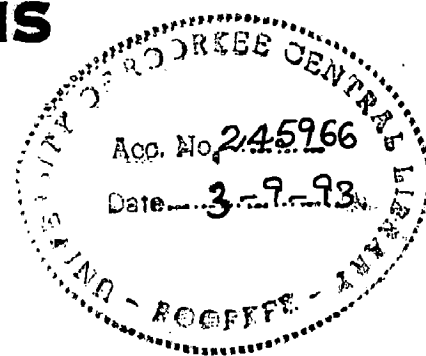


SIMULATION OF KINETIC MODELLING OF CAUSTICIZING REACTOR

A MASTER'S THESIS

BY:- PRADEEP KUMAR



Under the guidance of

Dr. A. K. RAY

&

Shri RAM KUMAR



INSTITUTE OF PAPER TECHNOLOGY

(UNIVERSITY OF ROORKEE)

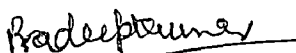
SAHARANPUR-247001 (INDIA)

JANUARY 1993

CANDIDATE'S DECLARATION

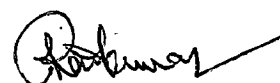
I hereby certify that the work which is being presented in the thesis entitled "SIMULATION OF KINETIC MODELLING OF CAUSTICIZING REACTOR" in partial fulfilment of the requirements for the award of the degree of MASTER OF ENGINEERING submitted at the Institute of Paper Technology, Department of the University of Roorkee, is an authentic record of my own work carried out during the period from July, 1992 to January, 1993 under the supervision of Dr.A.K.Ray and Sri Ram Kumar, at Institute of Paper Technology(University of Roorkee), Saharanpur.

The matter embodied in this thesis has not been submitted by me for the award of any other degree.


(PRADEEP KUMAR)

This is to certify that the above statement made by the candidate is correct to the best of my knowledge.


(DR. A.K. RAY)


(RAM KUMAR)

Dated: Jan.25, 1993

A C K N O W L E D G E M E N T

I am highly indebted to my guide Dr. A.K.Ray and Sri Ram Kumar for their sincere help and indispensable guidance to me throughout my dissertation work.

I am thankful to Prof. M.C.Bansal, for useful discussions and providing study providing study material related to the topic.

Sincere thanks are also due to Pulp Laboratory Staff, Institute of Paper Technology, Saharanpur for their cooperation and assistance rendered during my experimental work.

SAHARANPUR

DATED: January 25, 1993

- PRADEEP KUMAR

ABSTRACT

P. 11. 11. 11. 11.

The final stage of the recovery process is the causticization of green liquor from the smelt dissolve r of the furnace section to reclaim the alkali in a form ready for reuse in the cooking cycle. The efficiency of causticizing process does have an important bearing on the overall recovery process. Higher causticizing efficiency means that the circulation of inert chemicals in system is reduced which directly influences the economy and efficiency of the recovery process.

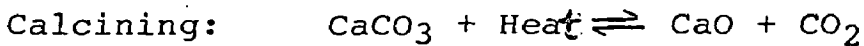
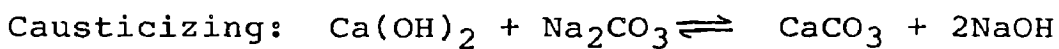
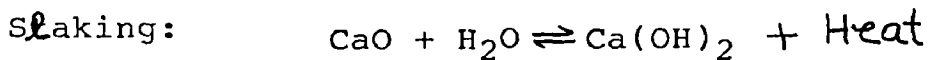
An attempt has been made in this work to study how the factors affect causticizing efficiency by preparing a model solution of approximately the same composition of Industrial Green Liquor from an integrated Pulp and Paper Industry.

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INTRODUCTION

Slaking, causticizing, and calcining form a closed loop process for converting the recovered green liquor (Na_2CO_3) into cooking or white liquor ($\text{NaOH} + \text{Na}_2\text{S}$). The major reactions are as follows:



Only the slaking and causticizing reactions are considered in this section. All sodium chemicals are expressed in terms of Na_2O .

The advantage of the Na_2O convention is that the TTA remains constant through the causticizing process. Causticizing then results in an increase in the active alkali content of the liquor. The advantage of basing the sulfidity on the TTA rather than the AA is that the sulfidity will remain constant through the causticizing process except for loss due to oxidation.

SLAKING:

The slaking reaction is the reaction of calcium oxide (reburned lime) and water to produce calcium hydroxide (slaked lime). Both the calcium oxide and calcium hydroxide are not very soluble in water, and behave as solid phases.

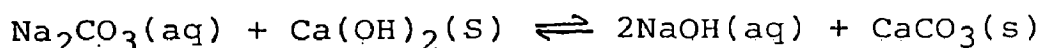
Slaking is an exothermic reaction. This heat of reaction is such that the stoichiometric addition of lime would raise the temperature of a typical green liquor about 1-5°C. The slaking reaction is retarded at low temperature and the recommended temperature for slaking is 90-100°C. If the slaking temperature is too low, unslaked lime particle will accumulate in the slaker. The slaking reaction is retarded in green liquor because of the development of a surface coating of carbonate.

carried out

When slaking with lime is carried out in hot green liquor, the most apparent changes occur during the first few minutes. The pellets begin to swell and may develop cracks from which steam may escape. Shortly after this, the pellets disintegrate into small particles. If this step does not occur, the unreacted pellets will fall to the bottom of the slaker and be removed with the grits. If the lime is not reactive enough, the exothermic slaking process will not proceed fast enough and the heating rate will not be sufficient to disintegrate the particle.

CAUSTICIZING:

The causticizing reaction begins in the slaker and is completed in the causticizers. The reaction can be written as:



Both the Na_2CO_3 and NaOH are in solution while $\text{Ca}(\text{OH})_2$ and CaCO_3 are of limited solubility and take part in the reaction essentially as solid phases. CaCO_3 is more insoluble than $\text{Ca}(\text{OH})_2$ and this is what drives the reaction to the right. The heat of reaction for the causticizing reaction itself is quite small. The temperature rise that occurs in slaking and causticizing is from the slaking reaction and not the causticizing reaction.

The causticizing reaction does not go to completion, but instead approaches equilibrium. This equilibrium can be described by the following equation:

$$K = \frac{[\text{OH}^-]^2}{[\text{CO}_3^{2-}]} = \frac{[\text{Ca}^{++}][\text{OH}^-]^2}{\text{Ca}^{++} \text{CO}_3^{2-}}$$

$$= \frac{K_{\text{Ca}(\text{OH})_2}}{K_{\text{CaCO}_3}} \quad (1)$$

where

$K_{\text{Ca}(\text{OH})_2}$ = solubility product of $\text{Ca}(\text{OH})_2$

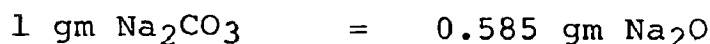
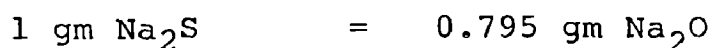
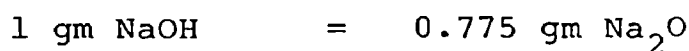
K_{CaCO_3} = solubility product of CaCO_3

The equilibrium constant, K , can be estimated from the solubilities of calcium hydroxide and calcium carbonate. At a temperature of 100°C , the solubility of calcium hydroxide in water is 10^{-2} g mol/l while the solubility of calcium carbonate is 2×10^{-4} g mol/l (2). The solubility

products for these two substances are then 4×10^{-6} and 4×10^{-8} , respectively. The value of the equilibrium constant is then of the order of 100. This means that equilibrium conversion efficiencies will tend to be of the order of 90%. The value of the equilibrium constant decreases with increasing sodium ion concentrations.

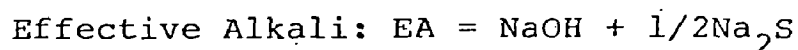
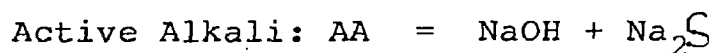
NOMENCLATURE:

The convention has developed of expressing alkali concentrations in white and green liquors in terms of the Na_2O equivalent. Thus,

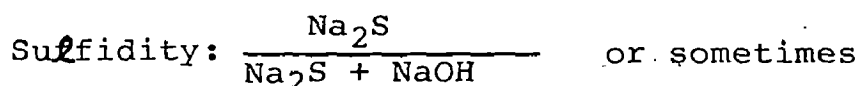
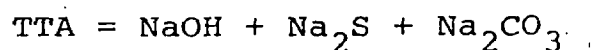


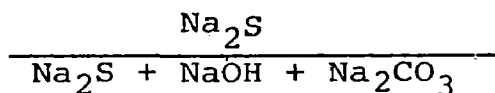
Concentrations are usually expressed in terms of g- $\text{Na}_2\text{O}/\text{l}$.

The following terms are frequently used, all expressed in terms of Na_2O .



Total Titratable Alkali:





Causticizing Efficiency: $\frac{\text{NaOH}}{\text{Na}_2\text{CO}_3 + \text{NaOH}}$

Conversion Efficiency:

$$\frac{\text{NaOH} - \text{NaOH}_{(\text{g.l.})}}{\text{Na}_2\text{CO}_3 + \text{NaOH} - \text{NaOH}_{(\text{g.l.})}}$$

Activity: $\frac{\text{NaOH} + \text{Na}_2\text{S}}{\text{TTA}}$

Causticity : $\frac{\text{NaOH}}{\text{TTA}}$

Causticizing the liquor results in an increase in the active alkali content of the liquor. The advantage of basing the sulfidity on the TTA rather than the AA is that the sulfidity will remain constant through^{out} the causticizing process except for loss due to oxidation.

LITERATURE SURVEY

Considerable early work has been published on causticization of sodium carbonate (1-20) Rydin and coworkers(21) studied the effect of lime quality on the equilibrium. Kojima⁽²⁰⁾ concluded that the equilibrium constant (K_e) calculated in concentration units which was the same for both carbonate solutions, with and without sodium sulfide. This equilibrium constant is calculated as:

$$K_e = \frac{[\text{OH}^-]^2}{[\text{CO}_3^{2-}]}$$

The units for (OH^-) and (CO_3^{2-}) are moles per liter of solution.

Lindberg and Ulmgren, (11) determined the effects of the major variables of concentration, composition, and temperature on the causticization equilibrium. The theoretical equilibrium constant for the reaction was expressed in terms of activity coefficients. The activity coefficients were assumed to be independent of the solution composition, provided the concentrations of inert cations Na and K. with opposite signs to the reactants OH^- and CO_3^{2-} , concentration. They concluded that the cation concentration was the parameter of greatest influence on the magnitude of the equilibrium constant and that temperature had little effect.

and Ulmgren were used to compare their data with the existing empirical equation.

The presence of hydrosulfide (HS) had no effect on the equilibrium constant but was shown to have a slight effect on the degree of causticizing as a result of the increase in the total cation concentration.

The values of equilibrium constant reported by Kobe and Williamson (19) and Dorris and Allen(23) studied equilibrium causticities as a function TTA. These equilibrium conversions are only obtained with large excess of lime and long reaction times. In the mill range of TTA concentrations the equilibrium causticity decreases by about 5 percent as the concentration is increased. Increase in sulfidity will decrease the causticity slightly, because the hydroxide produced by the hydrolysis of sodium sulfide suppresses the conversion of sodium carbonate.

Lindberg and Ulmgren (11) showed that the apparent equilibrium constant is a decreasing function of the total cation concentration which can be expressed as:

$$\log_{10} K_e = 2.95 - 0.62 \{ (\text{Na}^+) + (\text{K}^+) \}^{0.5}$$

Where $K_e = (\text{OH}^{-2}) / (\text{CO}_3^{--})$ and concentrations are in g-mol per lit.

The effect of temperature on the causticizing equilibrium constant is given by the Van't Hoff equation

$$\frac{d \ln K}{dT} = \frac{\Delta H}{RT^2}$$

Since the heat of reaction for causticizing is negligible the equilibrium would not be expected to be influenced by temperature. Kojo (20) studied the effect of temperature on the causticizing equilibrium and concluded that increasing the temperature tends to lower the equilibrium conversion efficiency slightly.

Jauhari . and Shiveshwar, R.M. (5) studied the effect of green liquor to lime ratio during slaking on the settling rate of Causticized slurry". They reported that green liquor to lime ratio during slaking is an important variable in determining the settling rate of the lime sludge. A ratio of 6:1 to 8:1 may be preferred. However it is advisable to determine the optimum ratio for the individual ^{mill} conditions to achieve the best results.

Ransdell and Genco (8) studied the effect of sodium sulfide on the equilibrium of the kraft causticizing reaction. They found that sulfidity has an effect on the equilibrium coefficients K_e . With sulfide ion added to green liquor, the reaction is somewhat suppressed, and the equilibrium coefficient K_e is lower. This less active reaction results in less carbonate ion being converted to the solid form and less hydroxyl ion being formed.

OBJECT OF STUDY

The work has been Planned on the following objectives:-

1. To study the effect of time of reaction on Causticizing efficiency.
2. To study the effect of green liquor temperature on causticizing efficiency.
3. To study the effect of quantity of lime on causticizing efficiency.
4. To study the effect of green liquor sulfidity on causticizing efficiency.
5. To study the effect of purity of lime on causticizing efficiency.
6. To study the effect of NaOH present in the green liquor on causticizing efficiency.
7. To study the effect of green liquor concentration on causticizing efficiency.
8. To study the effect of lime quantity on the settling rate of the lime mud solids.
9. To develop a kinetic model which can predict the effect of variables ^{S.no's} (1-7) on the causticizing efficiency.
10. To determine the order of the causticizing reaction.

EXPERIMENTAL PROCEDUREEXPERIMENTS:

The following experiments were carried out in the laboratory:

1. Kinetics of the causticizing reaction of 70 gpl Na_2CO_3 solution with four different stoichiometric amounts of lime (80 %, 90 %, 100 %, 110 %) was studied at four levels of temperature (50°C, 60°C, 70°C, 80°C).
2. Experiments were performed at sulfidity levels of 15 %, 20 %, 25 % with Na_2CO_3 : CaO = 1:1 g mole: g mole. Na_2CO_3 = 70 gpl at three levels of temperature (70°C, 80°C and 90°C). for the reaction kinetics.
3. Effect of time on causticizing efficiency was determined with 20% sulfidity, Na_2CO_3 :CaO = 1:1 g mole: g mole, MgO dosage (.5%, 1%, 1.5%) at 90°C temperature. The same experiment was also carried out for Na_2SiO_3 dosage of 1.5 %, 2 % and 2.5 %.
4. Reaction kinetics was studied for the Na_2CO_3 :CaO = 1:1 g mole: g mole. Na_2CO_3 = 70 gpl as Na_2O solution at a temperature 90°C with the three levels of NaOH dosage 5 gpl, 7.5 gpl, 10 gpl as Na_2O .
The same experiments were carried out for the 1% MgO and 1% Na_2SiO_3 dosage.
5. To study the effect of green liquor concentration nine solutions of different strengths (40, 50, 60, 70, 80, 90,

100, 110, 120 gpl as Na_2O TTA) were prepared. These solutions were than analysed (for $\text{Na}_2\text{CO}_3:\text{CaO} = 1:1$ g.mole: g.mole, $\text{NaOH} = 0$ at temperature 90°C) for two levels of sulfidity 0% and 20%.

6. Effect of lime dosage (90%, 100%, 110%) based on stoichiometric requirement) on the settling rate of the lime mud solids with $\text{Na}_2\text{CO}_3 = 70$ gpl as Na_2O solution, volume of slurry = 115 CC at temperature 20°C (room temperature) was studied.

PROCEDURE:

The water bath was maintained at a desired temperature. Lime (according to theoretical requirement) was taken in a 500 ml beaker and added 50 ml of water and the beaker was put into the water bath for slaking reaction for half an hour with constant agitation with the help of a glass rod. At the same time a solution of required amounts of Na_2CO_3 , Na_2S , NaOH , MgO , Na_2SiO_3 making the volume 200 ml in water was taken in another beaker. Maintaining the desired temperature the green liquor prepared was then poured into the beaker containing slaked lime, at this temperature the causticizing reaction was confined for a period of time with constant agitation with the help of a mechanical agitator. At different time periods a sample of the solution was taken out. The liquor obtained after the different causticizing reaction times was analysed by the following procedure:-

1. 5 ml of clear liquor was pipetted out and taken in a 200 ml. conical flask.
2. Then the solution was diluted with 30 ml of distilled water.
3. Now 20 ml of 20% BaCl_2 solution was added.
4. And Titration was done immediately with 0.5 NHCl using 8 drops of thymolphthalein as an indication. The consumption of acid was noted down as 'a' reading.
5. Now 5 ml of neutralized formaldehyde solution was added to the solution and kept for half minute.
6. Titrated upto a faint blue colour appear.
7. Added 8 drops of phenolphthalein for getting a sharp end point.
8. Titration was continued to the end point. The acid consumption was noted as 'b' reading.
9. Now 8 drops of Bromophenol-blue solution was added.
10. And completed the titration by running the burette. The acid consumption was noted as 'c' reading.

CALCULATIONS:

It has been assumed that the water evaporated during experiments is negligible.

(Based on TAPPI Standard method T6240S-68)

The causticizing efficiency and sulphidity has been calculated by the following formulae:

$$\text{Causticizing efficiency} = \frac{(\text{NaOH} - X) \times 100}{\text{NaOH} + \text{Na}_2\text{CO}_3}$$

where, X is the amount of NaOH already present in green liquor

$$\% \text{ sulphidity} = \frac{\text{Na}_2\text{S}}{\text{NaOH} + \text{Na}_2\text{S}} \times 100$$

All the chemicals expressed as Na_2O

From the acid consumption the contents of NaOH, Na_2S and Na_2CO_3 has been calculated as follows:

$$\text{NaOH} = 6.2(2a-b)n \text{ gpl as } \text{Na}_2\text{O}$$

$$\text{Na}_2\text{S} = 12.4(b-a)n \text{ gpl as } \text{Na}_2\text{O}$$

$$\text{Na}_2\text{CO}_3 = 6.2 (c-b)n \text{ gpl as } \text{Na}_2\text{O}$$

where, n is the strength of the HCl solution.

EXPERIMENTAL RESULTS AND DISCUSSION

Experimental results have been given in the tables (1-40) and figures (1-27). The following are the result of the experiments:

1. EFFECT OF TIME OF REACTION:

Fig. (1-4, 7-9, 14, 15, 19, 20) indicates that the causticizing efficiency increase with the increase of time and reaches to a state of equilibrium after a certain period. (20 to 30 minutes). It has been observed that total reaction time of about 30 minutes sufficient to achieve the maximum possible causticizing efficiency. A further increase in time there is no significant change in the causticizing efficiency as can be seen from the graph.

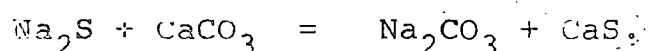
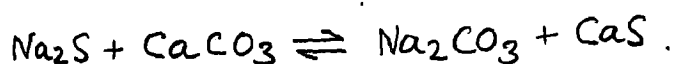
2. EFFECT OF TEMPERATURE:

Experimental results indicates that the causticizing efficiency increases with the increase of temperature. The slaking reaction is exothermic in nature but in case of causticizing reaction ΔH is nearly zero. Therefore temperature has greater influence of slaking reaction and proper slaking is the key to the success of causticizing operation. Slaking conditions govern the size of calcium hydroxide particles which in turn govern the size settling properties and filtering characteristics of calcium carbonate mud. For this reason the temperature should be kept as high as possible with due regard to safety. It has

been found that good slaking takes place if the temperature are above 90°C.

The best temperature for causticizing reaction has been found to be 95°C where the lime mud produced has good settling characteristics, at this temperature side reactions are suppressed below 90°C. There is always a possibility of formation of a double compound Na_2CO_3 , CaCO_3 , H_2O or $\text{Na}_2\text{CO}_3 \cdot 5\text{H}_2\text{O}$. These compounds are difficult to decomposed and they result in loss of soda and lime both. They also affect the settling characteristics of lime mud.

At temperature below 60°C, Na_2S may react with CaCO_3 to produce CaS .



This results in lower sulphidity and causticity.

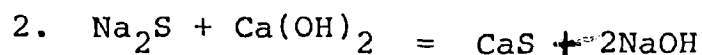
3. EFFECT OF LIME QUANTITY:

Figs. 1 to 4 indicate the effect of lime quantity on the causticizing reaction. It is observed that 5 to 10 percent of the excess lime over and above the stoichiometric requirement must be supplied for obtaining best result. Still higher quantities of lime do not increase the recausticizing efficiency rather they deteriorate the performance of the clarification equipment and causes:-

- a) Higher turbidities in the white liquor obtained.
- b) Lower filtration rate on the drum filter medium.
- c) Accelerating blinding of the filter medium.
- d) Washing of soda from the filter cake is impaired due to which alkali losses will increase.
- e) Cake moisture runs higher which again accounts for the alkali losses.

4. EFFECT OF SULFIDITY:

Figs. 7, 8 and 9 indicate the effect of sulfidity on the causticizing efficiency. It is clear that the causticizing efficiency decreases with the increase of sulfidity. In the sulphate process sodium sulphide present in green liquor does not come into reaction and hence does not require lime. This has an advantage over pure soda process as far as lime consumption for the total active alkali available for cooking the fibrous raw material is concerned. However, sodium sulphide present does not allow the reaction to proceed to completion as much as in the soda process due to the increase in hydroxyl ions by the hydration of sodium sulphide as per following equations:



The molar solubility of calcium sulphide is about six times than that of calcium hydroxide and therefore the second reaction is not likely to take place unless the

sulphide concentration is very high. In practice it has been found that extent to which the efficiency is lowered is more than that can be accounted by assuming complete hydrolysis of Na_2S .

5. EFFECT OF PURITY OF LIME:

The lime coming from the kiln may be containing many impurities depending upon the source of lime stone. Besides, the unburnt calcium carbonate, the other impurities may be silica, magnesia, alumina, iron oxides and other metallic oxides.

Figures 14, and 15 indicate the effect of present of MgO and Na_2SiO_3 in the Calcium oxide. It is clear that the causticizing efficiency decreases as the presence of MgO and sodium silicate increases during the causticizing reaction. It's also clear that the MgO decreases the causticizing efficiency more than the sodium silicate. For achieving highest recausticizing efficiency it is desirable that lime should contain maximum available CaO with minimum of the impurities. These impurities should be restricted to the limits as mentioned below:

Na_2SiO_3	2 % not more than
MgO	1% not more

6. EFFECT OF NaOH PRESENT IN THE GREEN LIQUOR:

Figs 19 and 20 indicate that the causticizing efficiency decreasing with the increasing amount of sodium hydroxide present in the green liquor.

7. EFFECT OF GREEN LIQUOR CONCENTRATION:

Fig. 24 represent the effect of green liquor concentration on the causticizing efficiency. It is clear that at constant green liquor sulfidity, the causticizing efficiency decreases with the increase of concentration of green liquor. It is also clear that for a given initial Sodium Carbonate concentration, the 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 . It was found that causticizing efficiency is higher when hydroxyl ion concentration in the green liquor is lower. In other words at low concentration of green liquor the causticizing efficiency are higher. But we can't lower the concentration of green liquor beyond certain limits because this would mean higher load on the black liquor evaporators. In the mills normally the green liquor concentration is around 100 gpl as Na_2O .

If the solubility product of calcium hydroxide is X and that of the calcium carbonate is Y the following equation can be formulated,

$$(\text{Ca})(\text{OH})_2 = X$$

$$(\text{Ca})(\text{CO}_3) = Y$$

At equilibrium, the concentration of Ca is the same in both the cases, consequently,

$$\frac{(\text{OH}^-)^2}{(\text{CO}_3^{--})} = \frac{X}{Y} = K$$

Accordingly

$$\frac{(\text{OH}^-)}{(\text{CO}_3^{--})} = \frac{K}{(\text{OH}^-)}$$

$$\text{or, } \frac{(\text{CO}_3^{--})}{(\text{OH}^-)} = \frac{(\text{OH}^-)}{K}$$

Accordingly

$$\text{or, } \frac{(\text{OH}^-) + (\text{CO}_3^{--})}{(\text{OH}^-)} = \frac{(\text{OH}^-) + K}{K}$$

$$\text{or, } \frac{(\text{OH}^-)}{(\text{OH}^-) + (\text{CO}_3^{--})} = \frac{K}{(\text{OH}^-) + K}$$

But evidently the fraction $(\text{OH}^-)/(\text{OH}^-) + (\text{CO}_3^{--})$ is nothing else than causticity. Consequently the causticity drops with increasing concentration of the hydroxyl ions or, may be more practically expressed with increasing concentration of the caustic soda.

This is of interest from two points of view. As the concentration of hydroxyl ions hinders the progress of the causticizing reaction from the point of view of demand for lime, it is uneconomical to drive the causticity of the white liquor higher than 82-85 %.

8. EFFECT OF LIME QUANTITY ON THE SETTLING RATE OF THE LIME MUD SOLIDS:

Fig. 25 is a typical plot of settled volume Vs Time. Its indicates that the excess lime dose given for the causticizing reaction decreases the settling rate of lime, mud solids.

9. MODEL: (as given on page 24)

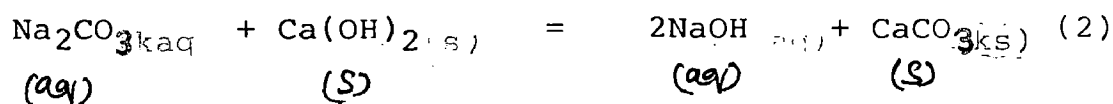
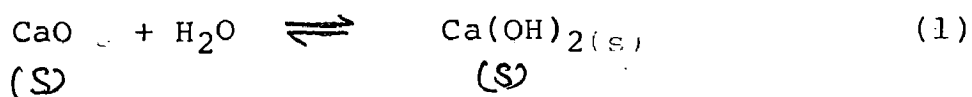
Equation No. 13 predicts the equilibrium behaviour of the causticizing reaction very near to the experimental results ^{is} which shown in the table 40.

KINETIC MODEL

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 would prevent the addition of excess lime and economize the operation of the causticizing plant.

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 quick lime. ^{As already indicated} the causticizing reaction proceeds in two stages, slaking and causticizing:



The slaking of CaO to calcium hydroxide is the first step in the causticizing process and is an exothermic reaction

($\Delta H = -65$ kJ/mole at 100°C): The causticizing reaction which follows the slaking reaction is slightly endothermic ($\Delta H=6\text{kJ}$ per 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 causticizing, if the overall rate of reaction is controlled by the causticizing reaction.

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

$$K = \frac{[a^2(\text{NaOH}) \cdot a(\text{CaCO}_3)]}{[a(\text{Na}_2\text{CO}_3) \cdot a(\text{Ca}(\text{OH})_2)]} \quad (3)$$

where

a = the activities of the respective species in the equilibrium mixture.

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

$$a_i = (\gamma_i C_i / f_i^\circ)$$

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 at moderately low pressures. In the reaction mixture, $\text{Ca}(\text{OH})_2$ 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:-

$$K = \frac{[\gamma^2(\text{NaOH}) [\text{NaOH}]^2]}{[\gamma(\text{Na}_2\text{CO}_3) [\text{Na}_2\text{CO}_3]]} \quad (4)$$

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:-

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

$$A = \frac{[\text{NaOH}]^2}{[\text{Na}_2\text{CO}_3]} \quad (6)$$

$$K' = \frac{[\text{NaOH}]^2}{[\text{Na}_2\text{CO}_3]} \quad (7)$$

At a given temperature, the value of 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 all equilibrium mixture.

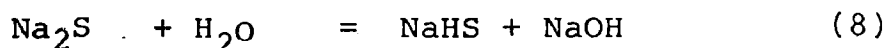
The presence of inert electrolytes (like sulfate, thiosulfate, chloride, and hydrosulfide) and their interactions have been studied by Lindberg and Ulmgren (11). They found that the presence of these inert anions had no appreciable effect on the value of K'. This absence of effect may be due to the fact that the hydroxide ion concentration in the equilibrium mixture is higher than that of all other anions. Therefore, the activity coefficients, $\gamma^2(\text{NaOH})$ and $\gamma(\text{Na}_2\text{CO}_3)$, may be assumed to be strongly dependent on the hydroxide ion concentration of the reaction mixture. Thus, if

$$A = f([\text{OH}^-])$$

then

$$K' = f([\text{OH}^-])$$

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



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

$$EA_0 = [\text{NaOH}]_0 + 1/2[\text{Na}_2\text{S}]_0 \quad (9)$$

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

$$E = ([\text{Na}_2\text{CO}_3]_0 - [\text{Na}_2\text{CO}_3]_e) / [\text{Na}_2\text{CO}_3]_0 \quad (10)$$

Therefore, the equilibrium concentration of NaOH becomes

$$\begin{aligned} [\text{NaOH}]_e &= [\text{Na}_2\text{CO}_3]_0 - [\text{Na}_2\text{CO}_3]_e + EA_0 \\ &= [\text{Na}_2\text{CO}_3]_0(E) + EA_0 \end{aligned} \quad (11)$$

The equilibrium concentration of Na_2CO_3 becomes

$$[\text{Na}_2\text{CO}_3]_e = [\text{Na}_2\text{CO}_3]_0(1-E) \quad (12)$$

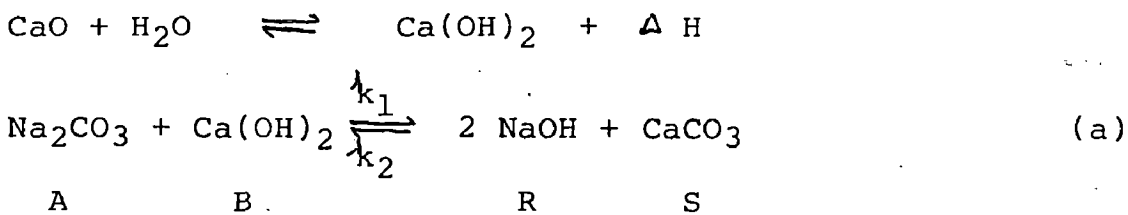
where both the initial concentration (subscript zero) and the equilibrium concentration are expressed in g/l, as Na_2O

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

$$K' = \frac{([\text{Na}_2\text{CO}_3]_0(E) + EA_0)^2}{[\text{Na}_2\text{CO}_3]_0(1-E)} \quad (13)$$

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.

ORDER OF THE CAUSTICIZING REACTION:



(i) If the reaction (a) is of first order than

$$\begin{aligned}
 \frac{dc_R}{dt} &= - \frac{dc_A}{dt} = C_{A0} \frac{dx_A}{dt} \\
 &= k_1 c_A - k_2 c_R \\
 &= k_1 (C_{A0} - C_{A0} x_A) - k_2 (C_{A0} M + C_{A0} x_A) \quad (14)
 \end{aligned}$$

Where $M = C_{RO}/C_{AO}$
 at equilibrium $\frac{dc_A}{dt} = 0$

Hence from eqn. (14) we find that

$$K_C = \frac{C_{Re}}{C_{Ae}} = \frac{M + X_{Ae}}{1 - X_{Ae}} = \frac{k_1}{k_2}$$

$$\text{Hence } \frac{dX_A}{dt} = \frac{k_1(M+1)}{M + X_{Ae}} (X_{Ae} - X_A) \quad (15)$$

Integrating eqn. (15)

We get

$$\begin{aligned}
 -\ln\left(1 - \frac{X_A}{X_{Ae}}\right) &= -\ln\frac{C_A - C_{Ae}}{C_{A0} - C_{Ae}} \\
 &= \frac{M+1}{M+X_{Ae}} k_1 t \quad (16)
 \end{aligned}$$

A plot of $-\ln\left(1 - \frac{X_A}{X_{Ae}}\right)$ Vs t should give a straight line.

where t is the reaction time and X_A is the conversion at time t and X_{Ae} is equilibrium conversion.

(ii) If the reaction (a) is of second order then with the restrictions that $C_{A0} = C_{B0}$ and $C_{R0} = C_{S0}$. The integrated rate equation is

$$\ln \frac{X_{Ae} - (2X_{Ae} - 1) X_A}{X_{Ae} - X_A} = 2k_1 \left(\frac{1}{X_{Ae}} - 1\right) C_{A0} t \quad (17)$$

A plot $-\ln\left(\frac{X_{Ae} - (2X_{Ae} - 1) X_A}{X_{Ae} - X_A}\right)$ Vs t should give a straight line

By knowing the slope of the curve we can find out the forward reaction rate $\overset{\text{Constant}}{k_1}$.

With this the back $\overset{\text{ward}}{}$ reaction rate $\overset{\text{constant}}{k_2}$ can be found out by the equation

$$k_2 = k_1/K \quad (18)$$

The value of K at any temperature can be determined with the help of following equation:

$$\frac{d \ln K}{dt} = \frac{\Delta H}{RT^2} \quad (19)$$

The value of equilibrium constant K at 100°C is 100 as already found out.

If the order of catalyzing reaction is known, then with the help of equation 18, and 19. the forward and backward reaction rates can be calculated.

DATA VALIDATION FOR MODEL

1. The experimental and predicted values of the causticizing efficiencies for different green liquor compositions are tabulated in Table 40. The predicted values were found to be within the range of experimental error.

2. The causticizing reaction has been tested for the order of the reaction $-\ln \left(1 - \frac{X_A}{X_{Ae}}\right)$ vs time t is plotted in the figure 26. The plot do not show the first order behaviour of the causticizing reaction as it is a curve against a straight line for the first order behaviour of the reaction. In Fig. 27 the test has been made for the second order behaviour. This is also a curve against a straight line for second order reaction. Hence causticizing reaction is a shifting order reaction.

CONCLUSION

The following conclusions have been made with the present study.

1. Causticizing efficiency increases with the increase in reaction time, and after a certain time it reaches to an equilibrium state.
2. With increase of green liquor temperature the causticizing efficiency increases. Best results are obtained at temperature ^{above} 90°C.
3. 5 to 10 per cent excess lime over and above the stoichiometric requirement results in maximum causticizing efficiency.
4. With the increase of sulfidity, causticizing efficiency decreases.
5. Causticizing efficiency decreases with the increase of impurities present in lime.
6. NaOH present in the green liquor decreases causticizing efficiency.
7. By increasing the green liquor concentration, causticizing efficiency decreases.
8. Increase lime quantity decreases the settling rate of the lime mud solid.

9. 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 per cent below the equilibrium condition. However, when too little lime is added, the white liquor is produced at a lower active alkali concentration ($\text{NaOH} + \text{Na}_2\text{S}$) than the target value. Conversely, if excess lime is added, poor settling and filtering conditions result because of the presence of unreacted $\text{Ca}(\text{OH})_2$.

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 feed forward 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.

FUTURE SCOPE OF THE STUDY

In the present study the order of the causticizing reaction and the forward and backward reaction rates could have not ~~be~~ obtained. The subsequent study to this work requires the determination of forward and backward reaction rates as well as the order of the causticizing reaction, so that the causticizing reaction can be controlled for the variation of different parameters during the causticization of green liquor.

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TABLE NO. 1

34

EFFECT OF TIME ON CAUSTICIZING EFFICIENCY WITH 80 % STOICHIOMETRIC
LIME DOSAGE TO 70 g/l Na_2CO_3 SOLUTION AT 50 °C.

TIME IN MINUTES	SET - I			SET - II			Average Causti- cizing Efficiency %
	NaOH as Na_2O g/l	Na_2CO_3 as Na_2O , g/l	Causti- cizing Efficiency E_1 %	NaOH as Na_2O g/l	Na_2CO_3 as Na_2O , g/l	Causti- cizing Efficiency E_1 %	
0	13.65	56.35	19.5	14.35	56.65	20.5	20.0
5	14.49	55.51	20.7	14.77	55.23	21.1	20.9
10	15.33	54.67	21.9	15.47	54.53	22.4	22.1
15	16.31	53.69	23.3	15.89	54.11	22.7	23.0
20	9.80	60.02	14.0	16.80	53.2	24.6	19.3
30	18.00	52.0	25.7	17.01	52.99	24.3	25.0
40	18.2	51.8	26.5	19.60	50.4	28.5	27.5
50	21	49	30.6	21	49	30.4	30.5

EFFECT OF TIME ON CAUSTICIZING EFFICIENCY WITH 80 % STOICHIOMETRIC LIME DOSAGE TO 70 g/l Na₂CO₃ SOLUTION AT 60 °C.

TIME IN MINUTES	SET - I			SET - II			Average Causticizing Efficiency %
	NaOH as Na ₂ O g/l	Na ₂ CO ₃ as Na ₂ O, g/l	Causticizing Efficiency E ₁ %	NaOH as Na ₂ O g/l	Na ₂ CO ₃ as Na ₂ O, g/l	Causticizing Efficiency E ₁ %	
0	14.07	55.93	20.1	14.35	55.65	20.5	20.3
5	16.59	53.41	23.7	17.01	52.99	24.3	24.0
10	20.23	49.707	28.9	21.77	48.23	31.1	30.0
15	20.65	49.35	29.5	21.49	48.51	30.7	30.1
20	29.96	40.04	42.8	31.64	38.35	45.2	44.0
30	31.43	38.57	44.9	31.57	38.47	45.1	45.0
40	32.97	37.03	47.1	32.83	37.17	46.9	47.0
50	38.01	31.99	54.3	37.59	32.43	53.7	54.0

TABLE NO.3

36

EFFECT OF TIME ON CAUSTICIZING EFFICIENCY WITH 80 % STOICHIOMETRIC LIME DOSAGE TO 70 g/l Na₂CO₃ SOLUTION AT 70 °C.

TIME IN MINUTES	SET - I			SET - II			Average Causti- cizing Efficiency %
	NaOH as Na ₂ O g/l	Na ₂ CO ₃ as Na ₂ O, g/l	Causti- cizing Efficiency E ₁ %	NaOH as Na ₂ O g/l	Na ₂ CO ₃ as Na ₂ O, g/l	Causti- cizing Efficiency E ₁ %	
0	14.49	55.51	20.7	14.77	55.23	21.1	20.9
5	17.99	52.01	25.7	17.01	52.9	24.3	25.0
10	21.84	48.16	31.2	22.54	47.46	32.2	31.7
15	25.69	44.31	36.7	25.13	44.87	35.9	36.3
20	27.58	42.42	39.4	27.16	42.84	38.8	39.1
30	37.66	32.34	53.8	38.08	31.92	54.4	54.1
40	42	28	60.0	42.28	27.72	60.4	60.2
50	42.14	27.86	60.2	42.14	27.86	60.2	60.2

TABLE NO.4

37

EFFECT OF TIME ON CAUSTICIZING EFFICIENCY WITH 80 % STOICHIOMETRIC LIME DOSAGE TO 70 g/l Na₂CO₃ SOLUTION AT 80°C.

TIME IN MINUTES	SET - I			SET - II			Average Causticizing Efficiency %
	NaOH as Na ₂ O g/l	Na ₂ CO ₃ as Na ₂ O, g/l	Causticizing Efficiency E ₁ %	NaOH as Na ₂ O g/l	Na ₂ CO ₃ as Na ₂ O, g/l	Causticizing Efficiency E ₁ %	
0	14.7	55.3	21.8	14.7	55.3	21.4	21.6
5	21.07	48.93	30.1	21.35	48.65	30.5	30.3
10	28.63	41.37	40.9	27.37	42.63	39.1	40.0
15	33.95	36.05	48.5	34.65	34.65	49.5	49.0
20	44.24	25.75	63.4	45.36	24.64	64.8	64.1
30	45.15	24.85	64.5	45.88	24.15	65.5	65.0
40	46.83	23.17	66.9	46.97	23.03	67.4	67.2
50	48.44	21.56	69.21	48.16	21.84	68.8	69.1

EFFECT OF TIME ON CAUSTICIZING EFFICIENCY WITH 90 % STOICHIOMETRIC LIME DOSAGE TO 70 g/l Na_2CO_3 SOLUTION AT 50 °C.

TIME IN MINUTES	SET - I			SET - II			Average Causti- cizing Efficiency %
	NaOH as Na_2O g/l	Na_2CO_3 as Na_2O , g/l	Causti- cizing Efficiency E_1 %	NaOH as Na_2O g/l	Na_2CO_3 as Na_2O , g/l	Causti- cizing Efficiency E_1 %	
0	14.14	55.86	20.2	14.42	55.58	20.6	20.4
5	15.05	54.95	21.5	14.63	55.37	20.9	21.2
10	15.26	54.74	21.8	15.82	54.18	22.6	22.2
15	16.1	53.9	23.0	16.1	53.9	23.0	23.0
20	16.8	53.2	24.0	11.34	58.66	10.2	20.1
30	20.23	49.77	28.9	22.91	48.09	31.3	30.1
40	21	49	30.0	22.4	47.6	32.0	31.0
50	25.2	44.8	36.0	27.3	42.7	39.0	37.5

TABLE NO. 6

39

EFFECT OF TIME ON CAUSTICIZING EFFICIENCY WITH 90% STOICHIOMETRIC LIME DOSAGE TO 70 g/l Na₂CO₃ SOLUTION AT 60°C.

TIME IN MINUTES	SET - I			SET - II			Average Causti- cizing Efficiency %
	NaOH as Na ₂ O g/l	Na ₂ CO ₃ as Na ₂ O, g/l	Causti- cizing Efficiency E ₁ %	NaOH as Na ₂ O g/l	Na ₂ CO ₃ as Na ₂ O, g/l	Causti- cizing Efficiency E ₁ %	
0	14.56	55.44	20.8	14.7	55.3	21.0	20.9
5	16.1	53.9	23.0	16.31	53.69	23.3	23.1
10	10.9	51.1	27.0	19.39	50.61	27.7	27.3
15	23.45	46.55	33.5	23.31	46.69	33.3	33.4
20	24.01	45.99	34.3	24.51	45.43	35.1	34.7
30	32.83	37.17	46.9	33.04	36.96	47.2	47.0
40	40.39	29.61	57.7	40.67	29.39	58.1	57.9
50	40.18	29.82	57.4	41.02	28.98	58.6	58

TABLE NO.7

40

EFFECT OF TIME ON CAUSTICIZING EFFICIENCY WITH 90 % STOICHIOMETRIC LIME DOSAGE TO 70 g/l Na₂CO₃ SOLUTION AT 70°C.

TIME IN MINUTES	SET - I			SET - II			Average Causticizing Efficiency %
	NaOH as Na ₂ O g/l	Na ₂ CO ₃ as Na ₂ O, g/l	Causticizing Efficiency E ₁ %	NaOH as Na ₂ O g/l	Na ₂ CO ₃ as Na ₂ O, g/l	Causticizing Efficiency E ₁ %	
0	15.4	54.6	22.0	15.54	54.46	22.2	22.1
5	17.57	52.43	25.1	18.97	51.03	27.1	26.1
10	25.13	44.87	35.9	26.53	43.47	37.9	36.9
15	30.1	39.9	43.0	30.8	39.2	44.0	43.5
20	32.41	37.59	46.3	32.06	37.94	45.8	46.1
30	42	28	60.0	42.14	27.86	60.2	60.1
40	42.69	27.51	60.7	42.77	27.23	61.1	60.9
50	48.09	21.91	68.7	47.18	22.82	67.4	68.1

TABLE NO. 8

41

EFFECT OF TIME ON CAUSTICIZING EFFICIENCY WITH 90% STOICHIOMETRIC LIME DOSAGE TO 70 g/l Na₂CO₃ SOLUTION AT 80 °C.

TIME IN MINUTES	SET - I			SET - II			Average Causticizing Efficiency %
	NaOH as Na ₂ O g/l	Na ₂ CO ₃ as Na ₂ O, g/l	Causticizing Efficiency E ₁ %	NaOH as Na ₂ O g/l	Na ₂ CO ₃ as Na ₂ O, g/l	Causticizing Efficiency E ₁ %	
0	15.47	54.53	22.1	15.47	54.53	22.1	22.1
5	23.1	46.9	33.0	23.24	46.76	33.2	33.1
10	28.77	41.23	41.1	29.33	40.67	41.9	41.5
15	39.62	30.38	56.6	40.6	29.4	58.0	57.3
20	44.38	25.62	63.4	44.52	25.48	63.6	63.5
30	46.2	23.8	66.0	47.04	22.6	67.2	66.6
40	56.54	19.46	72.2	50.96	19.04	72.8	72.5
50	51.45	18.55	73.5	51.87	18.13	74.1	73.8

TABLE NO.9

EFFECT OF TIME ON CAUSTICIZING EFFICIENCY WITH 100% STOICHIOMETRIC LIME DOSAGE TO 70 g/l Na₂CO₃ SOLUTION AT 50 °C.

TIME IN MINUTES	SET - I			SET - II			Average Causti- cizing Efficiency %
	NaOH as Na ₂ O g/l	Na ₂ CO ₃ as Na ₂ O, g/l	Causti- cizing Efficiency E ₁ %	NaOH as Na ₂ O g/l	Na ₂ CO ₃ as Na ₂ O, g/l	Causti- cizing Efficiency E ₁ %	
0	13.65	56.44	19.5	13.93	56.07	19.9	19.7
5	15.05	54.5	21.5	15.19	54.81	21.7	21.6
10	13.65	56.35	19.5	14.21	55.79	20.3	19.9
15	17.99	52.01	25.7	17.99	52.01	25.7	25.7
20	18.41	51.59	26.3	19.81	50.19	28.3	27.3
30	22.61	47.39	32.3	23.03	46.97	32.9	32.6
40	30.66	39.34	43.8	29.96	40.04	42.8	43.3
50	31.36	38.64	44.8	31.5	38.5	45.0	44.9

EFFECT OF TIME ON CAUSTICIZING EFFICIENCY WITH 100 % STOICHIOMETRIC LIME DOSAGE TO 70 g/l Na₂CO₃ SOLUTION AT 60°C.

TIME IN MINUTES	SET - I			SET - II			Average Causticizing Efficiency %
	NaOH as Na ₂ O g/l	Na ₂ CO ₃ as Na ₂ O, g/l	Causticizing Efficiency E ₁ %	NaOH as Na ₂ O g/l	Na ₂ CO ₃ as Na ₂ O, g/l	Causticizing Efficiency E ₁ %	
0	14.7	55.3	21.0	14.84	55.16	21.2	21.1
5	15.47	54.53	22.1	15.75	54.25	22.5	22.3
10	24.08	45.92	34.4	23.94	46.05	34.2	34.3
15	29.61	40.39	42.3	29.89	41.11	42.7	42.5
20	34.44	35.56	49.2	34.86	35.14	49.8	49.5
30	40.25	29.75	57.5	40.25	29.75	57.5	57.5
40	50.54	19.46	72.2	51.38	18.62	73.4	72.8
50	48.65	21.35	69.5	48.93	21.07	69.9	69.7

EFFECT OF TIME ON CAUSTICIZING EFFICIENCY WITH 100 % STOICHIOMETRIC LIME DOSAGE TO 70 g/l Na₂CO₃ SOLUTION AT 70 °C.

TIME IN MINUTES	SET - I			SET - II			Average Causticizing Efficiency %
	NaOH as Na ₂ O g/l	Na ₂ CO ₃ as Na ₂ O, g/l	Causticizing Efficiency E ₁ %	NaOH as Na ₂ O g/l ↔	Na ₂ CO ₃ as Na ₂ O, g/l	Causticizing Efficiency E ₁ %	
0	15.5	54.95	21.5	54.81	15.17	21.7	21.6
5	21.14	48.86	30.2	49	21.0	30.0	30.1
10	32.41	37.59	46.3	37.17	32.83	46.9	46.6
15	39.9	30.1	57.0	30.24	39.76	56.8	56.9
20	40.95	29.05	58.5	28.77	41.23	58.9	58.7
30	56.64	13.36	75.2	17.22	52.78	75.4	75.3
40	52.75	17.25	75.4	15.82	54.18	77.4	76.4
50	54.04	15.96	77.2	14.28	55.72	79.6	78.4

EFFECT OF TIME ON CAUSTICIZING EFFICIENCY WITH 100% STOICHIOMETRIC LIME DOSAGE TO 70 g/l Na₂CO₃ SOLUTION AT 80°C.

TIME IN MINUTES	SET - I			SET - II			Average Causticizing Efficiency %
	NaOH as Na ₂ O g/l	Na ₂ CO ₃ as Na ₂ O, g/l	Causticizing Efficiency E ₁ %	NaOH as Na ₂ O g/l	Na ₂ CO ₃ as Na ₂ O, g/l	Causticizing Efficiency E ₁ %	
0	15.47	54.53	22.1	15.75	54.25	22.5	22.3
5	35.7	34.3	51.0	36.12	33.88	51.6	51.3
10	51.92	18.08	74.2	52.67	17.33	75.2	74.7
15	56.0	14	80.0	56.56	13.44	80.8	80.4
20	57.47	12	82.1	58.03	11.97	82.9	82.5
30	58.1	12.53	83.0	58.1	11.9	83.0	83.0
40	60.02	9.8	86.0	60.34	9.63	86.2	86.1
50	60.2	9.8	86.0	61.18	8.82	87.4	86.7

EFFECT OF TIME ON CAUSTICIZING EFFICIENCY WITH 110 % STOICHIOMETRIC LIME DOSAGE TO 70 g/l Na₂CO₃ SOLUTION AT 50°C.

TIME IN MINUTES	SET - I			SET - II			Average Causti- cizing Efficiency %
	NaOH as Na ₂ O g/l	Na ₂ CO ₃ as Na ₂ O, g/l	Causti- cizing Efficiency E ₁ %	NaOH as Na ₂ O g/l	Na ₂ CO ₃ as Na ₂ O, g/l	Causti- cizing Efficiency E ₁ %	
0	13.37	56.63	19.1	13.93	56.07	19.9	19.5
5	16.59	53.49	23.7	17.15	52.25	24.5	24.1
10	20.3	49.7	29.0	20.72	49.28	29.6	29.3
15	24.78	45.22	35.4	25.34	44.66	36.2	35.8
20	25.2	44.8	36.0	25.2	44.8	36.0	36.0
30	35.84	34.16	51.2	36.26	33.74	51.8	51.5
40	37.17	32.83	53.1	37.24	32.76	53.2	53.1
50	39.97	30.03	57.1	40.11	29.89	57.3	57.2

TABLE NO. 14

47

EFFECT OF TIME ON CAUSTICIZING EFFICIENCY WITH 110 % STOICHIOMETRIC LIME DOSAGE TO 70 g/l Na₂CO₃ SOLUTION AT 60°C.

TIME IN MINUTES	SET - I			SET - II			Average Causticizing Efficiency %
	NaOH as Na ₂ O g/l	Na ₂ CO ₃ as Na ₂ O, g/l	Causticizing Efficiency E ₁ %	NaOH as Na ₂ O g/l	Na ₂ CO ₃ as Na ₂ O, g/l	Causticizing Efficiency E ₁ %	
0	14.07	55.3	20.1	14.91	55.09	21.3	20.7
5	18.9	51.1	27.0	19.04	50.6	27.2	27.1
10	25.62	44.38	36.6	26.04	43.96	37.2	36.9
15	30.87	39.13	44.1	31.15	38.85	44.5	44.3
20	33.6	33.4	48.0	34.16	35.84	48.8	48.4
30	47.6	22.4	68.0	48.44	21.56	69.2	68.6
40	50.05	19.95	71.5	49.77	20.23	71.1	71.3
50	34.6	15.4	78.0	54.6	15.4	78.0	78.0

TABLE NO.15

48

EFFECT OF TIME ON CAUSTICIZING EFFICIENCY WITH 110% STOICHIOMETRIC LIME DOSAGE TO 70 g/l Na₂CO₃ SOLUTION AT 70°C.

TIME IN MINUTES	SET - I			SET - II			Average, Causti- cizing Efficiency %
	NaOH as Na ₂ O g/l	Na ₂ CO ₃ as Na ₂ O, g/l	Causti- cizing Efficiency E ₁ %	NaOH as Na ₂ O g/l	Na ₂ CO ₃ as Na ₂ O, g/l	Causti- cizing Efficiency E ₁ %	
0	15.4	54.6	22.0	16.38	53.62	23.4	22.7
5	23.1	46.9	33.0	23.94	46.6	34.2	33.6
10	32.83	37.17	46.9	31.85	38.15	45.5	46.2
15	38.78	31.22	55.4	39.2	30.8	56.0	55.7
20	44.38	22.52	63.4	44.94	22.6	64.2	63.8
30	56.0	14	80.0	56.14	13.86	80.2	80.1
40	56.0	14	80.0	56.0	14	80.0	80.0
50	56.0	14	80.0	56.14	13.86	80.2	80.1

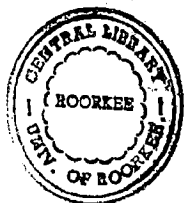
EFFECT OF TIME ON CAUSTICIZING EFFICIENCY WITH 110 % STOICHIOMETRIC LIME DOSAGE TO 70 g/l Na_2CO_3 SOLUTION AT 80 °C.

TIME IN MINUTES	SET - I			SET - II			Average Causti- cizing Efficiency %
	NaOH as Na_2O g/l	Na_2CO_3 as Na_2O , g/l	Causti- cizing Efficiency E_1 %	NaOH as Na_2O g/l	Na_2CO_3 as Na_2O , g/l	Causti- cizing Efficiency E_1 %	
0	15.47	54.53	22.1	16.31	53.69	23.3	22.7
5	35.7	34.3	51.0	36.4	33.6	52.0	51.5
10	49.0	21	70.0	49.0		70.0	70.0
15	55.79	14.21	79.7	55.93	14.7	79.9	79.8
20	54.6	15.4	78.0	54.74	15.26	78.2	78.1
30	63.98	6.02	91.4	64.26	5.74	91.8	91.6
40	63.14	6.86	90.2	62.86	7.14	89.8	90.0
50	63.07	6.93	90.1	63.49	6.51	90.7	90.4

TABLE NO.17

EFFECT OF TIME ON CAUSTICIZING EFFICIENCY WITH 15% SULPHIDITY,
 $\text{Na}_2\text{CO}_3 : \text{CaO} = 1:1$ g moles Na_2O , Na_2CO_3 70 g/l as Na_2O at 70°C .

TIME IN MINUTES	SET - I			SET - II			Average Causti- cizing Efficiency %
	NaOH as Na_2O g/l	Na_2CO_3 as Na_2O , g/l	Causti- cizing Efficiency E_1 %	NaOH as Na_2O g/l	Na_2CO_3 as Na_2O , g/l	Causti- cizing Efficiency E_1 %	
0	14.42	55.58	20.6	14.84	55.16	21.2	20.9
5	18.96	54.04	22.8	16.38	53.62	23.4	23.1
10	21	49	30.0	21.56	48.44	30.8	30.4
15	23.45	46.55	33.5	23.73	46.27	33.9	33.7
20	27.23	42.77	38.9	27.79	42.21	39.7	39.3
30	37.45	32.55	53.5	37.87	32.13	54.1	53.8
40	48.72	21.28	69.6	49.28	20.72	70.4	70.0
50	48.93	21.07	69.9	49.21	20.79	70.3	70.1



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TABLE NO. 18

EFFECT OF TIME IN CAUSTICIZING EFFICIENCY WITH 15% SULPHIDITY,

Na_2CO_3 : $\text{CaO} = 1.1$ g moles Na_2O , Na_2CO_3 70 Spl as Na_2O at 80°C

TIME IN MINUTES	SET - I			SET - II			Average Causti- cizing Efficiency %
	NaOH as Na_2O g/l	Na_2CO_3 as Na_2O , g/l	Causti- cizing Efficiency E_1 %	NaOH as Na_2O g/l	Na_2CO_3 as Na_2O , g/l	Causti- cizing Efficiency E_1 %	
0	18.76	51.24	26.8	19.18	50.82	27.4	27.1
5	23.66	46.34	33.8	24.36	45.64	34.8	34.3
10	27.44	42.56	39.2	27.72	42.28	39.6	39.4
15	35.49	34.51	56.7	36.19	33.81	51.7	51.2
20	45.85	24.15	65.5	46.13	23.87	65.9	65.7
30	54.81	15.19	78.3	54.53	15.47	77.9	78.1
40	54.95	15.05	78.5	54.32	15.68	77.6	78.1
50	57.47	12.53	82.01	57.75	12.25	82.5	82.3

TABLE NO. 19

EFFECT OF TIME IN CAUSTICIZING EFFICIENCY WITH 15% SULPHIDITY,

Na₂CO₃: Cao = 1.1 g moles Na₂O, Na₂CO₃ 70 g/l as Na₂O at 90°C

TIME IN MINUTES	SET - I			SET - II			Average Causti- cizing Efficiency %
	NaOH as Na ₂ O g/l	Na ₂ CO ₃ as Na ₂ O, g/l	Causti- cizing Efficiency E ₁ %	NaOH as Na ₂ O g/l	Na ₂ CO ₃ as Na ₂ O, g/l	Causti- cizing Efficiency E ₁ %	
0	22.12	47.88	31.6	21.7	48.3	31.0	31.3
5	32.27	37.73	46.1	32.41	37.59	46.3	46.2
10	50.75	19.25	72.5	51.03	18.97	72.9	72.7
15	56.7	13.3	81.0	57.12	12.88	81.6	81.3
20	61.67	8.33	88.1	62.23	7.77	88.9	88.5
30	60.62	9.38	86.6	61.04	8.96	87.2	86.9
40	62.09	7.91	88.7	62.37	7.63	89.1	88.9
50	62.3	7.7	89.0	62.86	7.14	89.8	89.4

TABLE NO. 20

53

EFFECT OF TIME ON CAUSTICITY EFFICIENCY WITH 20% SULPHITITY,

Na₂CO₃: CaO = 1:1 g moles, Na₂O, Na₂CO₃ 70 gpl as Na₂O at 70°C

TIME IN MINUTES	SET - I			SET - II			Average Causti- cizing Efficiency %
	NaOH as Na ₂ O g/l	Na ₂ CO ₃ as Na ₂ O, g/l	Causti- cizing Efficiency E ₁ %	NaOH as Na ₂ O g/l	Na ₂ CO ₃ as Na ₂ O, g/l	Causti- cizing Efficiency E ₁ %	
0	13.79	56.21	19.7	14.35	55.65	20.5	20.1
5	16.94	53.06	24.2	17.22	52.78	24.6	24.4
10	20.86	49.14	29.8	21.56	48.44	30.8	30.3
15	27.37	42.63	39.1	27.09	42.91	38.7	38.9
20	30.24	39.76	43.2	30.66	39.34	43.8	43.5
30	35.63	34.37	50.9	36.05	33.95	51.5	51.2
40	48.02	21.98	68.6	48.44	21.56	69.2	68.9
50	47.95	22.05	68.5	48.65	21.35	69.5	69.0

TABLE NO. 21

EFFECT OF TIME ON CAUSTICITY EFFICIENCY WITH 20% SULPHIDITY,

Na₂CO₃; CaO = 1:1 g moles Na₂O, Na₂CO₃ 70 gpl as Na₂O at 80°C

TIME IN MINUTES	SET - I			SET - II			Average Causticizing Efficiency %
	NaOH as Na ₂ O g/l	Na ₂ CO ₃ as Na ₂ O, g/l	Causticizing Efficiency E ₁ %	NaOH as Na ₂ O g/l	Na ₂ CO ₃ as Na ₂ O, g/l	Causticizing Efficiency E ₁ %	
0	17.01	52.99	24.3	17.43	52.57	24.9	24.6
5	23.24	46.76	33.2	23.1	46.9	33	33.1
10	34.16	35.84	46.8	33.32	36.68	47.6	47.2
15	39.9	30.1	57.0	40.32	29.68	57.6	57.3
20	47.74	22.26	68.2	48.16	21.84	68.8	68.5
30	54.04	15.96	77.2	54.32	15.68	77.6	77.4
40	56.14	13.86	80.2	56.84	13.16	81.2	80.7
50	54.91	15.09	78.5	55.37	14.63	79.1	78.8

TABLE NO.22

EFFECT OF TIME ON CAUSTICITY EFFICIENCY WITH 20% SULPHIDITY,

Na_2CO_3 : CaO = 1:1 g moles Na_2O , Na_2CO_3 70 gpl as Na_2O at 90°C

TIME IN MINUTES	SET - I			SET - II			Average Causticizing Efficiency %
	NaOH as Na_2O g/l	Na_2CO_3 as Na_2O , g/l	Causticizing Efficiency E_1 %	NaOH as Na_2O g/l	Na_2CO_3 as Na_2O , g/l	Causticizing Efficiency E_1 %	
0	21.14	48.86	30.2	22.12	17.88	31.6	30.9
5	30.38	39.62	43.4	30.8	39.2	44.0	43.7
10	47.95	22.05	68.5	48.37	21.63	69.1	68.8
15	55.65	14.35	79.5	55.37	14.63	79.1	79.3
20	58.94	11.06	84.2	59.15	16.85	84.6	84.4
30	59.92	10.08	85.6	57.33	12.67	81.4	83.5
40	60.13	9.87	85.9	59.85	10.15	85.5	85.7
50	60.13	9.87	85.9	60.34	96.6	86.2	86.1

TABLE NO. 23

56

EFFECT OF TIME ON CAUSTICITY EFFICIENCY WITH 25% SULPHIDITYNa₂CO₃ : CaO = 1:1 g moles Na₂O, Na₂CO₃ 70 gpl as Na₂O at 90°C

TIME IN MINUTES	SET - I			SET - II			Average Causti- cizing Efficiency %
	NaOH as Na ₂ O g/l	Na ₂ CO ₃ as Na ₂ O, g/l	Causti- cizing Efficiency E ₁ %	NaOH as Na ₂ O g/l	Na ₂ CO ₃ as Na ₂ O, g/l	Causti- cizing Efficiency E ₁ %	
0	18.9	51.1	27.0	19.46	50.54	27.8	27.4
5	26.95	43.05	38.5	26.53	43.47	37.9	38.2
10	46.11	29.88	57.3	39.55	30.45	56.5	56.9
15	47.46	22.54	67.8	48.02	21.98	68.6	68.2
20	58.51	14.43	79.3	55.93	14.07	79.9	79.6
30	56.07	13.93	80.1	56.63	13.37	80.9	80.5
40	56.28	13.72	80.4	56.84	13.16	81.2	80.9
50	56.84	13.16	81.2	53.62	16.38	76.6	78.9

TABLE NO. 24

EFFECT OF TIME ON CAUSTICITY EFFICIENCY WITH 25% SULPHIDITY,

$\text{Na}_2\text{CO}_3 : \text{CaO} = 1:1$ g moles Na_2O , Na_2CO_3 70 gpl as Na O at 80°C

TIME IN MINUTES	SET - I			SET - II			Average Causti- cizing Efficiency %
	NaOH as Na_2O g/l	Na_2CO_3 as Na_2O , g/l	Causti- cizing Efficiency E_1 %	NaOH as Na_2O g/l	Na_2CO_3 as Na_2O , g/l	Causti- cizing Efficiency E_1 %	
0	17.22	52.78	24.6	16.8	53.2	24.0	24.3
5	21.98	48.02	31.4	21.84	48.16	31.2	31.3
10	25.83	44.17	36.9	25.69	44.31	36.7	36.8
15	30.24	39.76	43.2	30.66	39.34	43.8	43.5
20	37.94	32.06	54.2	38.64	31.36	55.2	54.7
30	47.53	22.47	67.9	48.09	21.91	68.7	68.3
40	48.02	21.98	68.6	48.58	21.42	69.4	69.0
50	48.65	21.35	69.5	49.49	20.51	70.7	70.1

EFFECT OF TIME ON CAUSTICITY EFFICIENCY WITH 25% SULPHIDITY,
 $\text{Na}_2\text{CO}_3:\text{CaO} = 1:1$ g moles Na_2O , Na_2CO_3 70 gpl as Na_2O at 70°C

TIME IN MINUTES	SET - I			SET - II			Average Causti- cizing Efficiency %
	NaOH as Na_2O g/l	Na_2CO_3 as Na_2O , g/l	Causti- cizing Efficiency E_1 %	NaOH as Na_2O g/l	Na_2CO_3 as Na_2O , g/l	Causti- cizing Efficiency E_1 %	
0	12.81	57.19	18.3	13.23	56.77	18.9	18.6
5	16.73	53.27	23.9	16.17	53.83	23.1	23.5
10	20.37	49.63	29.1	21.56	48.44	30.8	29.9
15	22.05	47.95	31.5	22.89	47.11	32.7	32.1
20	24.15	45.85	34.5	23.87	46.13	34.1	34.3
30	32.83	37.17	46.9	33.11	36.89	47.3	47.1
40	36.28	33.74	51.8	36.96	33.04	52.8	52.3
50	43.89	26.11	62.7	42.91	27.09	61.3	62.0

TABLE NO. 26

59

EFFECT OF TIME ON CAUSTICIZING EFFICIENCY WITH 20% SULPHIDITY,
 Na_2CO_3 : CaO = 1:1 g-mole as Na_2O , Mgo dosage = .5% at temp. 90°C

TIME IN MINUTES	SET - I			SET - II			Average Causti- cizing Efficiency %
	NaOH as Na_2O g/l	Na_2CO_3 as Na_2O , g/l	Causti- cizing Efficiency E_1 %	NaOH as Na_2O g/l	Na_2CO_3 as Na_2O , g/l	Causti- cizing Efficiency E_1 %	
0	20.86	49.14	29.8	21.28	48.72	30.4	30.1
5	25.9	44.1	37.0	26.18	43.82	37.4	37.2
10	32.62	37.38	46.6	33.04	36.96	47.2	46.9
15	41.65	28.35	59.5	42.35	27.65	60.5	60.0
20	46.41	23.59	66.3	46.55	23.45	66.5	66.4
30	52.15	17.85	74.5	52.71	17.29	75.3	74.9
40	55.65	14.35	79.5	56.07	13.93	80.1	79.8
50	57.33	12.67	81.9	56.91	13.09	81.3	81.6

TABLE NO. 27

EFFECT OF TIME ON CAUSTICIZING EFFICIENCY WITH 20% SULPHIDITY,

Na_2CO_3 : CaO = 1.1 g mole as Na_2O , Mgo dosage = 1% at temp. 90°C

TIME IN MINUTES	SET - I			SET - II			Average Causti- cizing Efficiency %
	NaOH as Na_2O g/l	Na_2CO_3 as Na_2O , g/l	Causti- cizing Efficiency E_1 %	NaOH as Na_2O g/l	Na_2CO_3 as Na_2O , g/l	Causti- cizing Efficiency E_1 %	
0	19.67	56.33	28.1	19.95	50.05	28.5	28.3
5	23.17	46.83	33.1	23.73	46.27	33.9	33.5
10	28.21	41.79	40.3	28.63	41.37	40.9	40.6
15	37.24	32.76	53.2	37.52	32.48	63.6	53.4
20	43.12	26.88	61.6	42.56	27.44	60.8	61.2
30	50.4	19.6	72.6	50.54	19.46	72.2	72.1
40	53.13	16.87	75.9	52.85	17.15	75.5	75.7
50	54.32	15.68	77.6	54.74	15.26	78.2	77.9

TABLE NO. 28

EFFECT OF TIME ON CAUSTICIZING EFFICIENCY WITH 20% SULPHIDITY,

Na₂CO₃: CaO = 1.1 g. mole as Na₂CO₃ Mgo dosage = 1.5% at temp. 90°C

TIME IN MINUTES	SET - I			SET - II			Average Causti- cizing Efficiency %
	NaOH as Na ₂ O g/l	Na ₂ CO ₃ as Na ₂ O, g/l	Causti- cizing Efficiency E ₁ %	NaOH as Na ₂ O g/l	Na ₂ CO ₃ as Na ₂ O, g/l	Causti- cizing Efficiency E ₁ %	
0	18.41	51.59	26.3	19.25	56.75	27.5	26.9
5	20.86	49.14	29.8	21.14	48.86	30.2	30.0
10	25.55	44.45	36.5	25.69	44.31	36.7	36.6
15	33.25	36.75	47.5	33.67	36.33	48.1	47.8
20	39.48	30.52	56.4	40.18	29.82	57.4	56.9
30	47.32	22.68	67.6	47.04	22.96	67.2	67.4
40	51.1	18.9	73.0	51.24	18.76	73.2	73.1
50	50.4	19.6	72.0	50.68	19.32	72.4	72.2

TABLE NO. 29

EFFECT OF TIME ON CAUSTIZING EFFICIENCY WITH 20% SULPHIDITY,

Na₂CO₃:CaO=1.1 g mole as Na₂O, Na₂SiO₃ dosage = 1.5% at temp. 90°C

TIME IN MINUTES	SET - I			SET - II			Average Causti- cizing Efficiency %
	NaOH as Na ₂ O g/l	Na ₂ CO ₃ as Na ₂ O, g/l	Causti- cizing Efficiency E ₁ %	NaOH as Na ₂ O g/l	Na ₂ CO ₃ as Na ₂ O, g/l	Causti- cizing Efficiency E ₁ %	
0	21.14	48.86	30.2	21.7	48.3	31	30.6
5	28.49	41.51	40.7	28.63	41.37	40.9	40.8
10	37.38	32.62	53.4	37.8	32.2	54	53.7
15	41.3	28.7	59.0	41.86	28.14	59.8	59.4
20	44.94	25.06	64.2	45.5	24.5	65	64.6
30	54.39	15.61	77.7	54.53	15.47	77.9	77.8
40	54.95	15.05	78.5	54.39	15.61	77.7	78.1
50	54.39	15.61	77.7	54.81	15.19	78.3	78.0

TABLE NO. 30

EFFECT ON TIME ON CAUSTIZING EFFICIENCY WITH 20% SULPHIDITY,

 $\text{Na}_2\text{CO}_3:\text{CaO}=1.1$ g mole as Na_2O , Na_2SO_3 dosage = 2% at temp. 90°C

TIME IN MINUTES	SET - I			SET - II			Average Causti- cizing Efficiency %
	NaOH as Na_2O g/l	Na_2CO_3 as Na_2O , g/l	Causti- cizing Efficiency E_1 %	NaOH as Na_2O g/l	Na_2CO_3 as Na_2O , g/l	Causti- cizing Efficiency E_1 %	
0	18.83	51.17	26.9	18.69	51.31	26.7	26.8
5	24.99	45.61	35.7	25.13	44.87	35.9	35.8
10	32.76	37.24	46.8	32.34	37.66	46.2	46.5
15	35.42	34.88	50.6	35.84	34.16	51.2	50.9
20	40.32	29.68	57.6	40.88	29.12	58.4	58.0
30	49.35	20.65	70.5	48.79	21.21	69.7	70.1
40	51.87	18.13	74.1	52.01	17.99	74.3	74.2
50	52.57	7.43	75.1	52.85	17.15	75.5	75.3

TABLE NO.31

EFFECT OF TIME ON CAUSTICING EFFICIENCY WITH 20% SULPHIDICITY,

Na₂CO₃ :CaO=1:1 g mole as Na₂O, Na₂SO₃ dosage = 2.5% at temp. 90^o2C

TIME IN MINUTES	SET - I			SET - II			Average Causti- cizing Efficiency %
	NaOH as Na ₂ O g/l	Na ₂ CO ₃ as Na ₂ O, g/l	Causti- cizing Efficiency E ₁ %	NaOH as Na ₂ O g/l	Na ₂ CO ₃ as Na ₂ O, g/l	Causti- cizing Efficiency E ₁ %	
0	15.47	54.53	22.1	15.61	54.39	22.3	22.2
5	19.25	50.75	27.0	18.97	51.03	27.1	27.3
10	26.6	43.4	38	26.74	43.26	38.2	38.1
15	30.87	39.13	44.1	31.43	38.57	44.9	44.5
20	38.22	31.78	54.6	38.78	31.22	55.4	55.0
30	46.39	23.66	66.2	46.9	23.1	67	66.6
40	49.14	20.86	70.2	49.42	20.58	70.6	70.4
50	49.21	20.79	70.3	48.79	21.21	69.7	70.0

TABLE NO.32

EFFECT OF TIME ON CAUSTICIZING EFFICIENCY WITH SULPHIDITY 20%,

Na₂CO₃ = 1:1 g ple a, Na₂CO₃ = 70 g ple, NaOH dosage = 5 g ple,
 at temp. = 90°C

TIME IN MINUTES	SET - I			SET - II			Average Causti- cizing Efficiency %
	NaOH as Na ₂ O g/l	Na ₂ CO ₃ as Na ₂ O, g/l	Causti- cizing Efficiency E ₁ %	NaOH as Na ₂ O g/l	Na ₂ CO ₃ as Na ₂ O, g/l	Causti- cizing Efficiency E ₁ %	
0	22.35	52.65	29.8	22.05	52.95	29.4	29.6
5	27.83	47.17	37.1	28.13	46.87	37.5	37.3
10	36.08	38.92	48.1	36.3	38.7	48.7	48.4
15	42.75	32.25	57	42.9	32.1	57.2	57.1
20	52.13	22.87	69.5	51.37	23.63	68.5	69.6
30	57.83	17.17	77.1	58.13	16.87	77.5	77.3
40	61.95	13.05	82.6	61.5	13.5	82.0	82.3
50	62.63	12.37	83.5	58.13	16.87	77.5	80.5

TABLE NO.33

EFFECT OF TIME ON CAUSTICIZING EFFICIENCY WITH SULPHIDITY 20%

$\text{Na}_2\text{CO}_3 = 1:1$ g mole as Na_2O $\text{Na}_2\text{CO}_3=70$ g ple, NaOH dosage = 7.5 g ple
at temp. = 90°C .

TIME IN MINUTES	SET - I			SET - II			Average Causti- cizing Efficiency %
	NaOH as Na_2O g/l	Na_2CO_3 as Na_2O , g/l	Causti- cizing Efficiency E_1 %	NaOH as Na_2O g/l	Na_2CO_3 as Na_2O , g/l	Causti- cizing Efficiency E_1 %	
0	21.39	56.11	27.6	21.85	55.64	28.2	27.9
5	26.42	51.07	34.1	26.89	50.60	34.7	34.4
10	32.47	45.02	41.9	32.16	45.34	41.5	41.7
15	41.77	35.72	53.9	41.62	35.88	53.7	53.8
20	49.6	27.9	64.0	49.91	27.59	64.4	64.2
30	57.35	20.15	74.0	57.82	19.68	74.6	74.3
40	59.21	18.29	76.4	59.52	17.98	76.8	76.6
50	59.90	17.59	77.3	59.59	17.90	76.9	77.1

TABLE NO.34

EFFECT OF TIME ON CAUSTICIZING EFFICIENCY WITH SULPHDTY 20%,

$\text{Na}_2\text{CO}_3 = 1:1$ as Na_2O , $\text{Na}_2\text{CO}_3 = 70$ g ple, NaOH dosage 10 g ple,
at temp. 90°C

TIME IN MINUTES	SET - I			SET - II			Average Causti- cizing Efficiency %
	NaOH as Na_2O g/l	Na_2CO_3 as Na_2O , g/l	Causti- cizing Efficiency E_1 %	NaOH as Na_2O g/l	Na_2CO_3 as Na_2O , g/l	Causti- cizing Efficiency E_1 %	
0	21.12	58.88	26.4	20.8	59.2	26.0	26.2
5	24.24	55.76	30.3	23.92	56.08	29.9	30.1
10	29.28	50.72	36.6	29.76	50.24	37.2	36.9
15	37.12	423.88	46.4	37.44	42.56	46.8	46.0
20	45.84	34.16	57.3	45.52	34.48	56.9	57.1
30	56.4	23.6	70.5	56.88	23.12	71.1	70.8
40	58.24	21.76	72.8	57.76	22.24	72.2	72.5
50	58.88	21.12	73.6	55.52	24.48	69.4	71.5

TABLE NO.35

EFFECT OF TIME ON CAUSTICIZING EFFICIENCY WITH 20% SULPHIDITY,
 Na_2CO_3 : CaO = 1:1 as $\text{Na}_2\text{CO}_3 = 70$ g pl $\&$,

MgO dosage = 1%, Na_2SiO_3 dosage = 1%, NaOH dosage = 5 g pl $\&$ at temp 90°C

TIME IN MINUTES	SET - I			SET - II			Average Causti- cizing Efficiency %
	NaOH as Na_2O g/l	Na_2CO_3 as Na_2O , g/l	Causti- cizing Efficiency E_1 %	NaOH as Na_2O g/l	Na_2CO_3 as Na_2O , g/l	Causti- cizing Efficiency E_1 %	
0	20.62	54.37	27.5	20.17	54.83	26.9	27.2
5	27.37	47.63	36.5	27.97	47.03	37.3	36.9
10	34.13	40.87	45.5	34.57	40.43	46.1	45.8
15	49.12	25.88	65.5	48.67	26.33	64.9	65.2
20	53.85	21.15	71.8	53.4	21.6	71.2	71.5
30	58.27	16.73	77.7	58.57	16.43	78.1	77.9
40	58.57	16.43	78.1	56.93	18.07	75.9	77.0
50	58.13	16.87	77.5	57.53	17.47	76.7	77.1

EFFECT OF TIME ON CAUSTICIZING EFFICIENCY WITH 20% SULPHIDITY,

Na₂CO₃ : CaO = 1:1 mole as Na₂O. Na₂CO₃ = 70 g/lMgO dosage = 1%, Na₂SiO₃ dosage = 1 %, NaOH dosage 7.5 g/l at temp.90°C

TIME IN MINUTES	SET - I			SET - II			Average Causti- cizing Efficiency %
	NaOH as Na ₂ O g/l	Na ₂ CO ₃ as Na ₂ O, g/l	Causti- cizing Efficiency E ₁ %	NaOH as Na ₂ O g/l	Na ₂ CO ₃ as Na ₂ O, g/l	Causti- cizing Efficiency E ₁ %	
0	19.68	57.82	25.4	19.84	57.66	25.6	25.5
5	25.96	51.54	33.5	25.49	52.01	32.9	33.2
10	33.55	43.94	43.3	33.86	43.64	43.7	43.5
15	45.42	32.08	58.6	45.10	32.40	58.2	58.4
20	51.84	25.66	66.9	51.38	26.12	66.3	66.6
30	57.89	19.61	74.7	58.20	19.30	75.1	74.9
40	58.44	19.06	75.4	57.82	19.68	74.6	75.0
50	57.58	19.92	74.3	57.89	19.61	74.7	74.5

TABLE NO.37

EFFECT OF TIME ON CAUSTICIZING EFFICIENCY WITH 20% SULPHIDITY,

Na₂CO₃: CaO = 1:1 Na₂CO₃ = 70 g/lMgO dosage = 1% Na₂SiO₃ dosage = 1%, NaOH dosage 10 g/l temp.90°C

TIME IN MINUTES	SET - I			SET - II			Average Causti- cizing Efficiency %
	NaOH as Na ₂ O g/l	Na ₂ CO ₃ as Na ₂ O, g/l	Causti- cizing Efficiency E ₁ %	NaOH as Na ₂ O g/l	Na ₂ CO ₃ as Na ₂ O, g/l	Causti- cizing Efficiency E ₁ %	
0	19.28	60.72	24.1	19.76	60.24	24.7	24.4
5	23.04	56.96	28.8	22.72	57.78	28.4	28.6
10	29.84	50.16	37.3	29.52	50.48	36.9	37.1
15	43.04	36.96	53.8	42.41	37.58	53.2	53.5
20	47.2	32.8	59.0	47.52	32.48	59.4	59.2
30	56.16	23.84	70.2	56.32	23.68	70.4	70.3
40	58	22	72.5	57.52	22.48	71.9	72.2
50	58	22	72.5	56.72	23.38	70.9	71.7

TABLE NO.38

EFFECT OF GREEN LIQUOR CONCENTRATION ON CAUSTICIZING

EFFICIENCY WITH $\text{Na}_2\text{CO}_3:\text{CaO} = 1:1$ g mole as Na_2O $\text{NaOH} = 0$ at temperature 90°C

Particulars/ Samples	Sulphidity = 0%		Sulphidity = 20%	
	TTA as Na_2O	Causticizing efficiency%	TTA as Na_2O	Causticizing efficiency %
1	40	94.0	40	91.8
2	50	93.1	50	91.1
3	60	91.3	60	88.5
4	70	91.4	70	87.6
5	80	90.2	80	86.3
6	90	87.5	90	82.7
7	100	86.2	100	81.0
8	110	82.0	110	76.1
9	120	81.6	120	75.3

TABLE NO. 39

EFFECT OF LIME DOSAGE ON THE SETTLING RATE OF THE LIME MUD
 SOLIDS WITH $\text{Na}_2\text{CO}_3 = 70$ gpl VOLUME OF SLURRY = 115 CC AT TEMP.
 20°C (ROOM TEMPERATURE)

Time Minutes	Settled volume CC	Settled volume in CC	Settled volume in CC
	For 90% lime used stoichiometrically	For stoichiometri- cally 100% lime used	For Stoichime- trically 110% lime used
0	115	114	115
5	80	92	108
10	58	74	102
15	42	47	97
20	27	38	86
25	16	33	84
30	16	30	73

TABLE NO. 40

EXPERIMENTAL AND PREDICTED CAUSTICIZING EFFICIENCIES FOR
DIFFERENT GREEN LIQUOR COMPOSITION AT TEMPERATURE 90°C

Experiment No.	Initial green liquor composition g/l as Na ₂ O			Causticizing efficiency	
	Na ₂ CO ₃	NaOH	Na ₂ S	Measured	Predicted
1	70	0	12	89.4	90.8
2	70	0	17.5	86.1	85.0
3	70	0	23.2	78.9	79.2
4	70	5	17.5	80.5	78.9
5	70	7.5	17.5	77.1	77.8
6	70	10	17.5	71.1	72.1
7	70	0	0	91.4	91.4
8	40	0	0	94.0	93.6
9	50	0	0	93.1	93.9
10	60	0	0	91.3	91.8
11	70	0	0	91.4	91.4
12	80	0	0	90.2	89.3
13	90	0	0	87.5	87.9
14	100	0	0	86.2	86.3
15	110	0	0	82.0	84.5
16	120	0	0	81.6	82.9
17	80	0	20	81	80.4

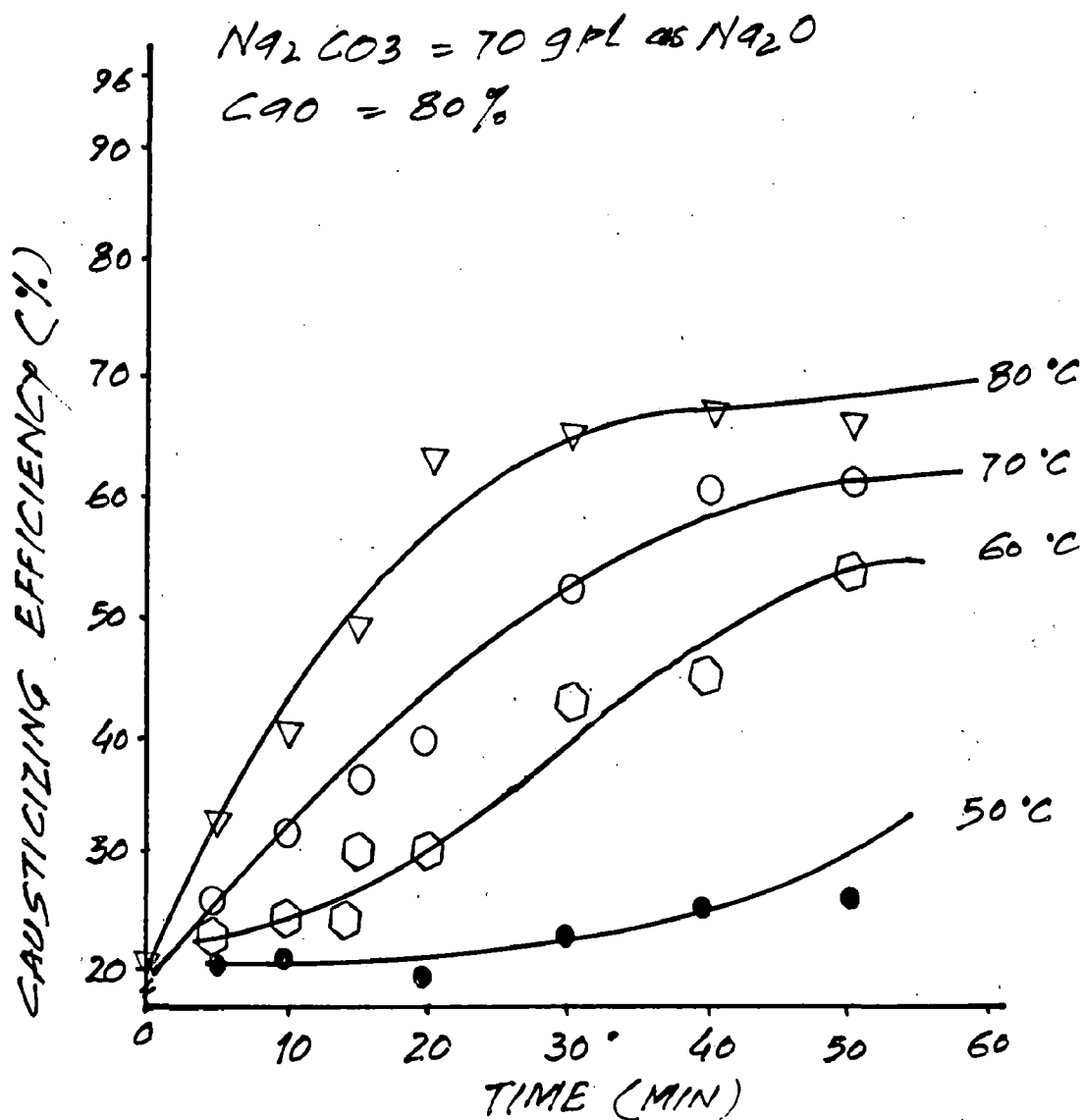


FIG. 1, VARIATION OF CAUSTICIZING EFFICIENCY WITH TIME AND TEMPERATURE AS A PARAMETER.

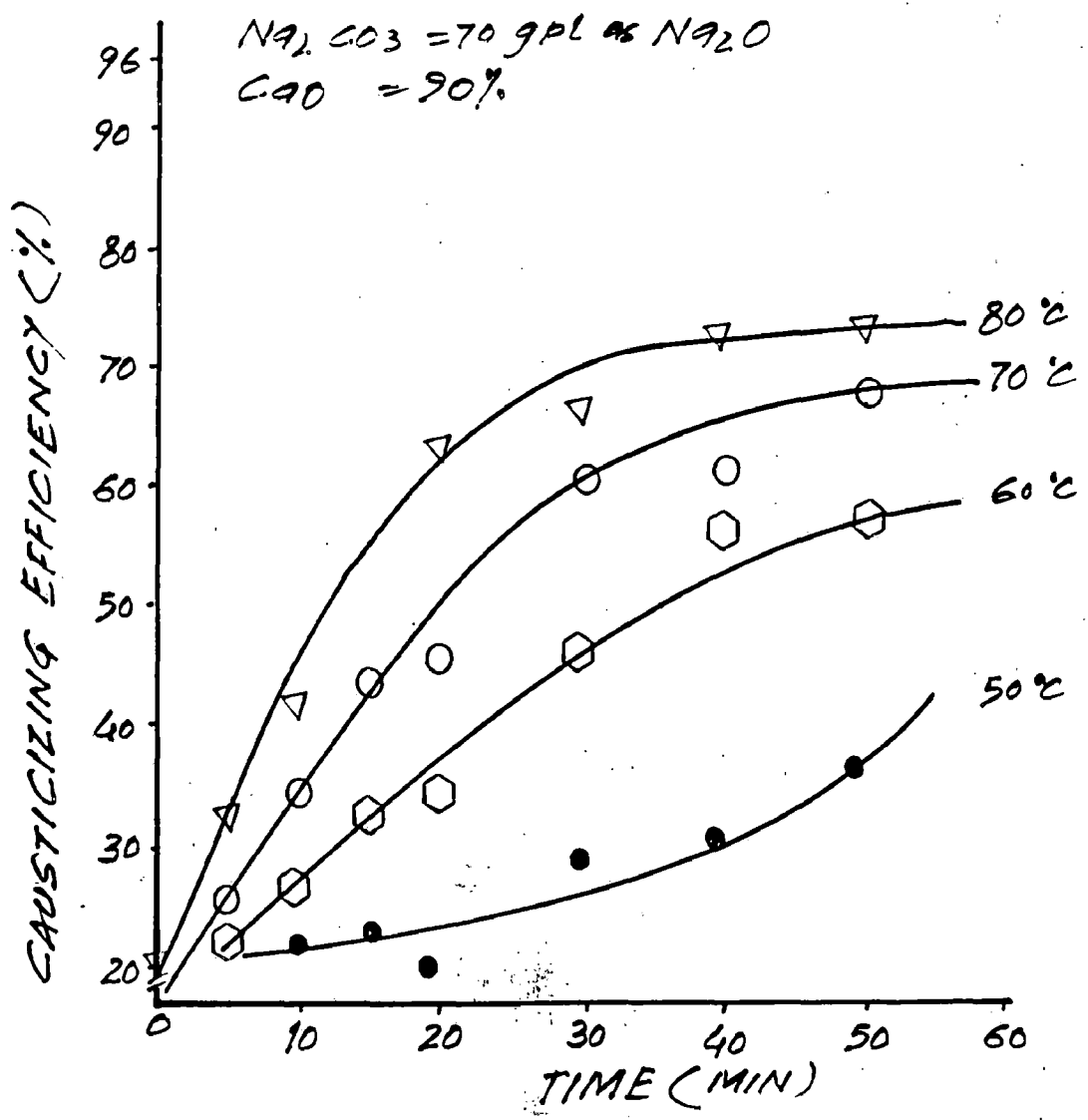


FIG. 2, VARIATION OF CAUSTICIZING EFFICIENCY WITH TIME AND TEMPERATURE AS A PARAMETER.

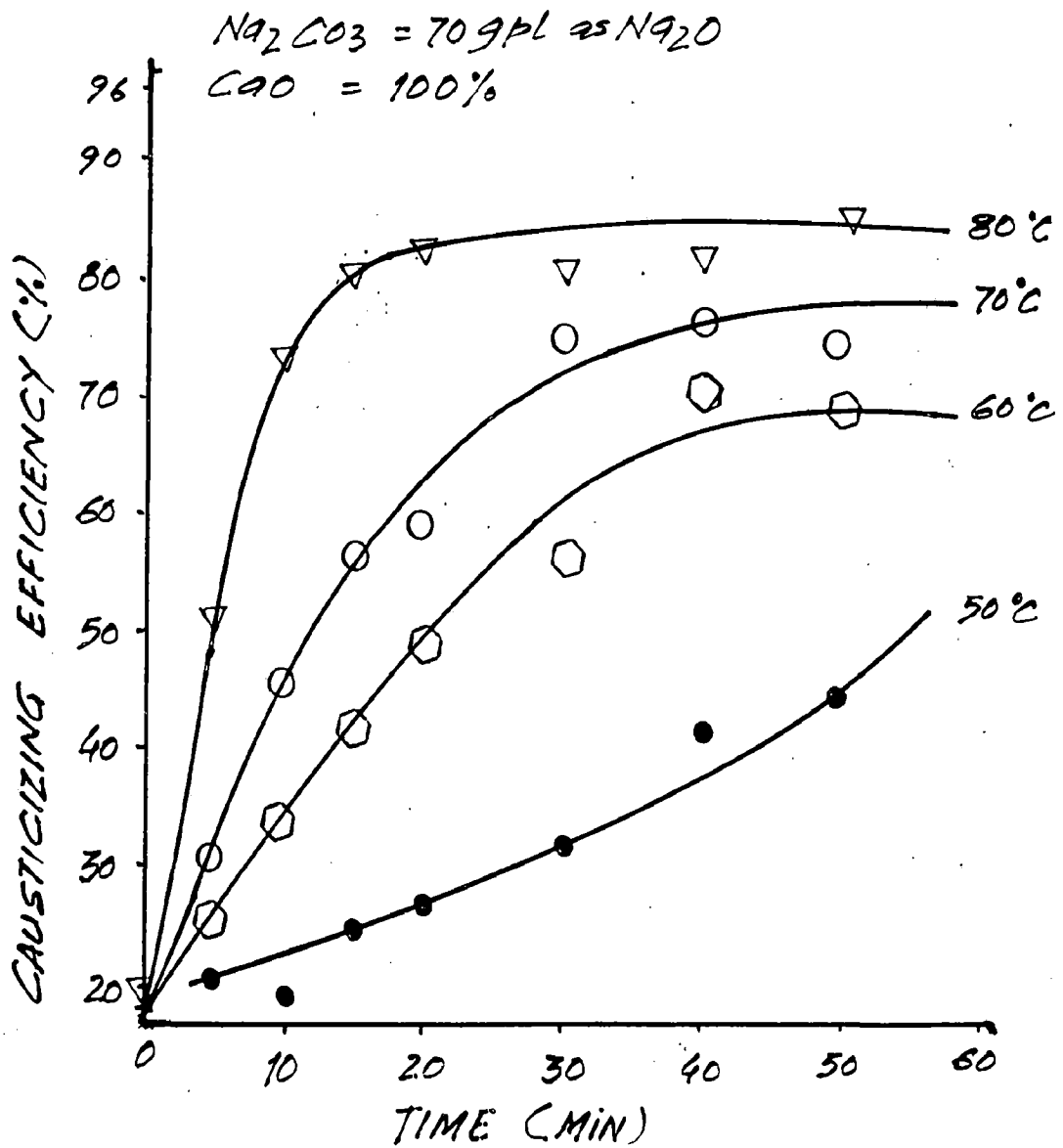


FIG. 3, VARIATION OF CAUSTICIZING
 EFFICIENCY WITH TIME & TEMPERATURE
 AS A PARAMETER

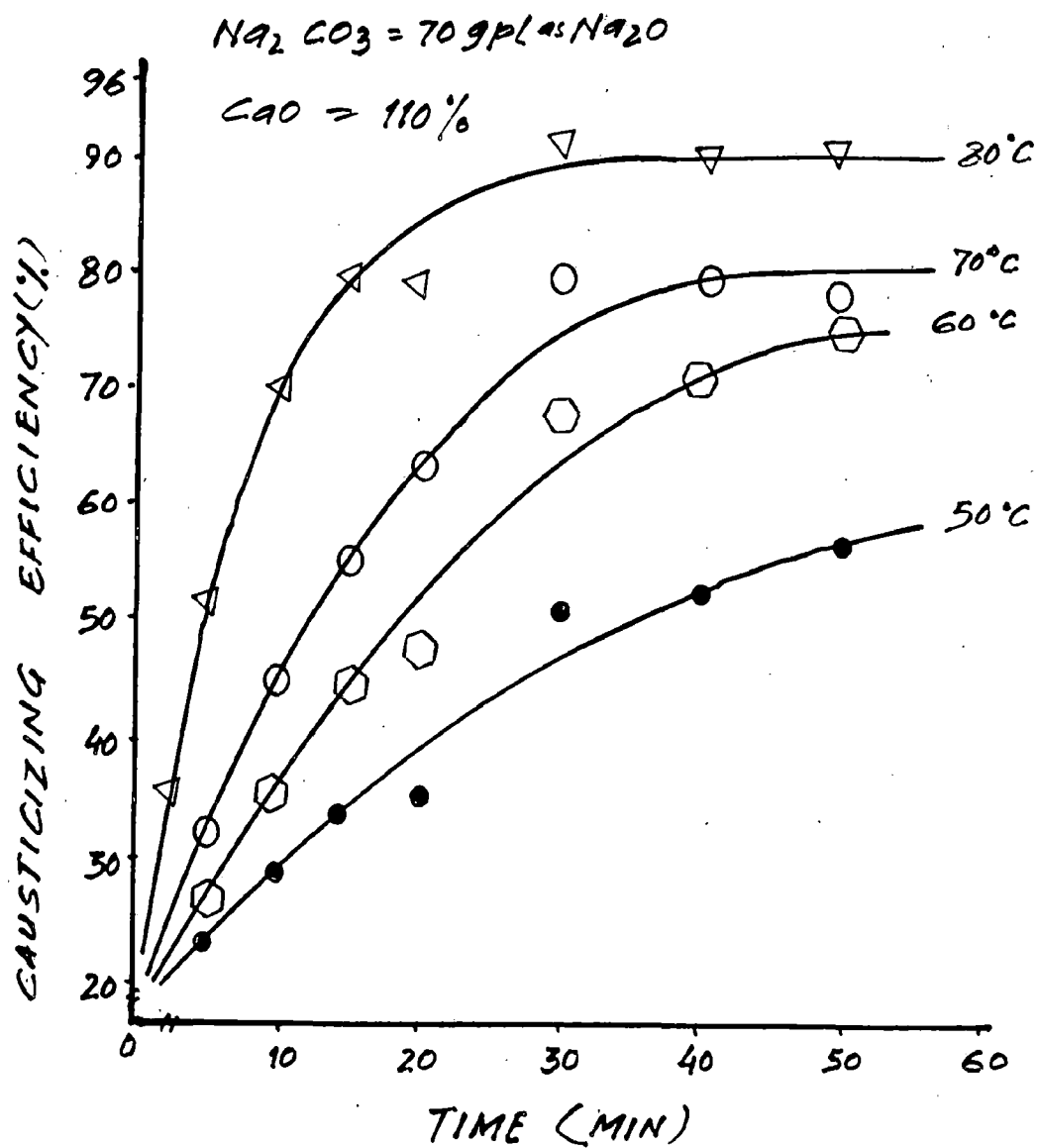


FIG. 4, VARIATION OF CAUSTICIZING EFFICIENCY WITH TIME & TEMPERATURE.

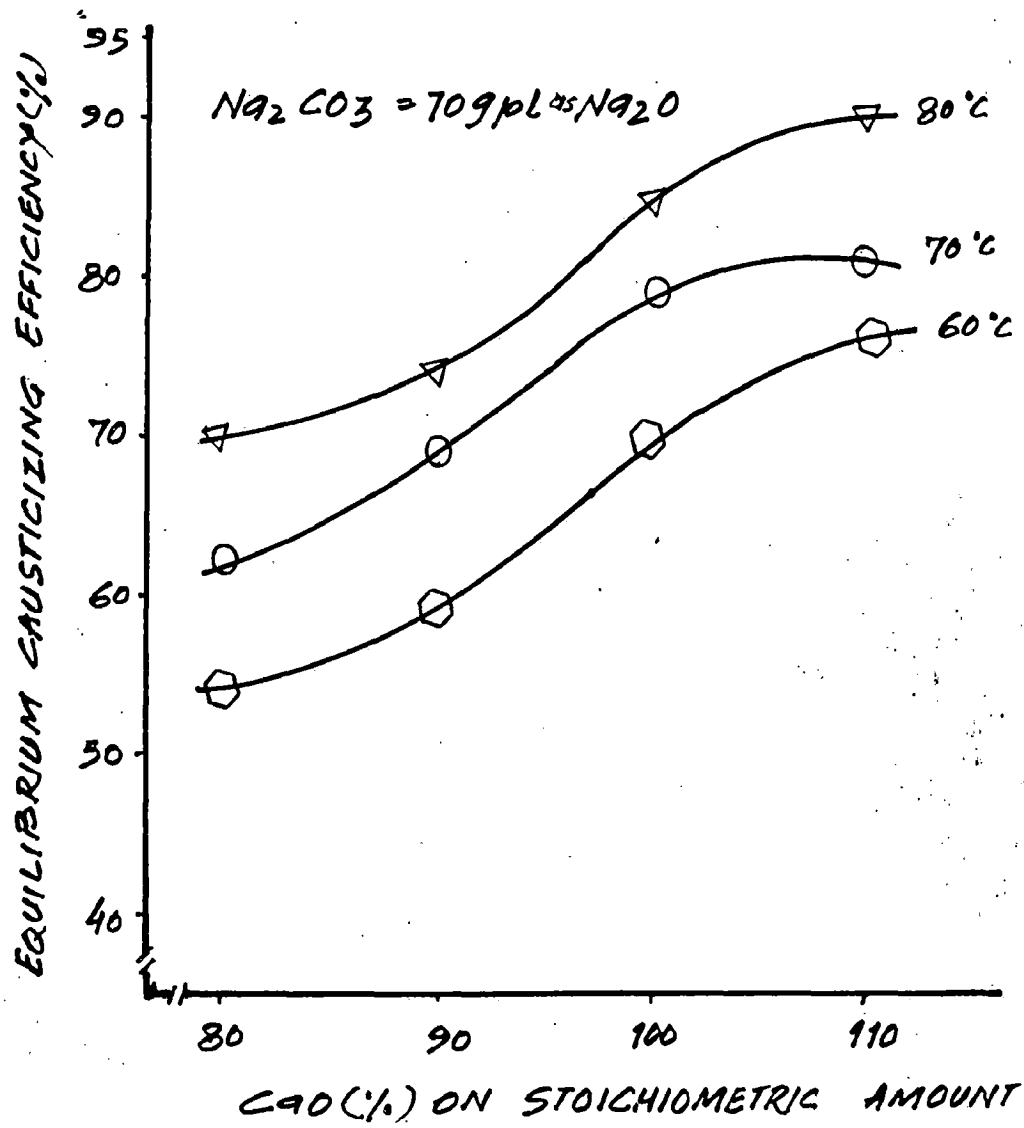


FIG. 5, EFFECT OF LIME DOSAGE ON CAUSTICIZING EFFICIENCY.

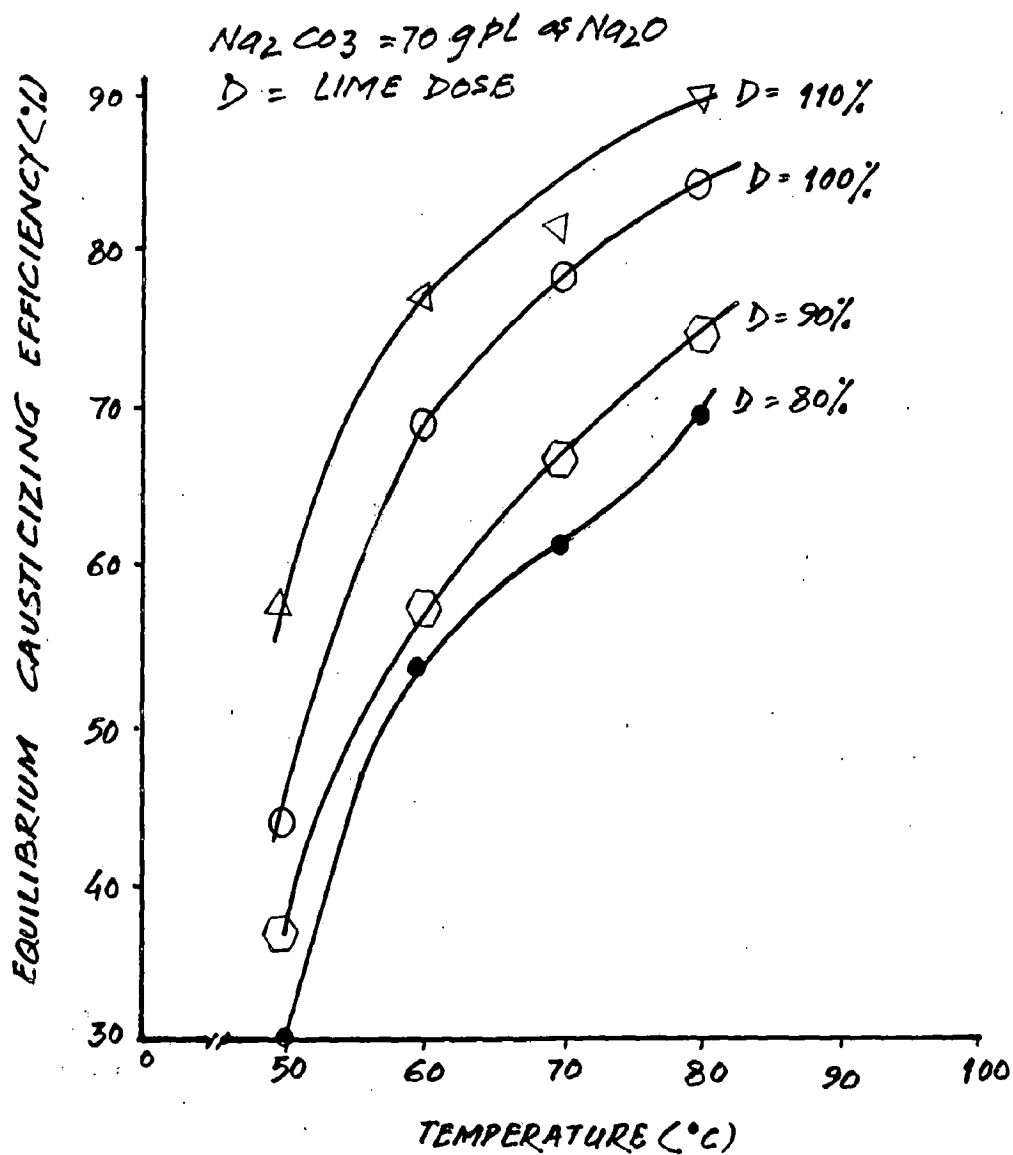


FIG. 6, EFFECT OF TEMPERATURE ON EQUILIBRIUM CAUSTICIZING EFFICIENCY WITH LIME DOSE AS A PARAMETER.

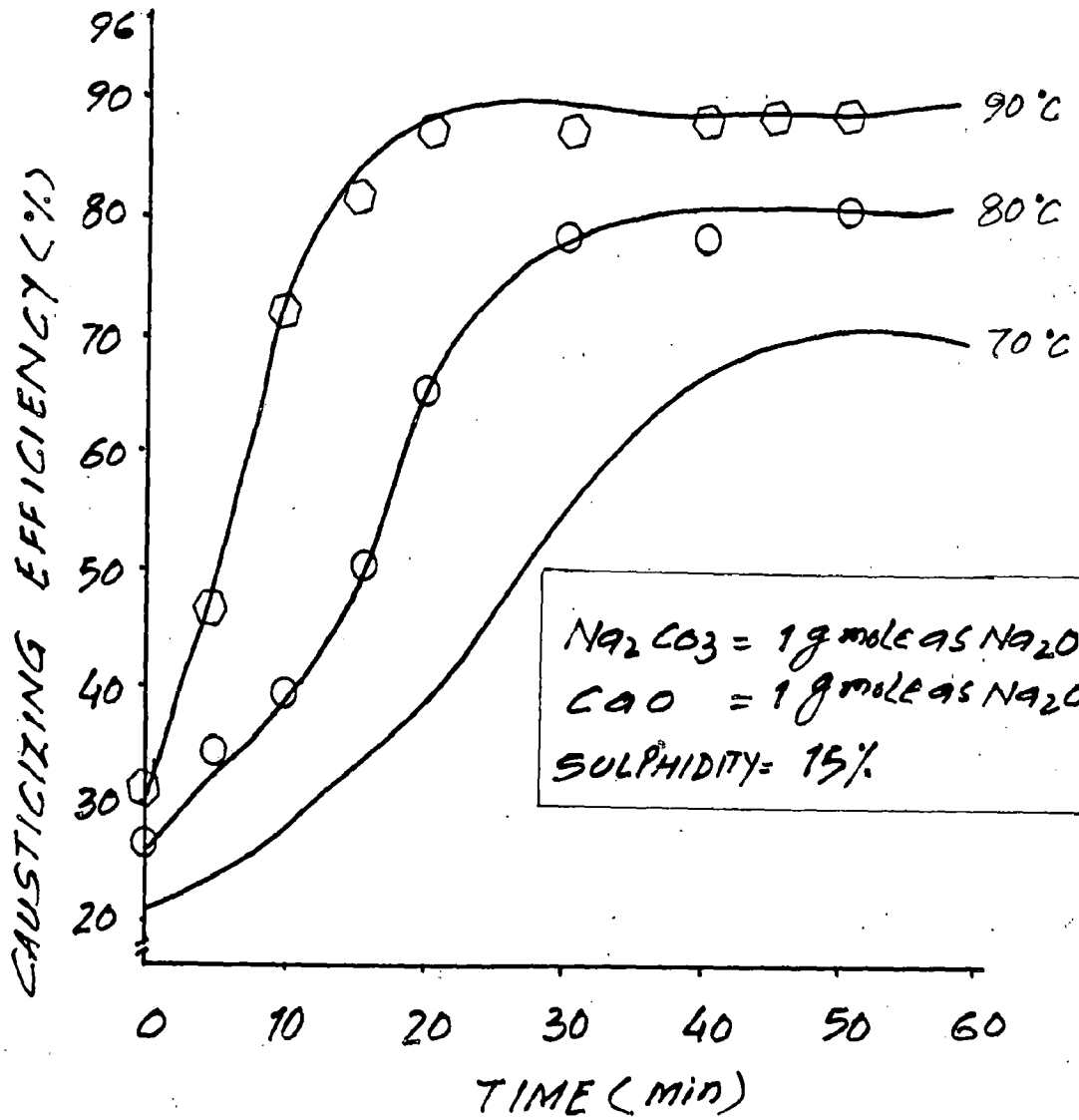


FIG. 7, VARIATION OF CAUSTICIZING EFFICIENCY WITH TIME AND TEMPERATURE.

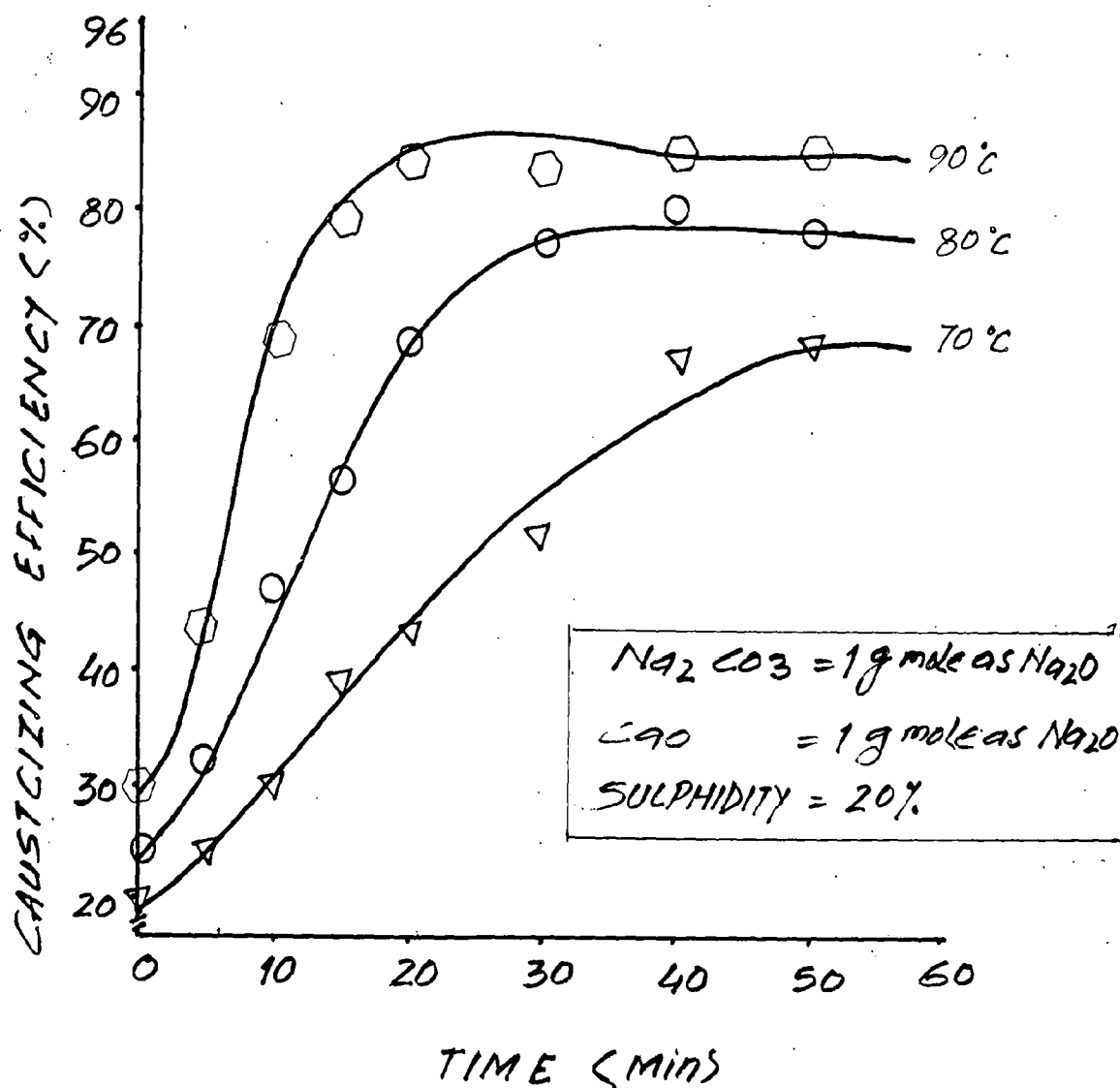


FIG. 8, VARIATION OF CAUSTICIZING EFFICIENCY WITH TIME AND TEMPERATURE.

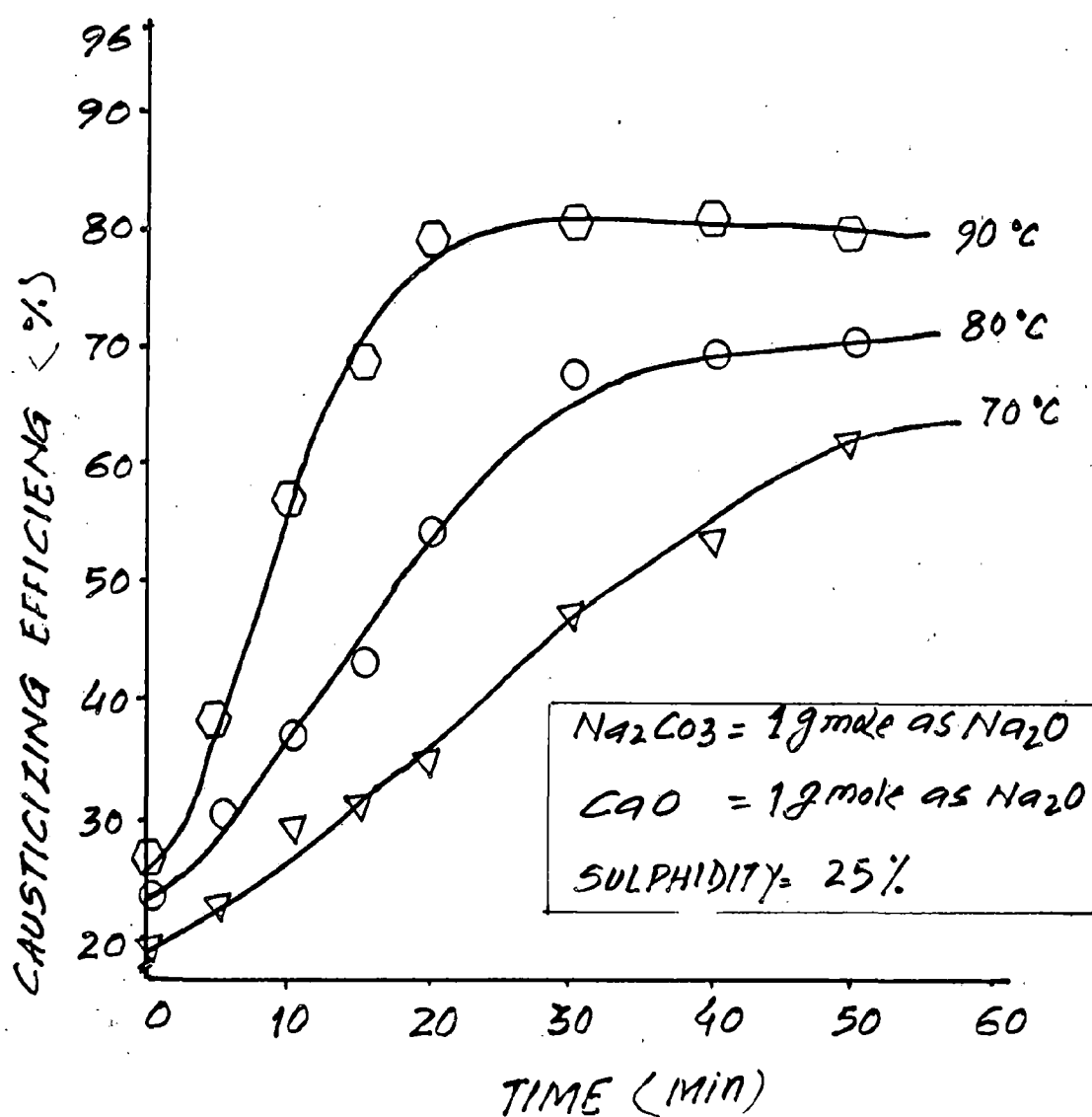


FIG. 9, VARIATION OF CAUSTICIZING EFFICIENCY WITH TIME AND TEMPERATURE.

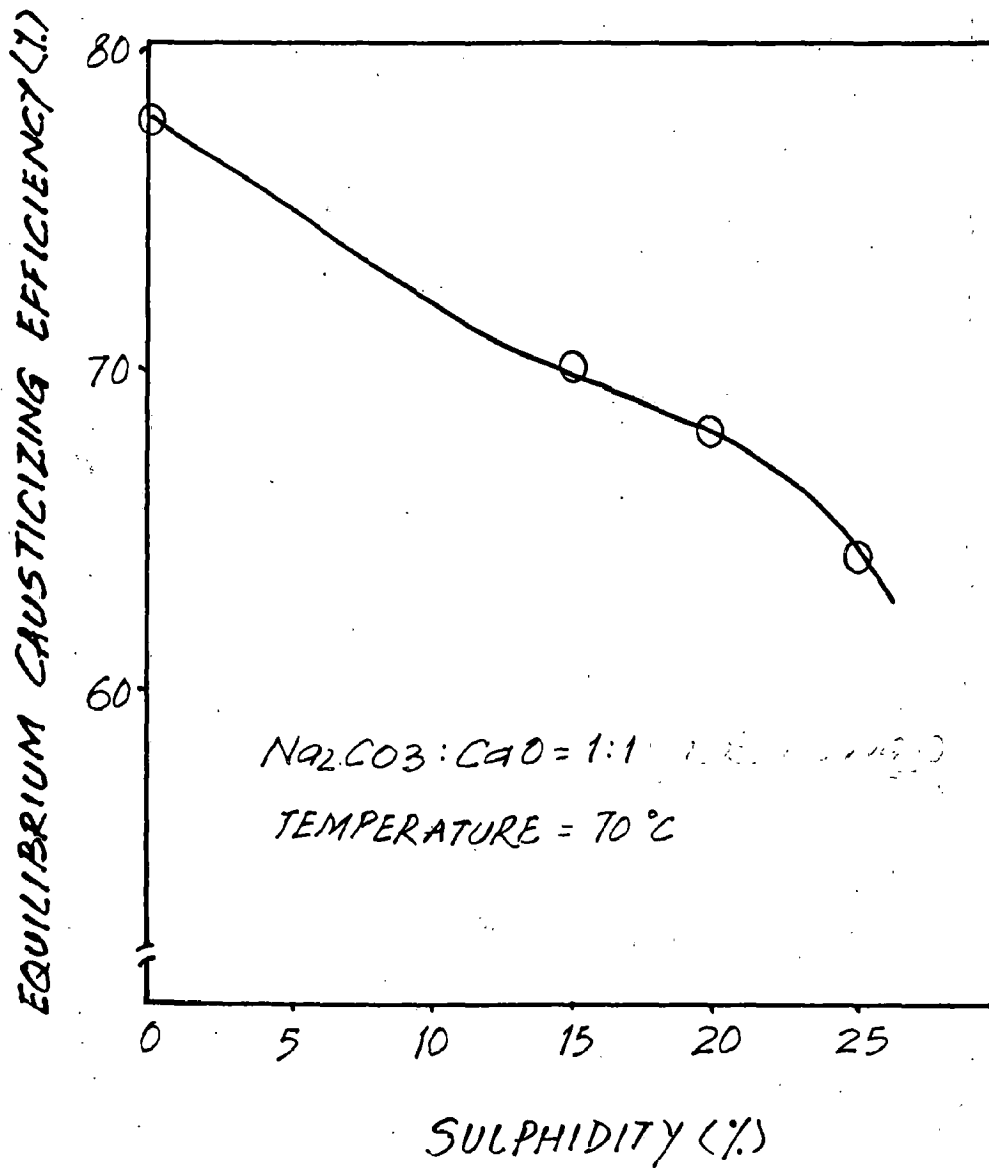


FIG. 10, EFFECT OF CHANGE OF
SULPHIDITY ON EQUILIBRIUM
CAUSTICIZING EFFICIENCY.

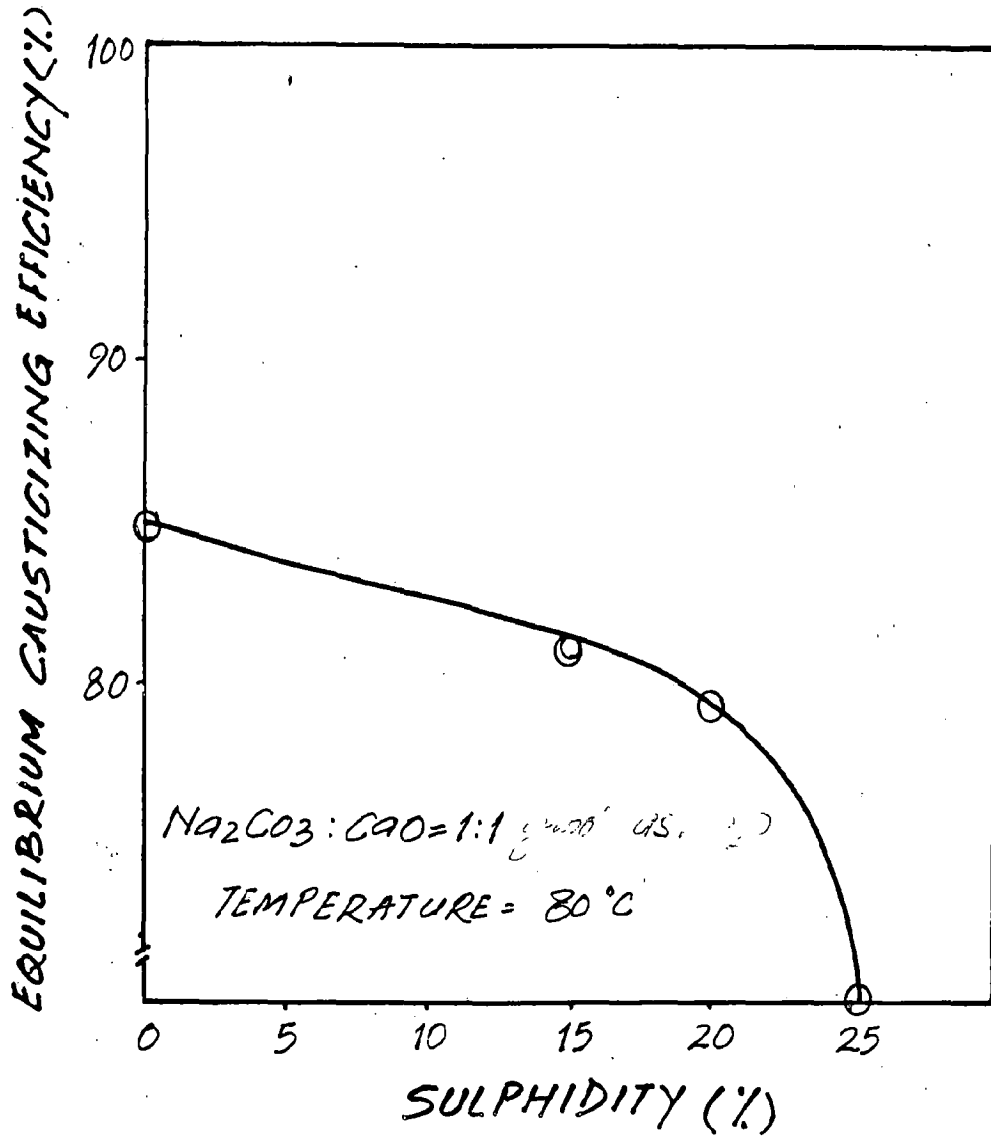


FIG. 11, EFFECT OF CHANGE OF
SULPHIDITY ON EQUILIBRIUM
CAUSTICIZING EFFICIENCY.

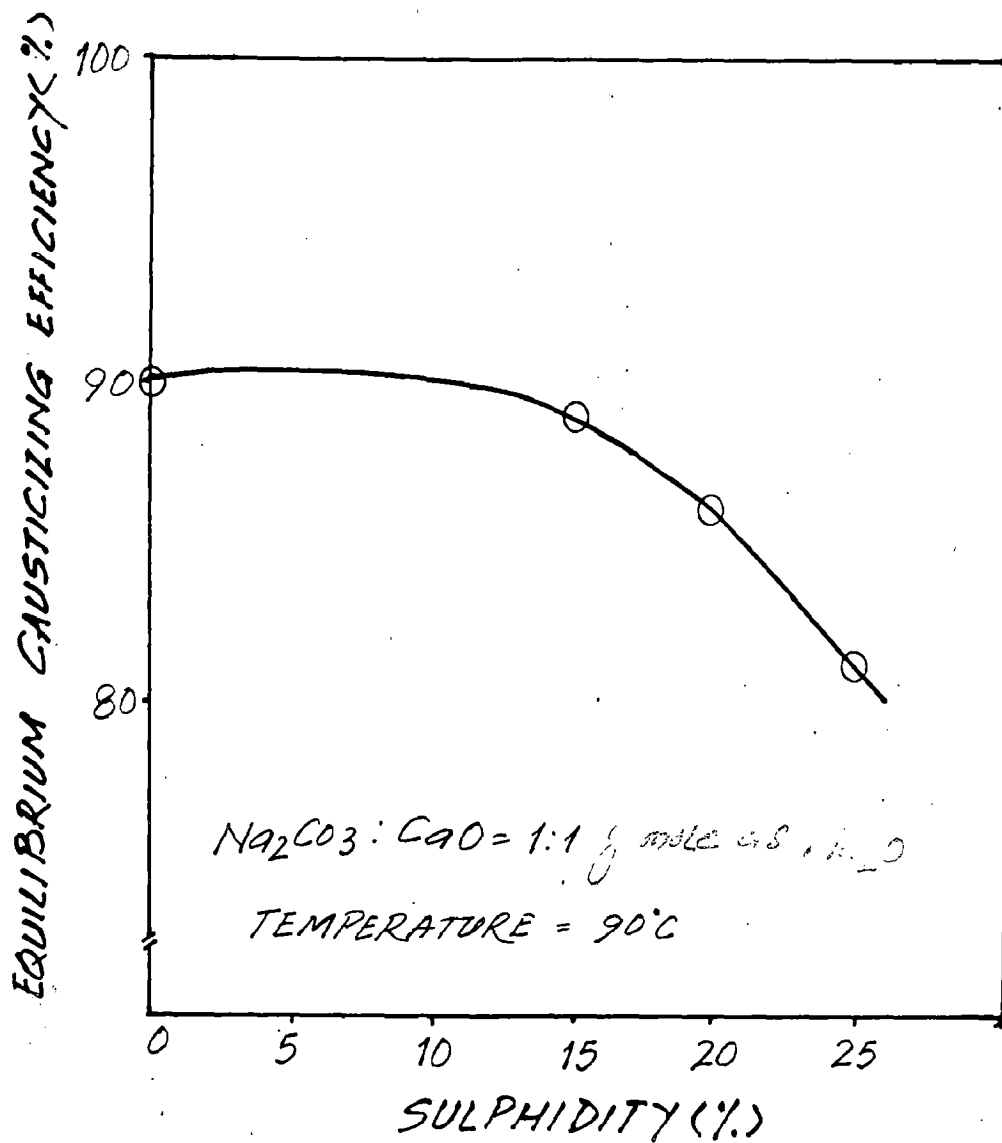


FIG. 12, EFFECT OF CHANGE OF
SULPHIDITY ON EQUILIBRIUM
CAUSTICIZING EFFICIENCY.

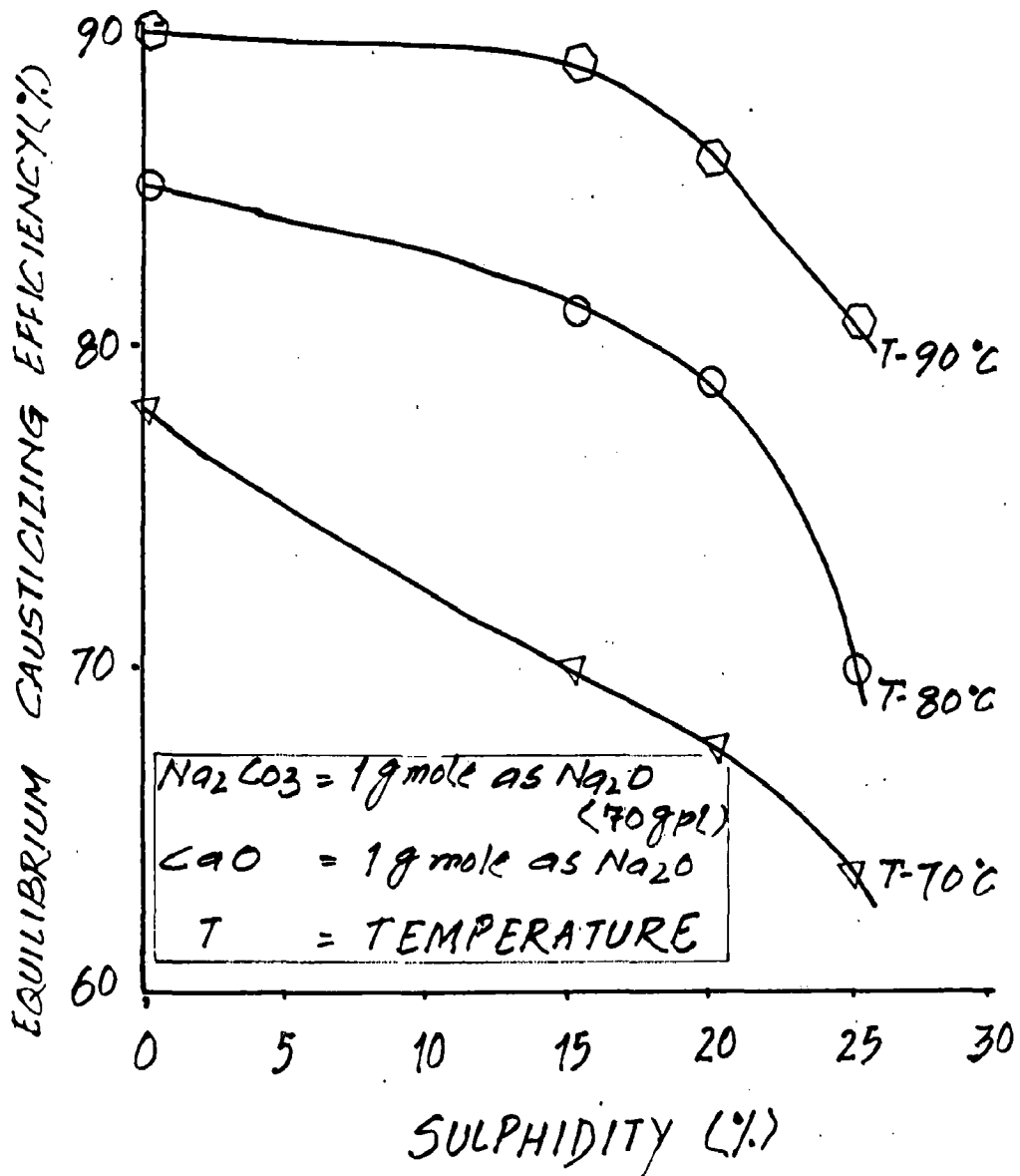


FIG. 13, COMPARISON OF EQUILIBRIUM
 CAUSTICIZING EFFICIENCY WITH
 CHANGE OF SULPHIDITY AT
 DIFFERENT TEMPERATURE.

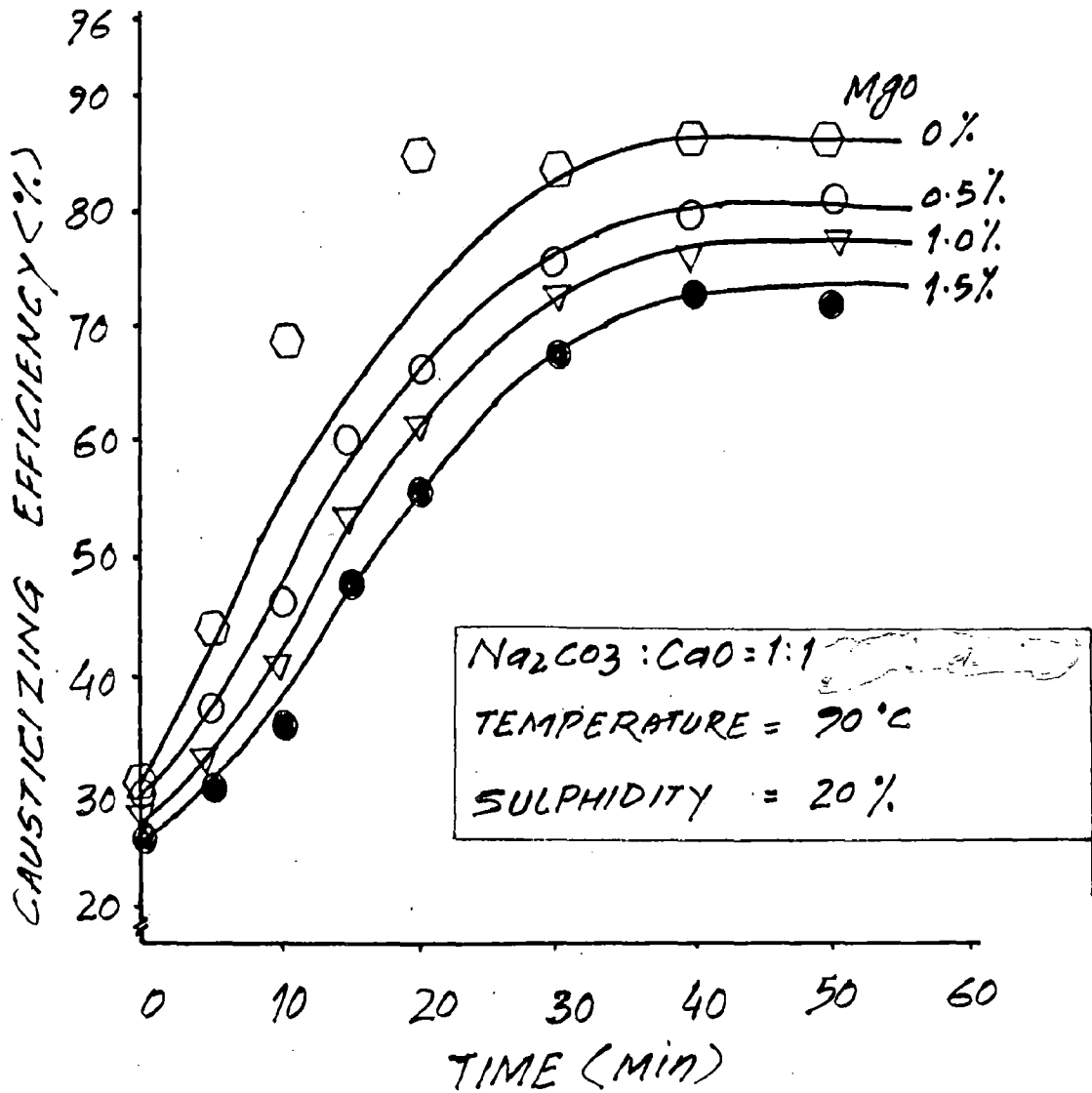


FIG. 14, VARIATION OF CAUSTICIZING EFFICIENCY WITH TIME AND MgO DOSAGE.

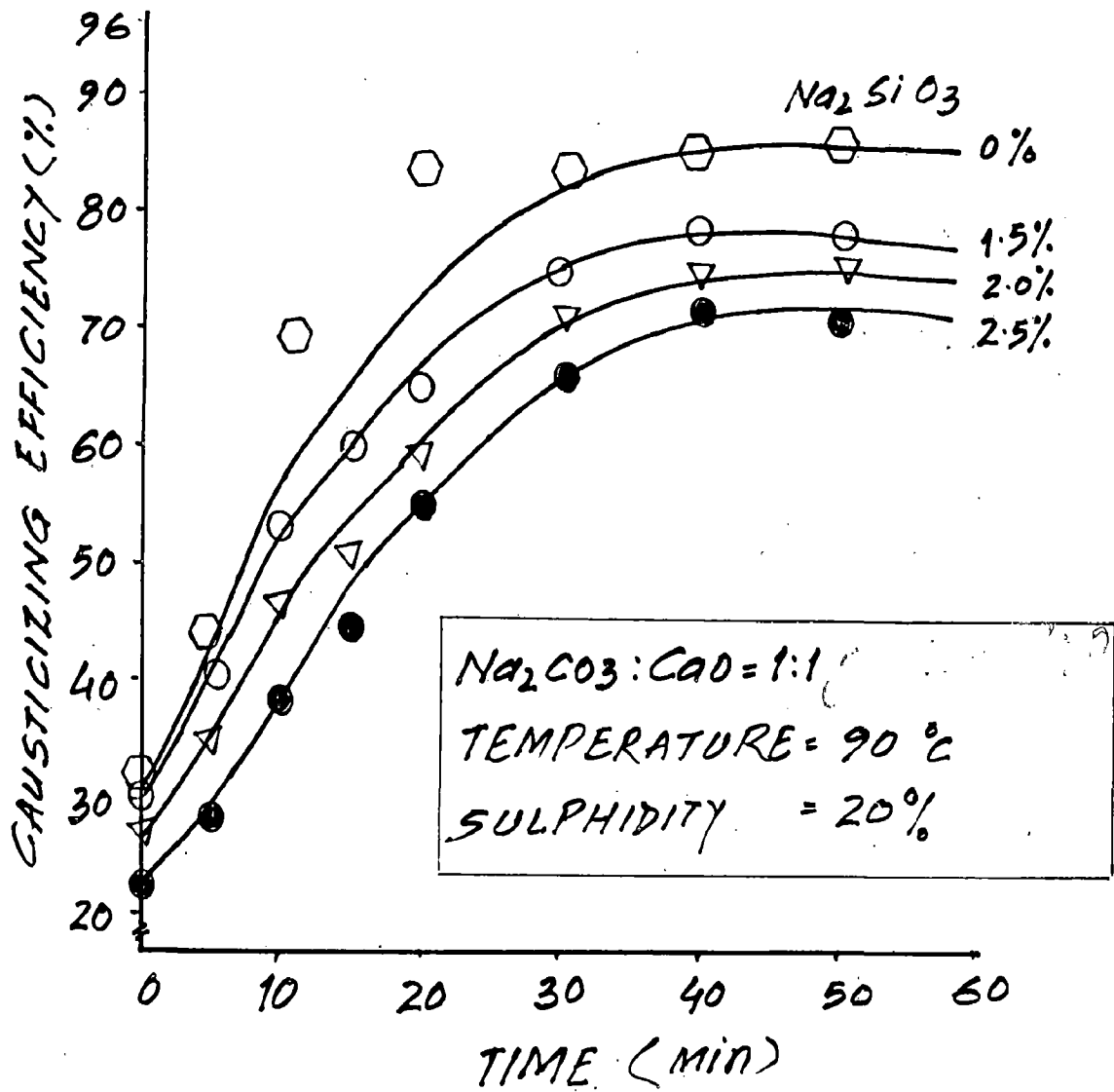


FIG. 15, VARIATION OF CAUSTICIZING EFFICIENCY WITH TIME AND Na₂SiO₃ DOSAGE.

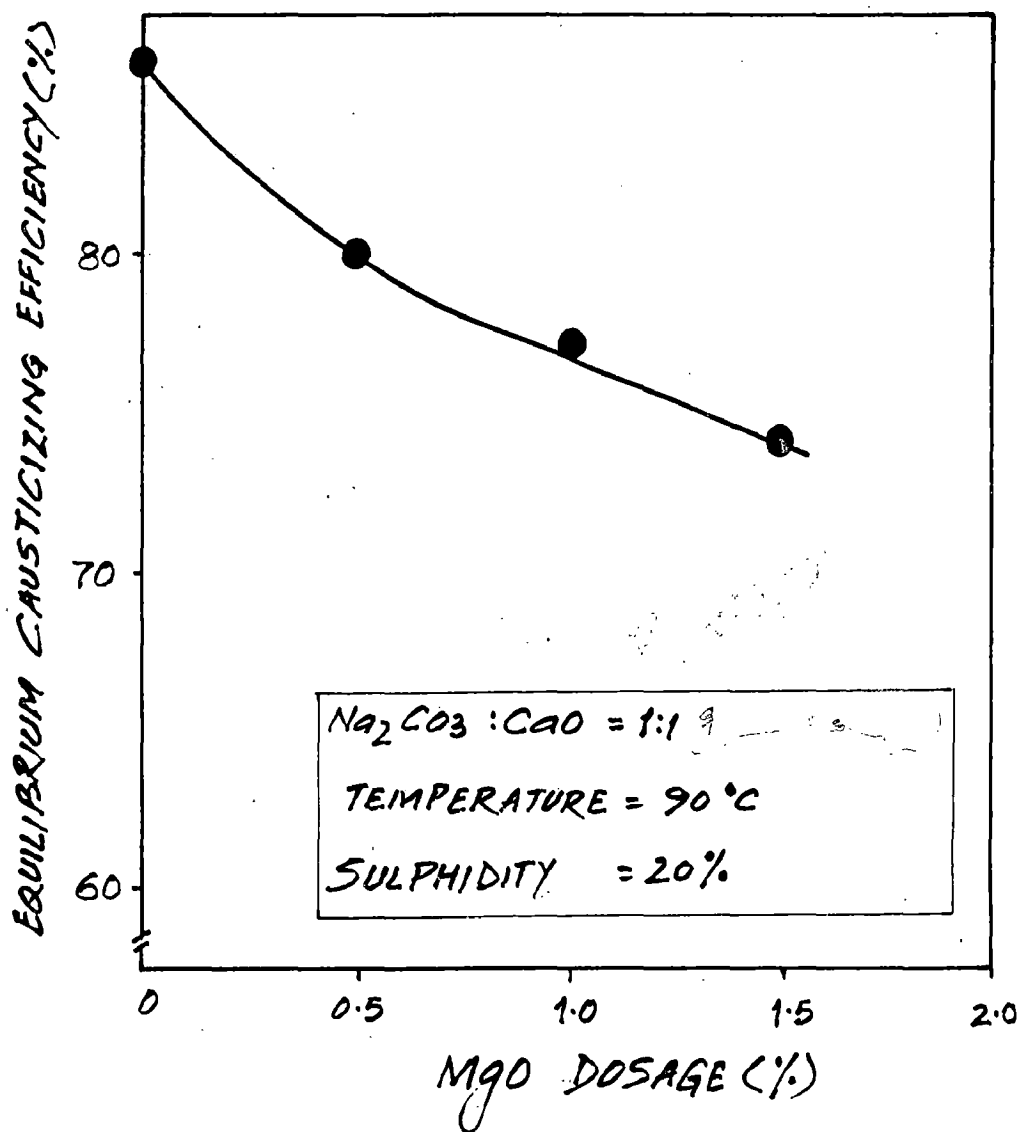


FIG. 16, EFFECT OF MgO DOSAGE ON EQUILIBRIUM CAUSTICIZING EFFICIENCY.

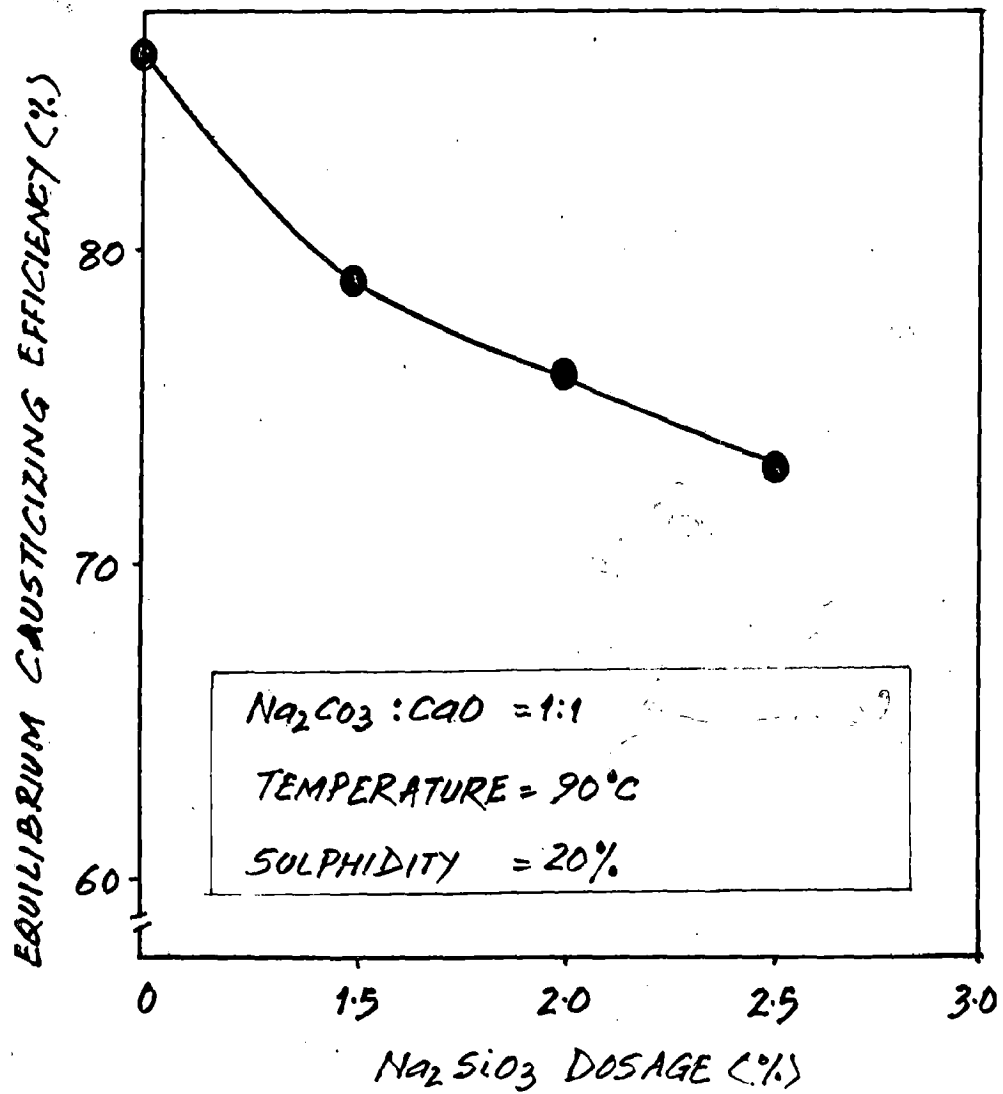


FIG. 17, EFFECT OF Na₂SiO₃ DOSAGE ON EQUILIBRIUM CAUSTICIZING EFFICIENCY.

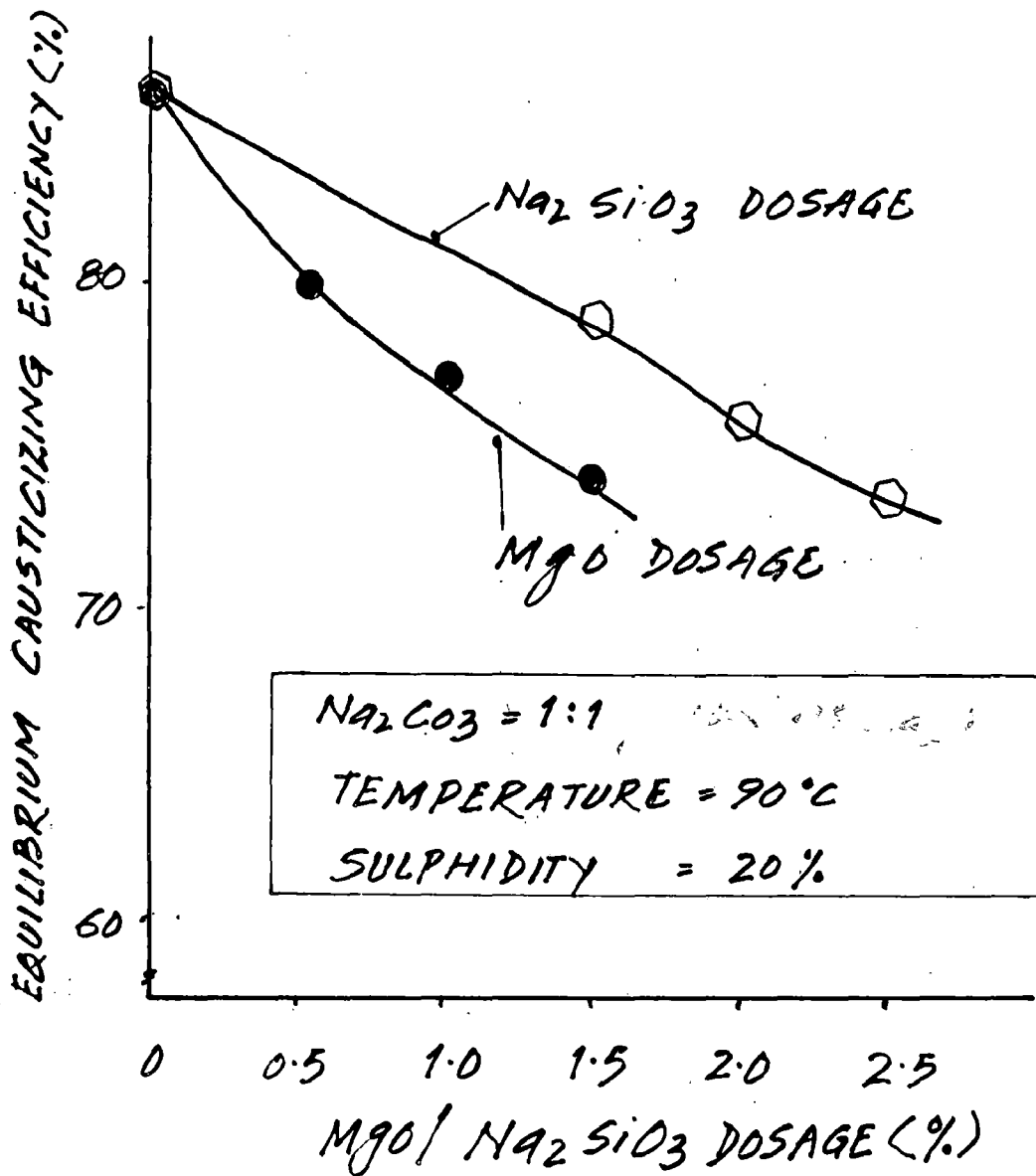


FIG. 18, COMPARISON OF EQUILIBRIUM CAUSTICIZING EFFICIENCY WITH MgO AND Na₂SiO₃ ADDITION.

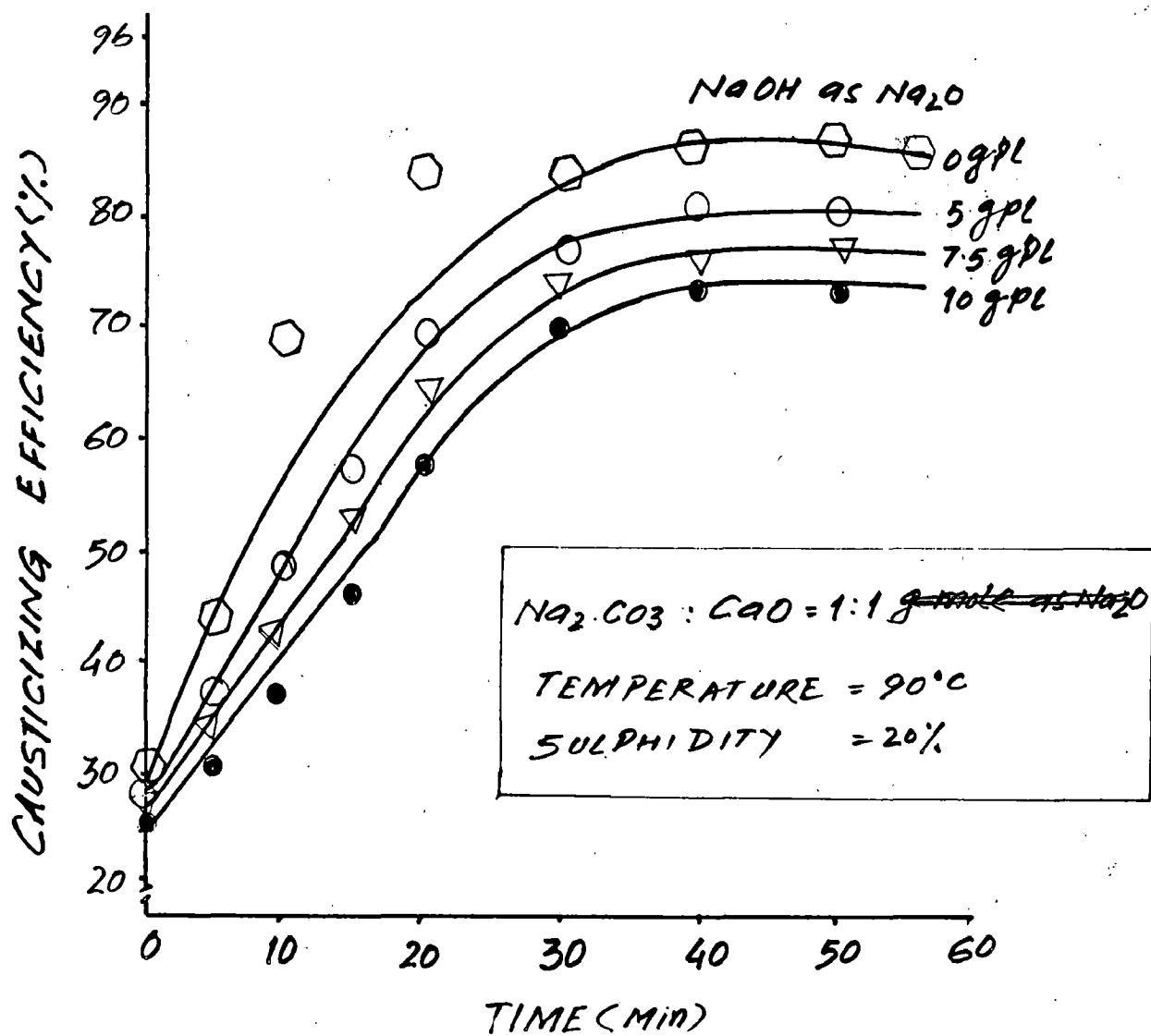


FIG. 19, VARIATION OF CAUSTICIZING EFFICIENCY WITH TIME AND NaOH DOSAGE.

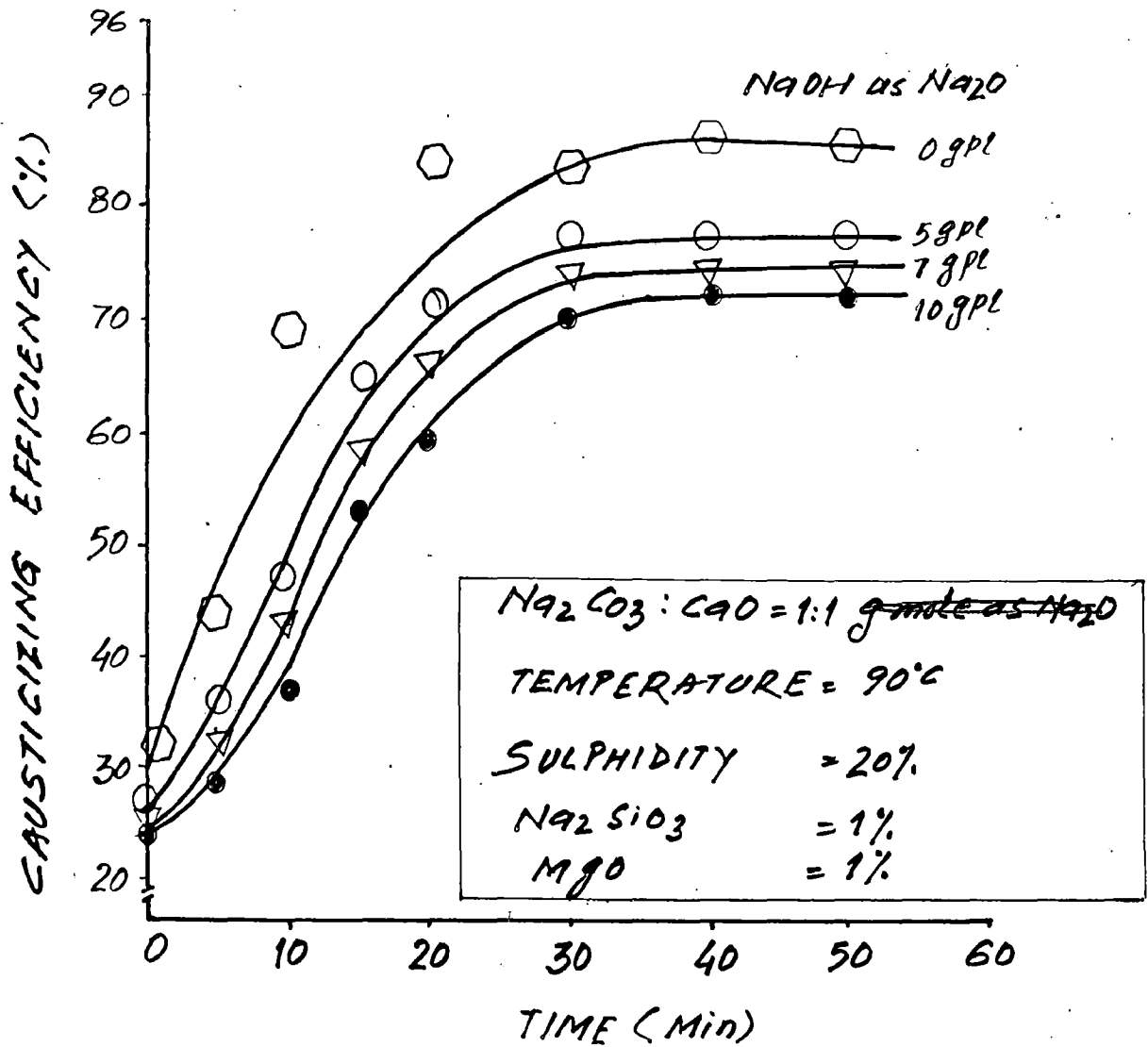


FIG. 20, VARIATION OF CAUSTICIZING EFFICIENCY WITH TIME AND NaOH DOSAGE.

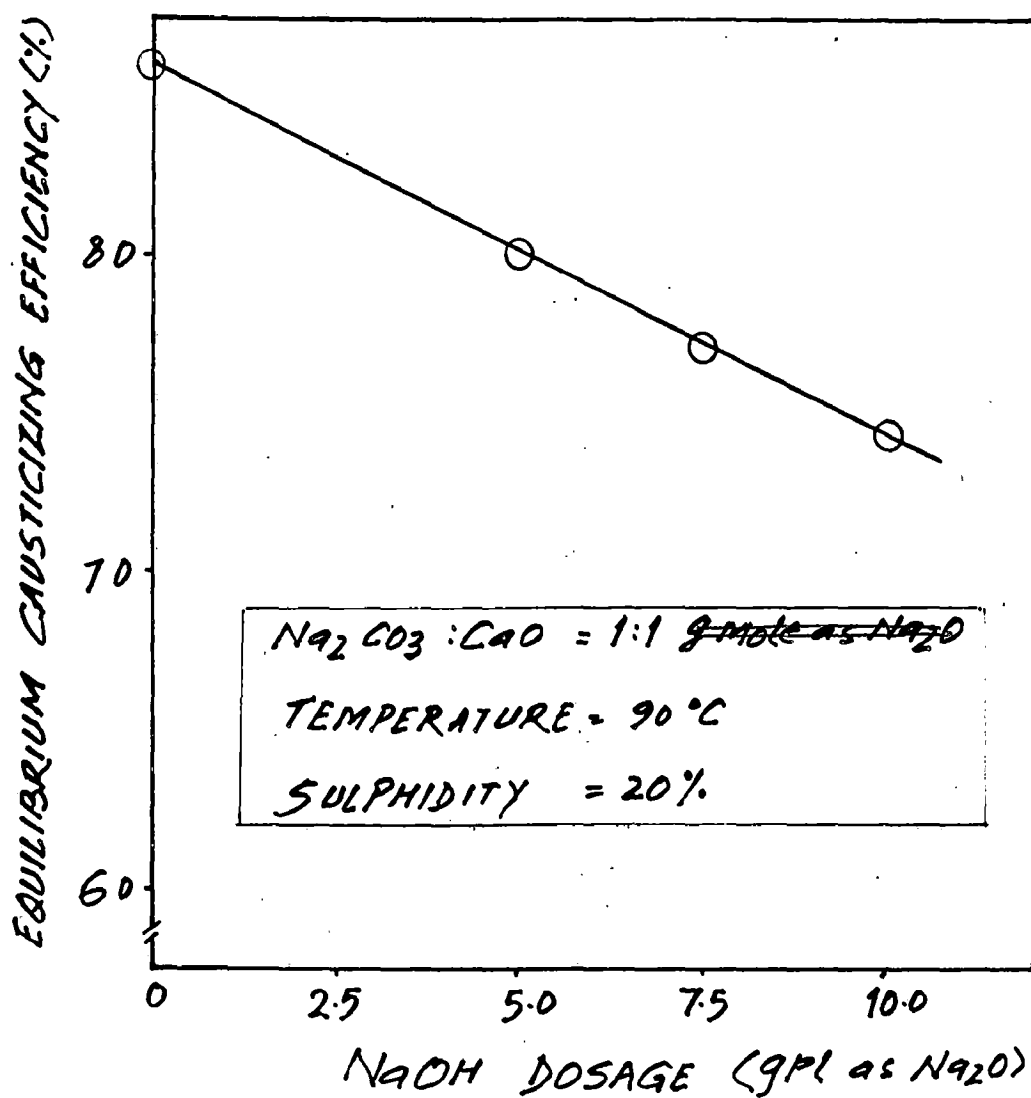


FIG. 21, EFFECT OF NaOH DOSAGE ON EQUILIBRIUM CAUSTICIZING EFFICIENCY.

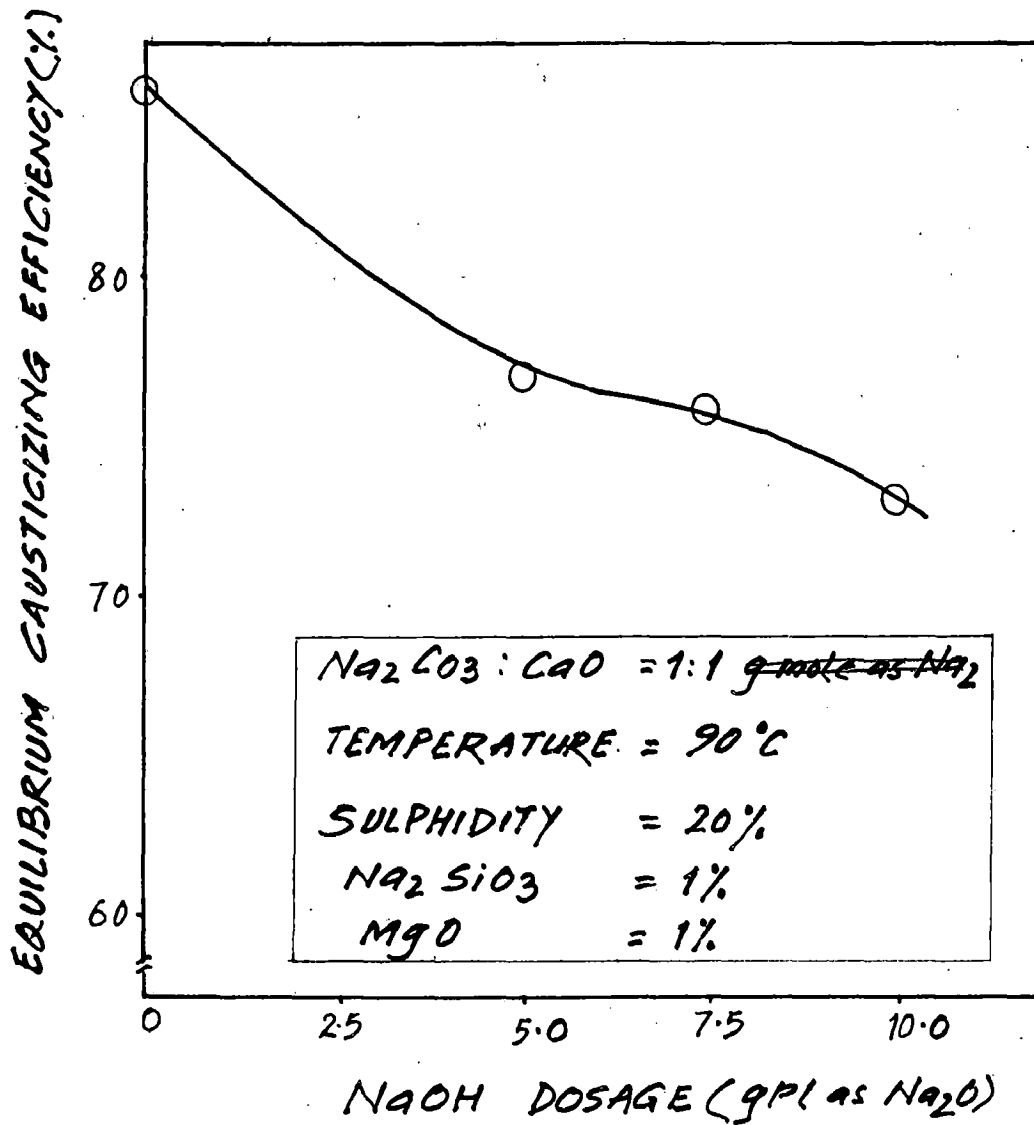


FIG. 22, EFFECT OF NaOH DOSAGE ON EQUILIBRIUM CAUSTICIZING EFFICIENCY.

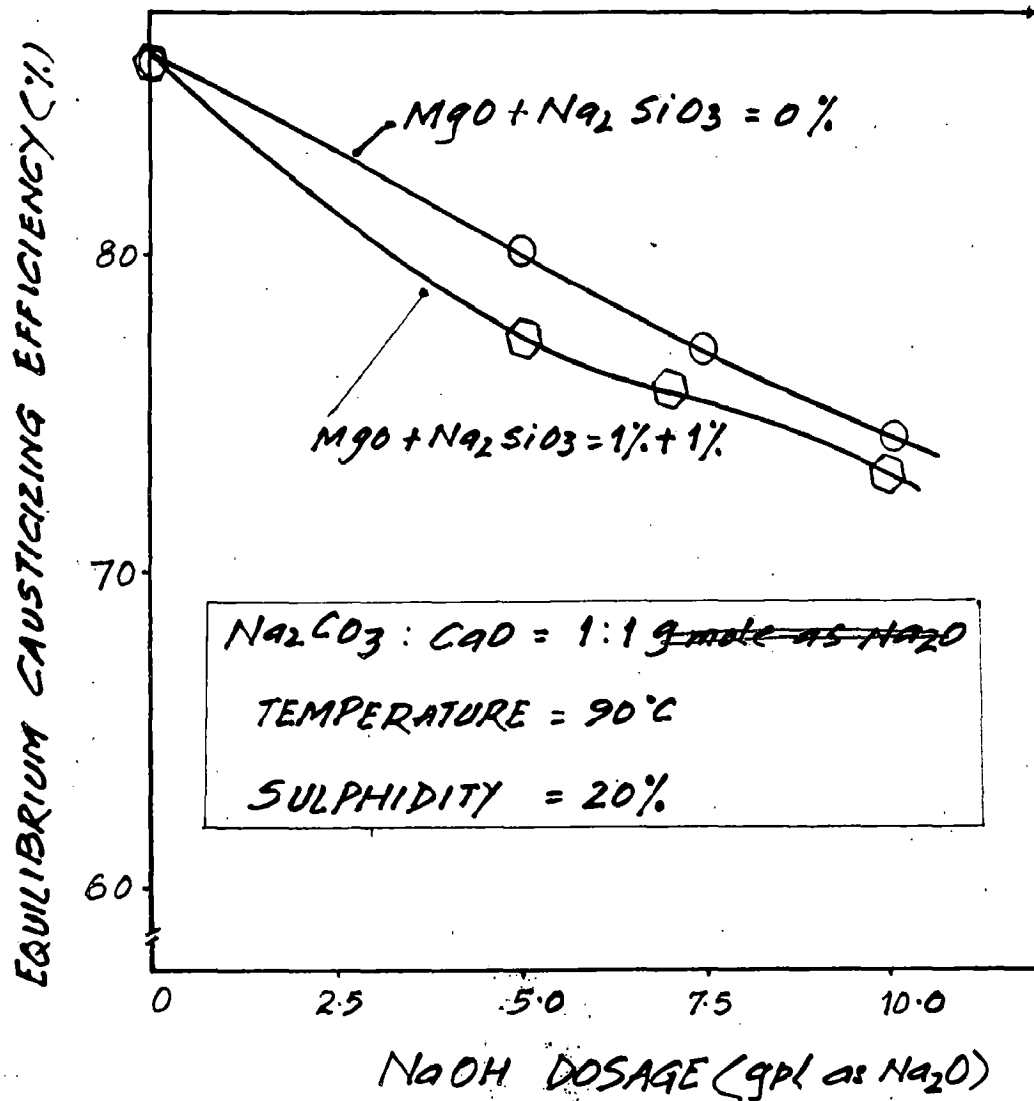


FIG. 23, COMPARISON OF EQUILIBRIUM
 CAUSTICIZING EFFICIENCY WITH
 AND WITHOUT ADDITION ON
 MgO AND Na_2SiO_3 .

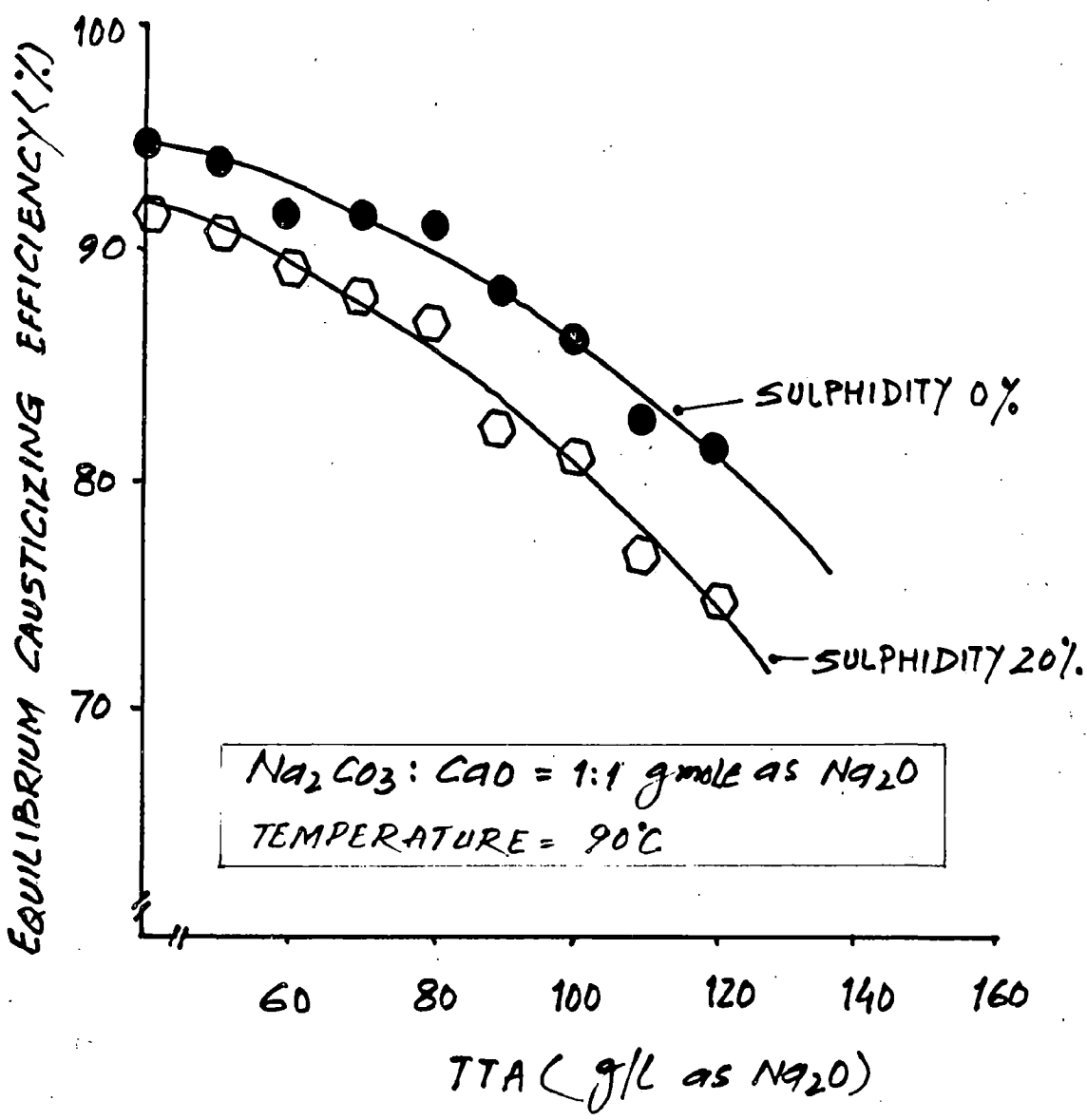


FIG. 24, EFFECT OF GREEN LIQUOR CONCENTRATION ON CAUSTICIZING EFFICIENCY.

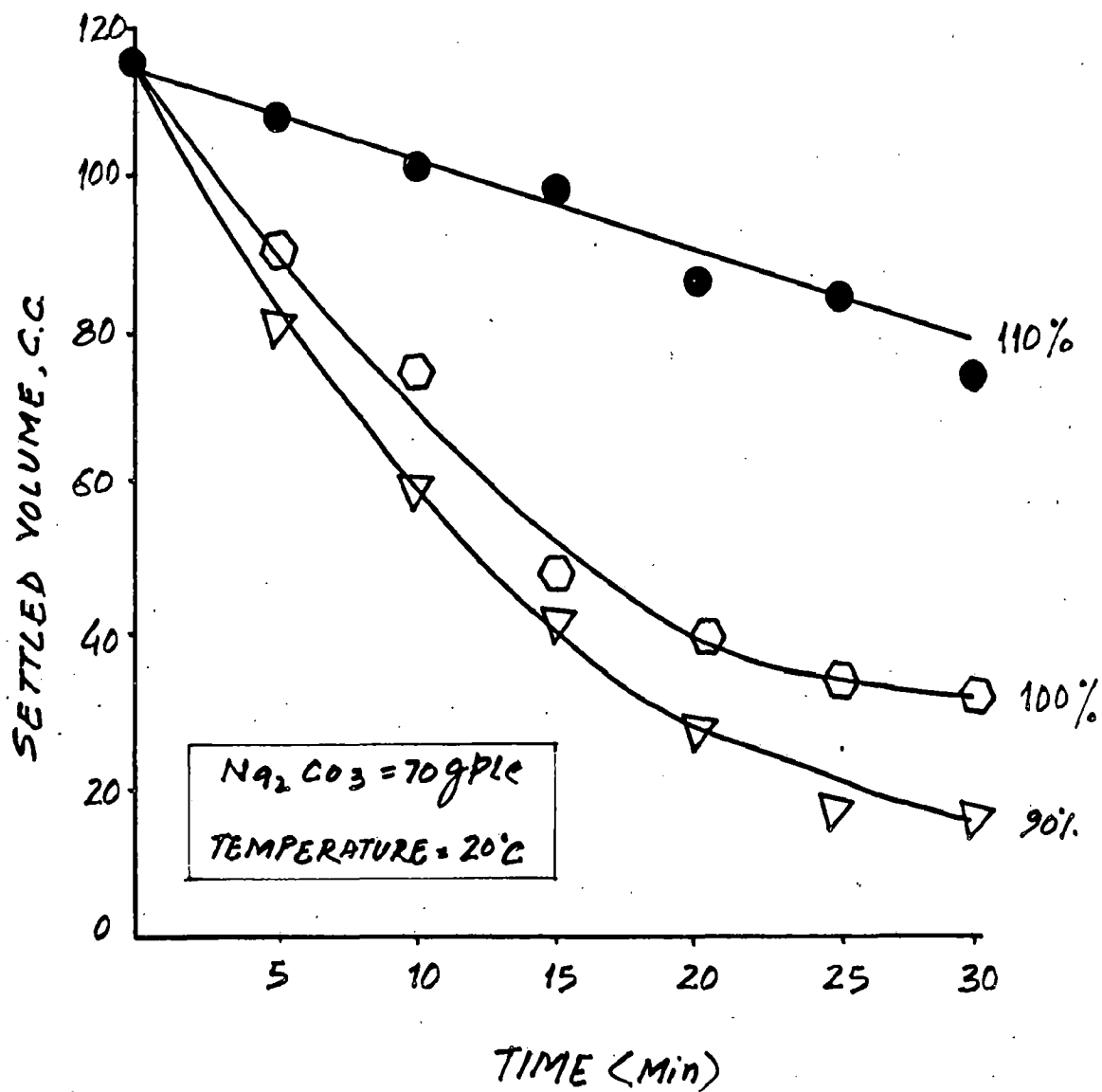


FIG. 25, EFFECT LIME QUANTITY ON THE SETTLING RATE OF THE LIME MUD SOLIDS.

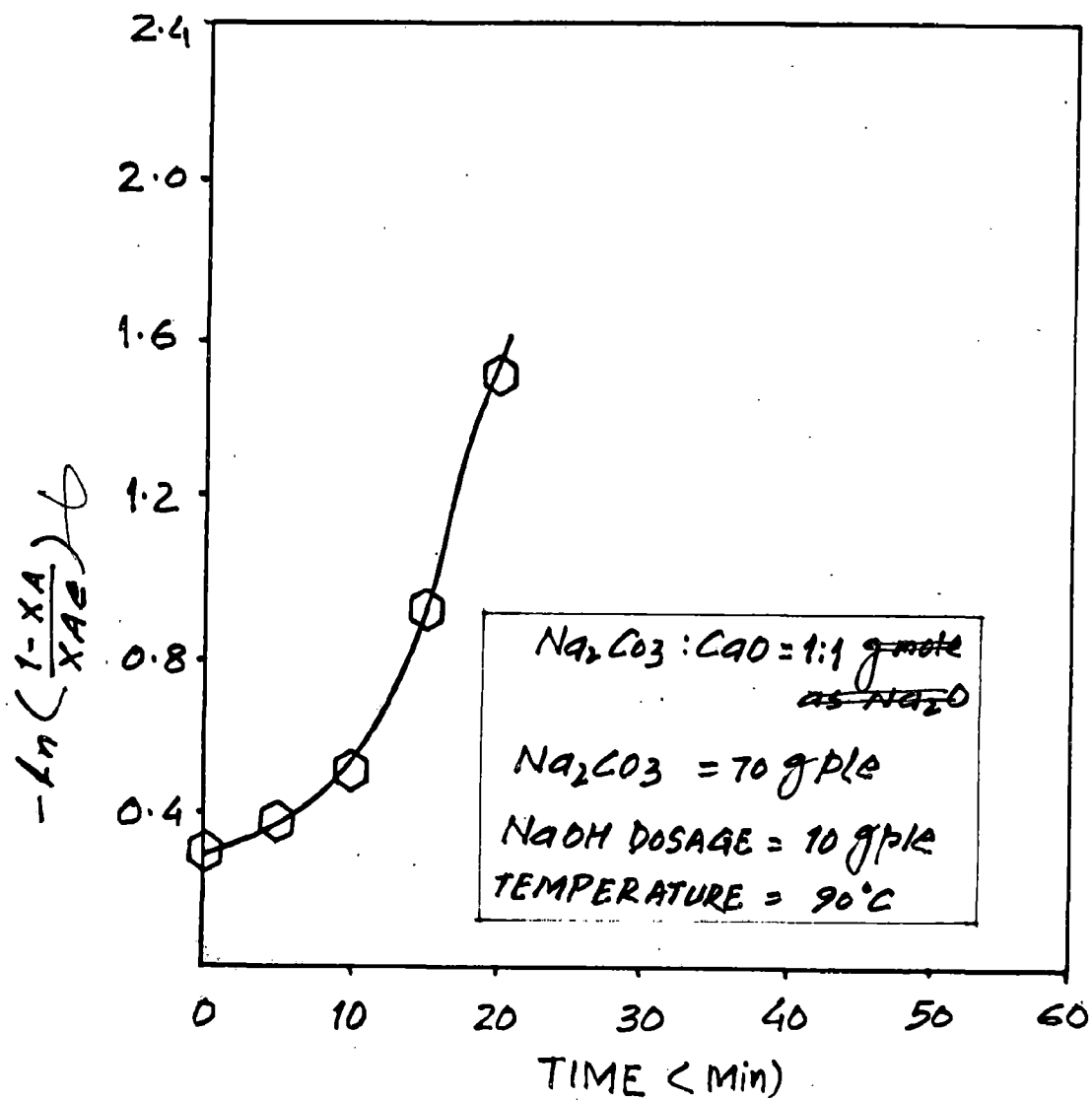


FIG. 26, TEST FOR THE FIRST ORDER
FOR CAUSTICIZING REACTIONS.

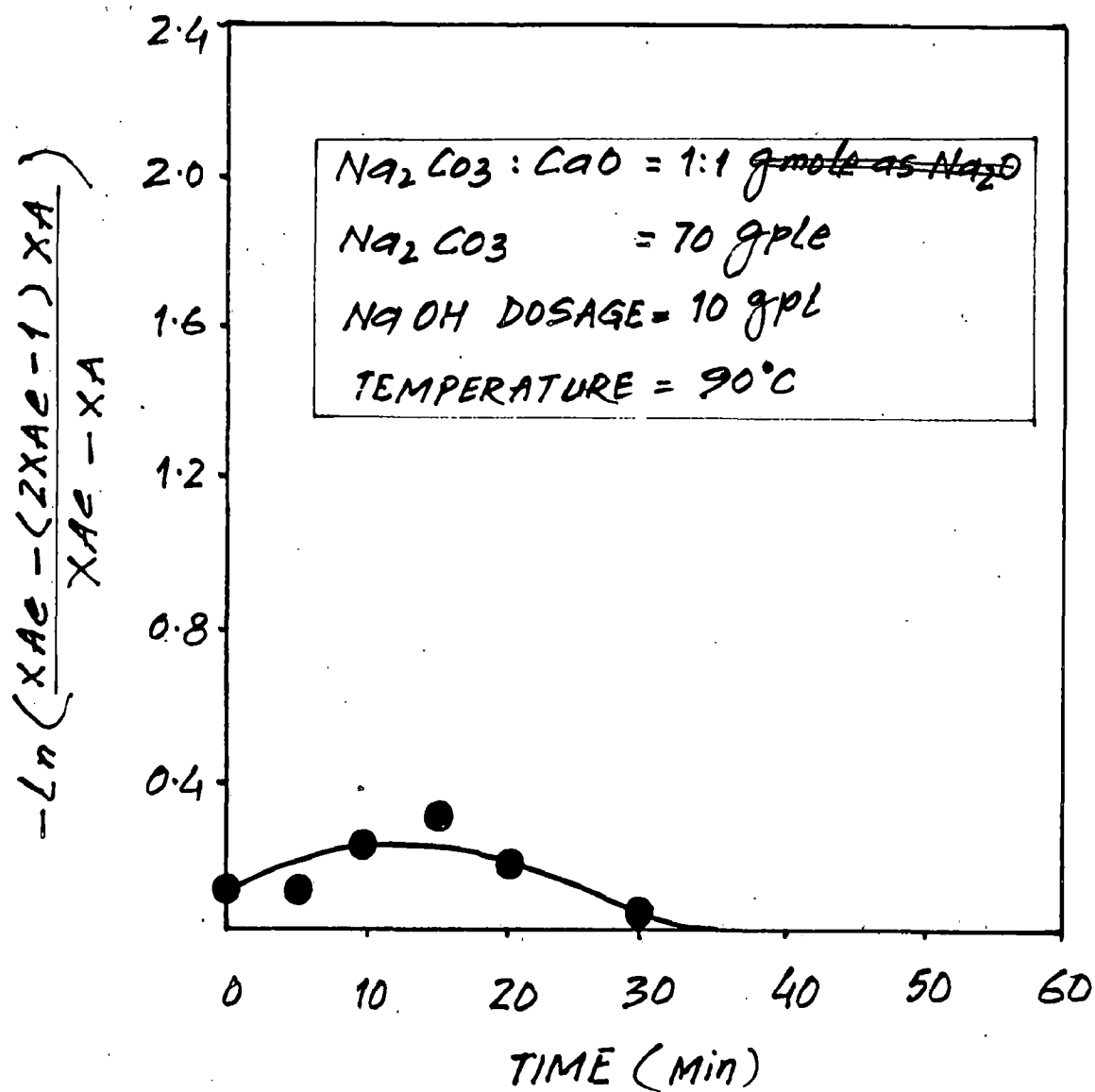


FIG. 27, TEST FOR THE SECOND ORDER FOR CAUSTICIZING REACTIONS.