrium dissociation constant. Δ = account for the shift of the various curves from zero intercept and is characteristic of the equilibrium dissociation constant. $\Delta C_A = C_A - C_{Ae}$, ($C_A$ = instantaneous soda ash concentration and C_{Ae}= equilibrium concentration of soda ash).

When $K_M\Delta C_A >> 1$, Equation 4 reduces to zero order

$$-r_A = \frac{k}{K_M} \qquad \text{.........Equation 5}$$

and when $K_M\Delta C_A$ (at low C_A concentrations)<< 1, Equation 4 reduces to 1st order.

$$-r_A = k\Delta C_A \qquad \text{.......Equation 6}$$

This shows that not only the product has the tendency to inhibit dissociation of lime, but even the co-reactant especially at higher concentrations of soda ash. Equation 5 shows that rate is simply dissociation constant dependent.

The parameters in the model Equation 4 were first optimized using the (EXCEL) non-linear least square method and then tested for kinetic consistency by comparing model predicted rate values with those obtained from experimental curves at times other than initial (i.e. at > 0) for various [Na_2CO_3].

To this end, k= 7017 (variance, σ =0.28099), and K_M is found to be a function of C_{Ao} as $K_M = 6.1351\ C_{AO}^{-1.1746}$. Typical values of k and K_M obtained are shown in Table 1. Figure 6 shows the consistency of Equation 4 with those obtained from experimental curves. There is sufficiently close agreement between the experimental data and model developed, apart from the turning point (asymptote) which possibly results from the limitation of the method used in determining the value of k/K_M.

Conclusion

The preliminary investigation of lime causticisation using locally derived soda ash (trona) and hydrated lime followed an existing Kinetic model. It provides deep insight into how lime-soda process can be optimized to address its common setbacks. The elucidated product inhibition phenomena suggest the use of spraying type-contacting pattern rather than the traditional batch process often used.

The need to operate at pseudo-homogeneous condition, by use of vigorous stirring to prevent the possible blanketing effect of $CaCO_3$ formed on lime is worth noting in the course of pilot and commercial scale plant design.

Current efforts on this subject are geared toward overcoming the lime dissociation barrier by use of different lime solubility enhancing agents and consideration of other relevant thermodynamic inputs during the dissociation process. The results of those studies will be reported later.

REFERENCES

1. Carvret, L.S., Tilak, V.B.(1992). Alkali and Chlorine Products. In: Mary H.G. et al (Ed) Kirk-Othmer Encyclopedia of Chemical Technology, 4th Edn, John Wiley and Sons Inc., New York. 1: 938-1025.

2. Edward, G.E. (1968). Alkali Metals and their Compounds. In: Thoor T.J.W (Ed) Material and Technology, Longmans, Green and Co. Ltd. and J.H. de Bussy, London 1: 429-445.

3. Ameh, A. O., Ahmed, A. S., Aderemi, B.O. (2004). Caustic Soda Production from Nigerian Trona and Hydrated Lime. 5th Annual Engineering Conference, FUT Minna. pp 8 – 16.

4. Fogler, H.S. (1992). Elements of Chemical Reaction Engineering 2nd Edn. Prentice-Hall Inc., New Jersey. pp 196.

5. Aderemi, B. O., Oludipe, J.O. (2000). Dealumination of Kankara Clay – Development of Governing Rate Equation, Nigerian Journal of Engineering. 8 (2): 22 – 25.

6. Levenspiel, O. (1986). Chemical Reaction Engineering, 3rd Edn, Replica Press Prt. Ltd. Delhi, India. pp 41-96.

7. Boynton, R. S. (1980). Chemistry and Technology of lime and limestone, Wiley Interscience Publishers, London.pp 324-358.

8. Oludipe, J. O., Iyuke, S. E., Aderemi, B. O. (1995). Kinetics of Mechanism of Maleic Acid Hydroxylation by Hydrogen Peroxide. Part I: Formal Kinetic Studies by Immobilized Catalysis in a