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REACTION OF LIME IN SODIUM ALUMINATE LIQUORS

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Abstract

The method of process carbonate removal from sodium aluminate liquors by sidestream reactions with lime has been reviewed. The paper summarizes original work on this subject and exemplifies the transition to the efficient technique now used by the Reynolds Metals Company. A comparative historical description of the causticization process is presented with emphasis placed on more recently developed systems, both domestic and foreign, in the alumina industry. The technology employed by Reynolds Metals Company for solving the problems of overcoming the accumulation of sodium carbonate in Bayer plant liquors is reviewed. A discussion of plant experimental work leading up to the installation of the causticization units is included. Critical parameters required for efficient causticization and the chemistry involved are emphasized.

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Introduction

In the aluminum industry, bauxite is refined using the Bayer process to produce alumina, the first step in manufacturing the metal. "Bauxite" describes an ore for which the mineral content is as follows: Iron 18-22 percent; Silica 0.5-4.5 percent; Titanium 2-4 percent; Phosphate Trace-1.0 percent; Calcium 0.5-3 percent; Alumina (total) 40-50 percent. The alumina which is extractable under normal modern techniques will average 35-48 percent. The compounds given above are easily identified by standard metallurgical techniques. There are, however, inorganic CO_2 bearing materials particularly in Caribbean ores which are extremely difficult to determine with precision. This paper is primarily concerned with the quantity of CO_2 which enters the Bayer process either through converting organic compounds to carbon dioxide or by direct reaction of the Bayer Liquor with CO_2 bearing inorganic compounds. Lime is an economical raw material generally used in the Bayer process for controlling impurities such as CO_2.

Lime is one of the three major raw materials which reflect heavily on the conversion cost for producing alumina. While this paper will basically describe reactions of lime with CO_2, lime is also used as a filter aid and to control P_2O_5 in sodium aluminate liquors.

In a 3000 tons per day alumina plant, using a mixture of Caribbean ores, the demand for CO_2 removal (as CaO) will be 50-200 tons per day. Additionally, P_2O_5 input would consume an additional 20-70 tons per day CaO. The lime is also consumed by competing reactions with $NaAlO_2$, NaF, Na_3PO_4, and sodium organics (1). Equations for some of the reactions include:

1. $CaO + H_2O \rightleftharpoons Ca(OH)_2$
2. $Na_2CO_3 + Ca(OH)_2 \rightleftharpoons 2NaOH + CaCO_3$
3. $2NaAlO_2 + 3Ca(OH)_2 + 4H_2O \rightleftharpoons 3CaO{\cdot}Al_2O_3{\cdot}6H_2O\downarrow + 2NaOH$
4. $2Na_3PO_4 + 3Ca(OH)_2 \longrightarrow Ca_2(PO_4)_2\downarrow + 6NaOH$
5. $Na_2C_2O_4 + Ca(OH)_2 \longrightarrow CaC_2O_4\downarrow + 2NaOH$
6. $2NaF + Ca(OH)_2 \longrightarrow 2NaOH + CaF_2\downarrow$

The reactions listed above form highly crystalline compounds when the holding temperature is in the range of 205-215 °F. In plant practice, however, the liquors being treated are at somewhat lower temperatures. It has been shown that multiple-hydrated forms of calcium aluminate hydrates actually result as shown in Table I.

Table I X-ray Diffraction Analysis of Spent Lime Sludge

Chemical Form	Molecular Form
$CaCO_3$	$CaCO_3$
$3CaO{\cdot}Al_2O_3{\cdot}CaCO_3{\cdot}11H_2O$	$3CaO{\cdot}Al_2O_3{\cdot}CaCO_3{\cdot}11H_2O$
$Ca_3Al_2O_6{\cdot}8\text{-}12H_2O$	$3CaO{\cdot}Al_2O_3{\cdot}8\text{-}12H_2O$
$Ca_3Al_2(OH)_{12}$	$3Ca(OH)_2{\cdot}2Al(OH)_3$
$Ca_{16}Al_8(OH)_{54}CO_3{\cdot}21H_2O$	$15Ca(OH)_2{\cdot}8Al(OH)_3{\cdot}CaCO_3{\cdot}21H_2O$
$Ca_2Al(OH)_7{\cdot}3H_2O$	$2Ca(OH)_2{\cdot}Al(OH)_3{\cdot}3H_2O$

It is clear that by use of X-ray diffraction techniques, the compound formed may be more readily identified, thus irregularities in the compounds formed can be explained; this is, additional loss of Al_2O_3 and a corresponding loss of lime efficiency for the CO_2 reaction.

In standard analytical techniques the composition is generally shown as the oxide, such as in Table II of a typical spent lime sludge.

Table II Chemical Analysis of Spent Lime Sludge

CaO	41.80 %
Al_2O_3	21.18 %
CO_2	5.24 %
LOI	35.98 %
SiO_2	0.49 %
Fe_2O_3	0.22 %
P_2O_5	Trace
TiO_2	Trace

Analytical

The reaction with lime which is the most costly is the tendency for lime to react with alumina in solution to form an insoluble precipitate of tricalcium aluminate or, at temperatures below 205 °F, compounds combining calcium and aluminum hydroxides in highly hydrated states. The rate of these reactions to proceed is controlled by the concentration of CaO, alumina, soda and temperature. Tricalcium aluminate is an insoluble scale-like material which forms on vessel walls and in pipe lines. It can not be chemically dissolved readily with the normal cleaning reagents found in the Bayer plant; therefore, the loss is not only that of materials, but manpower is required to remove this scale from vessels and pipe lines.

A second important reaction is the combination of calcium with titanium. Relatively little is known about the chemistry of this reaction, however, by experience it has been shown that the reaction forms a compound when the mixture is subjected to temperatures in the range of 400-490 °F. As the sodium aluminate liquor temperature reaches the upper limits of this range, a calcium titanate scale is formed which is very hard, brittle, insoluble precipitate or "scale". These temperature conditions are normally found in the "digestion" process. The scaling surface will normally be the digester vessel walls or the tubes of heat exchangers preceding the digester vessels. For this reason, CaO can not be effectively used to control impurities if the process temperature is elevated. A typical analysis of the calcium-titanate scale is shown in Table III.

Table III Typical Calcium Titanate Scale

LOI	4.0 - 5.5 %
SiO_2	5.5 - 7.0 %
R_2O_3	59.0 - 62.5 %
Fe_2O_3	18.6 - 22.5 %
TiO_2	28.5 - 30.5 %
P_2O_5	0.5 - 1.5 %
Al_2O_3	8.5 - 11.5 %
CaO	19.0 - 21.5 %
Na_2O	3.0 - 7.5 %

CO_2 Control Systems

Methods for reacting CaO with CO_2 have been reported by many companies in the alumina industry. Originally, sodium aluminate liquors were treated as two-phase systems of only soda ash and caustic in a water solution (2). Gross discrepancies were observed due to the many side reactions.

Most major manufacturers of alumina have at one time used the "inside causticization" process probably introduced by Hall (3). This method consists of charging lime, soda ash and bauxite along with the recycled Bayer liquor to convert Na_2CO_3 to NaOH in the digesters. This method has several disadvantages, some of which are: 1. The causticization efficiency is very poor, possibly as low as 20-30%. This results in an excess lime consumption with accompanying additional cost; 2. The caustic to soda ratio (C/S) in a Bayer liquor system using "inside causticization" ranges from 0.700 to about 0.800. These liquors contain an undue quantity of CO_2 as Na_2CO_3. This sodium carbonate serves no useful purpose and therefore multiplies the processing cost. It lowers the efficiency of the alumina extraction and recovery process; 3. In more modern plants processing mono-hydrate bauxite, elevated temperatures cause a side reaction with TiO_2; and 4. The efficiency of lime causticization in the inside causticizing circuit is low due to the high degree of reversibility which is caused by the presence of relatively high concentrations of caustic and alumina in solution. Additionally, the causticization efficiency is lowered by the presence of bauxite residue (red mud) which deposits on the particles of lime and prevents them from entering into reaction with the sodium carbonate present.

A more modern approach to CO_2 removal was first published in 1965 (4) and is shown on Fig. 1. This method of sidestream causticization consists of taking a portion of the overflow from the first mud washing step, which is relatively clear liquor, injecting steam into a stirred tank reactor to which unslaked lime is added by a weight controller to effect causticization of the sodium carbonate in this liquor stream. The chemical reactions involved include slaking of the lime to form calcium hydroxide with sodium carbonate present in the stream being causticized. Additionally, a side reaction occurs in which calcium hydroxide reacts with sodium aluminate to form sodium hydroxide and calcium aluminate. The effluent from the first stage stirred tank reactor is pumped to a

second stage stirred tank reactor where additional liquor is introduced for causticization by reaction with any excess calcium hydroxide that is present.

The effluent from the second stage stirred tank reactor is pumped through the filter presses to wash the mud residue from filtration of the Bayer liquor slurry. The second stage causticization reactor effluent passes through the mud removing a large portion of the caustic liquor which is left in this mud at the end of a filter press cycle. The dilute liquor, after passing through the mud to recover liquor and/or valuable chemical contents from this mud, is added into the main clarified liquor stream which is then routed to the precipitation area.

Lime efficiency in this causticization circuit is reported to be affected by liquor temperature, reaction time, liquor flow rate, lime particle size and liquor clarity.

A plot of lime efficiency versus liquor temperature is shown in Fig. 2. Percent lime efficiency increases with liquor temperature almost linearly. Reaction time was held constant at ten minutes during this phase of the study and liquor temperature was varied from 124 °F to 212 °F.

Plots of lime efficiency versus reaction time are also shown in Fig. 2 for three liquor temperatures. At 180 °F the lime efficiency increased from about 60% after ten minutes reaction time to 75% with twenty minutes reaction. At 200 °F the lime efficiency increased from about 80% after ten minutes reaction time to 88% with twenty minutes reaction time. At 212 °F the lime efficiency increased from about 83% after ten minutes reaction time to 90% with twenty minutes reaction time.

Another sidestream system in operation in the Caribbean area reportedly adds lime slaked in a diluted process liquor to a portion of the overflow from the first stage red mud washers, Fig. 3. This stream is at a concentration of 85-90 g/kg soda and a C/S ratio of 0.830. A live-steam heater raises the temperature from about 170 °F to near 200 °F. This heated liquor then goes to a causticizer where the slaked lime is introduced and the C/S ratio is brought up to near 0.890. The greater portion of this causticized solution is then sent to the second stage red mud presses where it is used as a filter aid in the filter presses. This plant also uses lime to react with sodium oxalate compounds.

Yet another system adds slaked lime to the lower soda concentration stages of the red mud washing circuit, Fig. 4, in order to take advantage of the reversible reaction of calcium aluminate reverting as shown below:

$$3CaO \cdot Al_2O_3 \cdot 6H_2O + 3Na_2CO_3 = 3CaCO_3 + 2NaAlO_2 + 4NaOH$$

Design Parameters

The Sherwin Plant of Reynolds Metals Company has modernized their sidestream system due to increased inputs of CO_2 from organic bearing bauxites. Laboratory data such as that shown on Table IV indicated that a controlling factor for design of the system would be the total soda

Table IV Typical Analytical Data

Sample No.	A	B	C	D	E	F	G	H
Solids Analysis (Percent)								
Moisture @ 110 °C	64.12	54.17	65.13	52.92	57.34	58.79	60.86	45.43
LOI @ 1000 °C	38.75	35.79	40.35	39.40	39.85	30.83	31.72	36.40
SiO_2	0.51	1.12	0.26	0.42	0.44	1.25	1.71	2.15
Fe_2O_3	0.99	8.79	0.10	0.16	0.12	17.01	11.02	8.14
TiO_2	0.13	1.16	0.04	0.22	0.04	2.12	1.69	1.05
P_2O_5	0.24	0.37	0.13	0.04	0.15	0.47	0.55	0.59
Al_2O_3	13.25	8.40	13.81	9.05	11.37	8.62	12.73	5.29
CaO	44.45	42.87	44.08	49.74	47.94	36.61	38.71	45.29
Na_2O	0.35	0.84	0.31	0.38	0.30	1.00	0.99	0.83
CO_2	15.55	23.27	16.00	24.67	20.48	18.66	15.12	26.49
$CaCO_3$ equivalent to CO_2	35.34	52.89	36.36	56.07	46.55	42.41	34.36	60.21
CaO equivalent to CO_2	19.79	29.62	20.36	31.40	26.07	23.75	19.24	33.72
% CaO reacted with CO_2	44.52	69.09	46.20	63.13	54.38	64.87	49.70	74.45
% CaO reacted with Al_2O_3	49.18	32.33	51.69	30.02	39.13	38.85	54.26	19.27
Liquor Analysis (g/kg)								
A	54.64	52.64	53.42	48.74	52.95	52.85	56.43	51.39
C	94.24	87.86	89.72	83.37	88.95	88.42	93.98	84.41
S	106.88	101.21	102.62	92.77	101.00	100.00	108.49	97.13
C/S (Treated)	0.882	0.868	0.874	0.899	0.881	0.884	0.867	0.869
C/S (Untreated)	0.845	0.826	0.832	0.845	0.834	0.834	0.847	0.835
Specific Gravity @ 80 °F	1.152	1.144	1.147	1.132	1.145	1.144	1.155	1.138

concentration. Without major expenditures the choices for CO_2 bearing streams to treat were limited to the first stage mud washer overflow or the sixth stage mud washer overflow. The amount of CO_2 to be removed made it clear that the high concentration liquor streams must be treated. A significant breakpoint was noted at a soda concentration of about 97-105 g/kg. This concentration is a result of underflow mud consistency and washwater rates. These conditions were examined in design calculations and analytical tests.

A second design parameter considered was retention time. Using selected laboratory data it appeared that the reaction is essentially first order up to sixty minutes retention time. After this time, side reactions and reversibility become important. The data after the sixty minutes time seem to fit the second order equation quite well. The reaction is:

$$Na_2CO_3 + Ca(OH)_2 \underset{K_2}{\overset{K_1}{\rightleftharpoons}} 2NaOH + CaCO_3$$

The rate constant K_2 is small until sixty minutes retention time is reached. After that, reaction tends to reverse.

It was also calculated that $K_1 = 0.0345\ Min^{-1}$ which gives a half-life of 20.1 minutes, or the reaction will go half way to completion in 20.1 minutes.

The second order curve is applicable after sixty minutes. For data collected at 210 °F the curve as a zero slope indicated a low rate constant.

$$K_2 = 0.0038\ Min^{-1} \text{ thus half-life} = 182\ Min$$

This shows how influential the back reaction can be after the sixty minutes retention time. It holds that the rate constant is a function of temperatures indicated in Table V.

Table V Lime Reaction Rate Constants

Temp °F	K_1, Min^{-1}	K_2, Min^{-1}
185	0.0184	0.0028
195	0.0217	0.0036
210	0.0345	0.0038

Further experimentation showed that an intimate mixing during the first ten to twenty minutes was essential to obtain maximum efficiency.

Lime efficiency calculations have been published by Adamson, Bloore and Corr (5) which are based on the experimental work of Goodwin (6), Littman and Gaspari (7), and Olsen and Direnga (8). This approach requires that soda concentration be on a total alkalinity basis. By assuming a two-hour total retention time and varying soda concentration, the equilibrium C/S ratio ($P\infty$) is determined. By determining the final C/S ratio (P_2) we compute the resulting ratio ($P_2/P\infty$).

With the ($P_2/P\infty$) value known, by using Fig. 5 we find the value of $Pa/P\infty$. Pa is defined as the theoretical C/S if all lime added was converted to $CaCO_3$. Once Pa is calculated substitute this value in $\frac{P_2-P_1}{Pa-P_1} \times 100$ to find the lime efficiency.

The theoretical lime efficiency is computed from $Pa/P\infty$.

A second method for determining lime efficiency is by analysis of the sludge formed from the reaction. A typical comparison of these expressions for efficiency with varying soda concentration is shown in Table VI.

Table VI Comparison of Lime Efficiency

Na_2CO_3 g/kg	UZA g/kg	Resultant C/S Pa	Efficiency by Liquor Analysis	Efficiency by Sludge Analysis
95	115	0.890	90 %	65 - 72 %
100	121	0.880	89 %	62 - 68 %
105	127	0.870	88 %	60 - 63 %

The system in use at Sherwin Plant provides for the following design conditions: 1. retention time - up to 2 hours; 2. temperature - up to atmospheric boiling; 3. soda concentration - not to exceed 110 g/kg; 4. resultant C/S - up to 0.900.

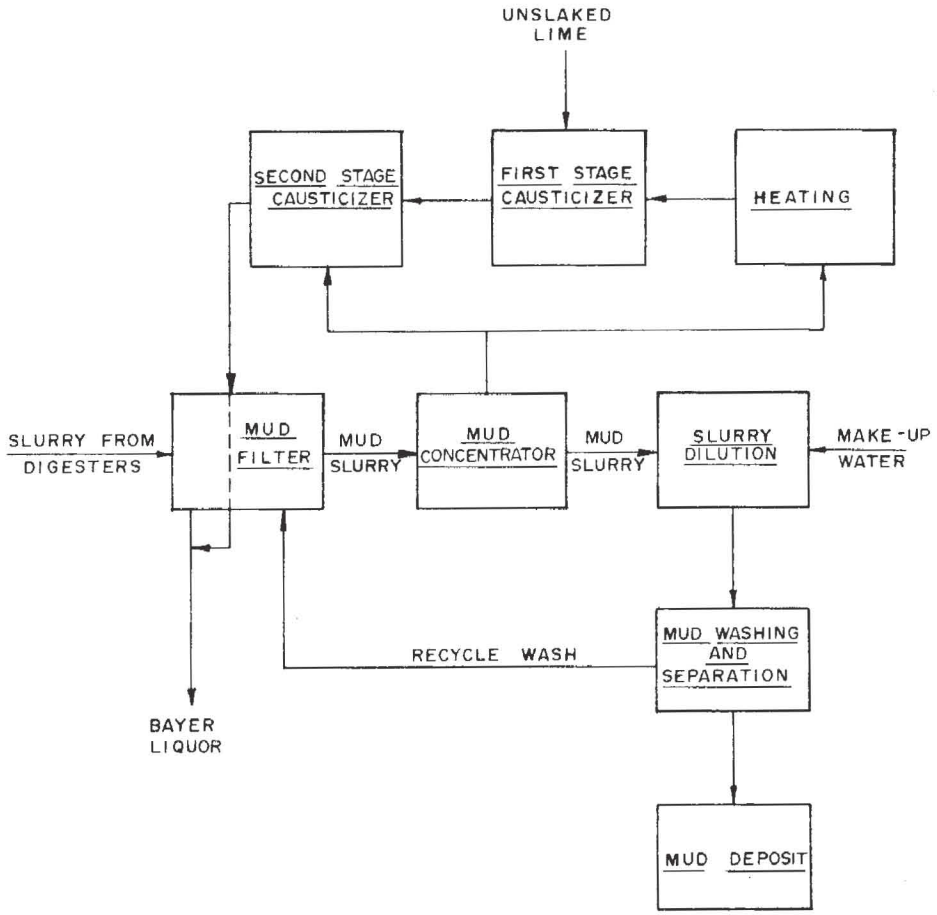
A premix tank (15' x 32') is equipped with a top entering mixer and draft tube. The holding tanks are equipped with side entering mixers. Approximately 175-200 Hp is consumed to provide adequate mixing.

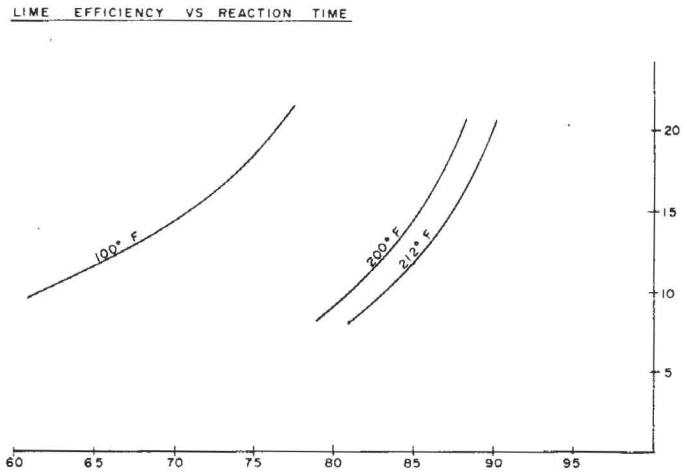
The schematic diagram, Fig. 6, shows this system.

Conclusion

The advantages of the "sidestream" systems over the "inside causticization" systems are primarily: 1. lower alumina loss; 2. greater efficiency due to fewer interfering side reactions; and 3. lower scaling of process equipment. The Sherwin Plant system is apparently more efficient than other "sidestream" systems due to the following factors. All the treated stream is handled in a "pre-mix" tank where simultaneous heating and addition of slaked lime result in low alumina loss. Additionally, the desired C/S ratio can be decreased as input of CO_2 decreases resulting in more efficient reaction rates. A side benefit has also been noted which was not expected from design data. The installed mixing equipment greatly reduces scaling rates by keeping particles of red mud and calcium aluminate in suspension.

FIG 2


UNSLAKED LIME
SECOND STAGE CAUSTICIZER
FIRST STAGE CAUSTICIZER
HEATING
SLURRY FROM DIGESTERS
MUD FILTER
MUD SLURRY
MUD CONCENTRATOR
MUD SLURRY
SLURRY DILUTION
MAKE-UP WATER
RECYCLE WASH
MUD WASHING AND SEPARATION
BAYER LIQUOR
MUD DEPOSIT


LIME EFFICIENCY VS REACTION TIME
100° F
200° F
212° F
20
15
10
5
60
65
70
75
80
85
90
95

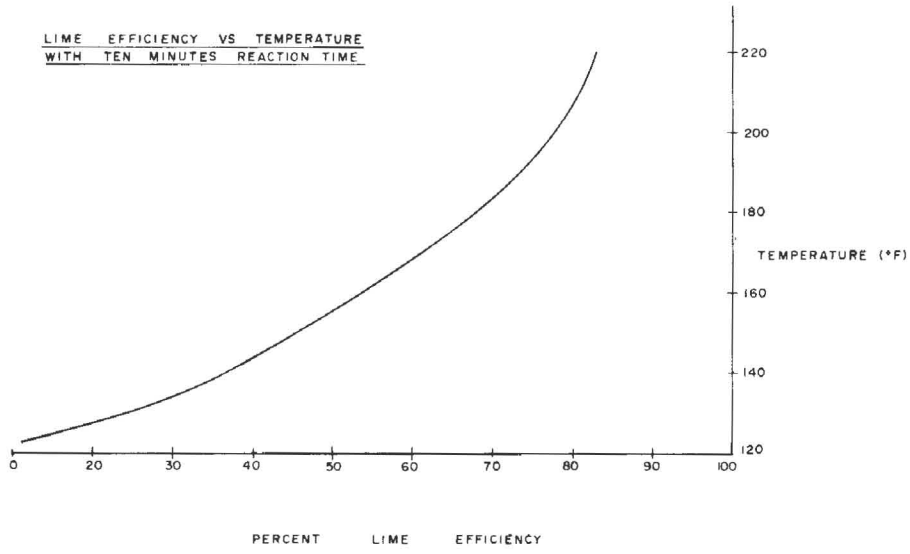

LIME EFFICIENCY VS TEMPERATURE
WITH TEN MINUTES REACTION TIME
220
200
180
160
140
120
TEMPERATURE (°F)
0
20
30
40
50
60
70
80
90
100
PERCENT LIME EFFICIENCY

FIG 3

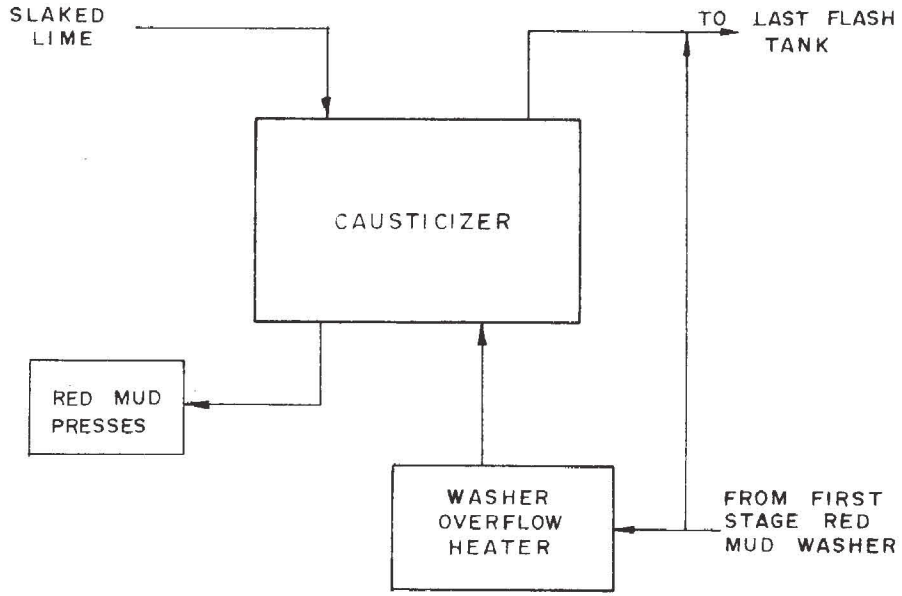
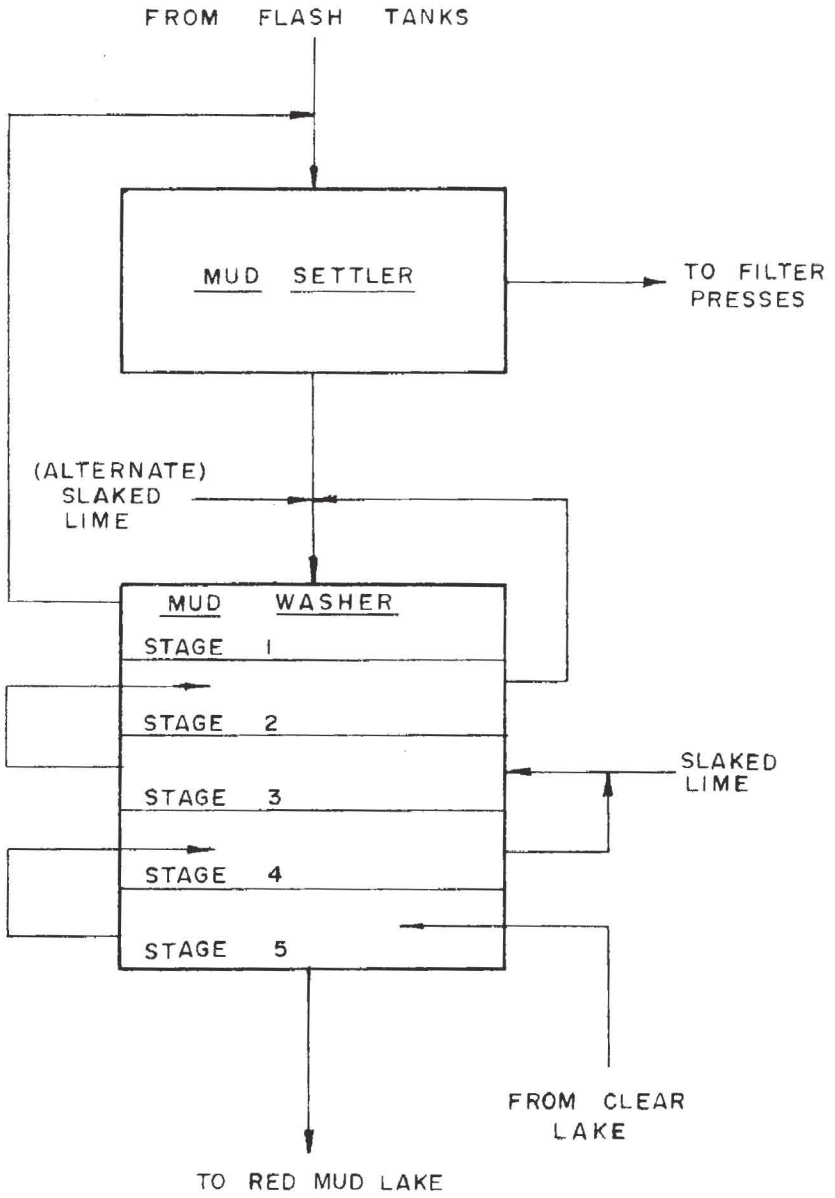

SLAKED LIME
TO LAST FLASH TANK
CAUSTICIZER
RED MUD PRESSES
WASHER OVERFLOW HEATER
FROM FIRST STAGE RED MUD WASHER

FIG 4


FROM FLASH TANKS
MUD SETTLER
TO FILTER PRESSES
(ALTERNATE) SLAKED LIME
MUD WASHER
STAGE 1
STAGE 2
STAGE 3
STAGE 4
STAGE 5
SLAKED LIME
FROM CLEAR LAKE
TO RED MUD LAKE

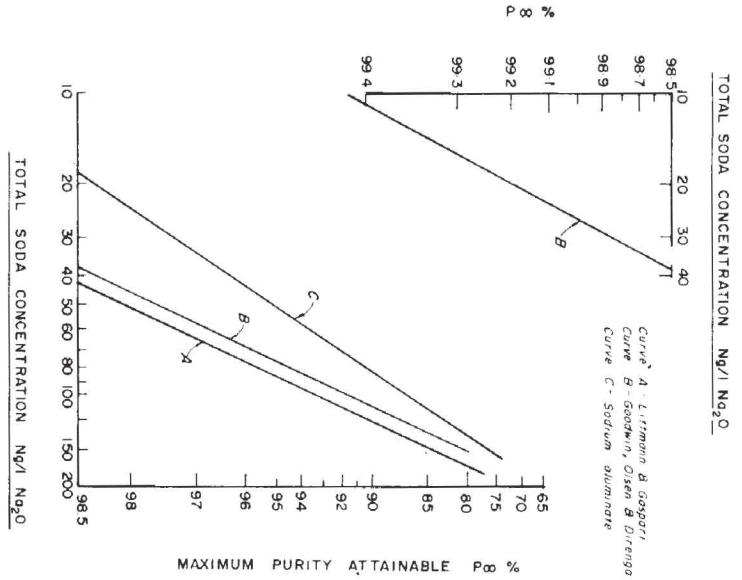

P ∞ %
TOTAL SODA CONCENTRATION Ng/l Na_2O
MAXIMUM PURITY ATTAINABLE P∞ %
Curve A - Lehmann & Gaspari
Curve B - Goodwin, Olsen & Direngo
Curve C - Sodium aluminate

FIG. 5

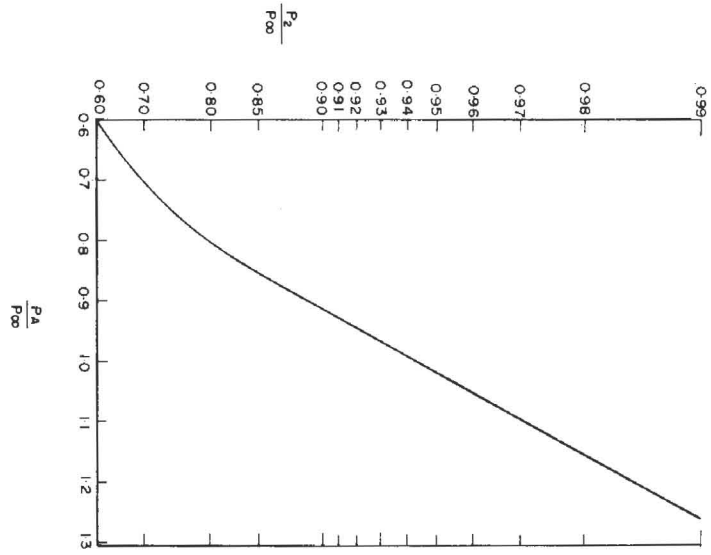
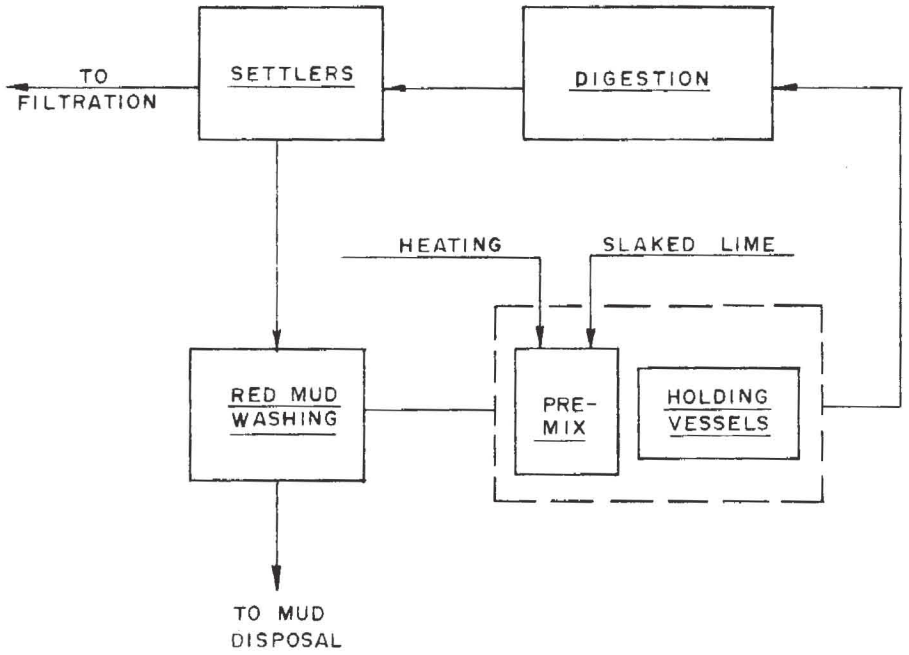

$\frac{P_2}{P_\infty}$
$\frac{P_A}{P_\infty}$

FIG. 6


TO FILTRATION
SETTLERS
DIGESTION
HEATING
SLAKED LIME
RED MUD WASHING
PRE-MIX
HOLDING VESSELS
TO MUD DISPOSAL

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