SO_2-SCRUBBER TECHNOLOGY - DOUBLE ALKALI MODE

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ABSTRACT

Double alkali (D/A) processes for the desulfurization of flue gases occupy an increasingly important role in applied technology.

D/A processes involve two steps, namely, scrubbing and regeneration. In the scrubbing step, the alkali (Na_2SO_3) reacts with SO_2. In the regeneration step the acid formed, $NaHSO_3$, reacts with an alkali to regenerate Na_2SO_3.

This study was focussed on the regeneration step. Regenerants investigated were slurries of lime and limestone. The major factors studied were reactor configuration and mixing patterns.

These systems were investigated in a batch, backmix, and plug-flow reactors. Reactants were mixed to effect a large range of degrees of mixing.

It was observed that if the lime and Na_2SO_3 were effectively mixed initially, the regeneration of Na_2SO_3 occurs instantaneously.

In the limestone system, efficient mixing obviated the need for further mixing of reactants to effect regeneration. It is conjuctured that further mixing may even be detrimental. These results indicate that optimum design of regenera-

tion must take into account the possible formation of agglomerations of "blinded" reactants. This "blinding" results from the deposition of solid insoluble products around clusters of solid reactants. This model explains why processes occur more efficiently with high initial mixing.

These are systems in which products are less soluble than the reactants. It is this difference which makes "blinding" occur to a significant degree.

These studies cannot be used to predict the optimum degrees of mixing necessary in a plant operation. The scale of these studies was too low. However, these studies uniquely point out the need for efficient initial mixing and also, a model to explain this need.

APPROVAL OF THESIS

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FACULTY COMMITTEE

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DEDICATION

To my parents:

This tribute for their selflessness

and

To my brothers, Sham and Balram:

With grateful thanks for their encouragement,

help and advice.

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CHAPTER I

Double Alkali Processes

One of the combustion products of a power plant operation - SO_2 - has been the subject of much investigation and technology aimed at preventing its entrance into the atmosphere because it is a harmful pollutant. It is one of the few air contaminants which has been subjected to regulation under the Clean-Air Act. This thesis will be mainly concerned with one of the major processes for removing SO_2, namely, the double alkali (D/A) process.

In the D/A processes, the flue gas is scrubbed with a homogeneous alkali solution of sodium. No precipitate forms in the scrubber. Therefore, scaling cannot occur and the absorption is simpler because a solid phase is not present.

Comparing the D/A process with its precursors, namely, the lime or limestone process, one observes that the reaction schemes are similar. In both processes, the SO_2 gas is absorbed to form a bisulfite (HSO_3^-) salt which is then converted to the insoluble calcium sulfite ($CaSO_3$). To some extent calcium sulfate ($CaSO_4$) forms because the HSO_3^- solution undergoes partial oxidation due to the oxygen present in flue gas. In the lime or limestone process, the scrubber operation contains a holding tank. HSO_3^- forms in the scrubber and the $CaSO_3$ mainly forms in the holding tank. For the D/A process, HSO_3^-, also, forms in the scrubber but the formation of insoluble $CaSO_3$ takes place in an external regenerator independent of the scrubber. Stabler plant operation is obtained because scaling and plugging does not occur since there are no solids present in the scrubber loop.

CHAPTER II

Literature Survey

Introduction. A number of feasible processes have been reported both on sodium/calcium[1-5] and other basic alkali ion/calcium double alkali process[7-11]. There has also been a distinction made between the modes of operation, namely, the dilute mode and concentrated mode of operations.

In the dilute mode the "throwaway" product is $CaSO_4$; in the concentrated mode $CaSO_3$. The terms "dilute" and "concentrated" refer to the active Na levels, i.e., the concentration of sodium associated with anionic species capable of reacting with SO_2. While Na associated with SO_3^{-2} is considered active because SO_3^{-2} can react with SO_2, Na associated with SO_4^{-2} is considered inactive because Na cannot react. When the active Na level is of the order of 1 molar Na, the mode is considered dilute, in contrast, at an active sodium level of 2 molar Na the mode is considered concentrated. Though there are two modes of operations available, the mode of operation is fixed for a given power plant of defined flue gas composition and is not interchangable.

For a low SO_2 content, it is necessary to operate dilute; but for a high SO_2 content the concentrated mode is preferred. Interchanging of modes is not possible because the nature of the process equipment differs significantly.

In spite of these differences, a "black box" view of these processes reveal that they are essentially the same in that they have identical unit operation steps, namely, absorption of SO_x from flue gas with a soluble scrubber liquor and an external regeneration loop to recycle the scrubber liquor[2] (Fig. 1).

The object of this literature search is to (1) document the reaction schemes in the absorption and regeneration steps for both the Na/Calcium and other basic alkali ion/calcium based double alkali processes (2) to discuss the dilute and concentrated modes of operations and (3) to analyze the available scrubber and regeneration data.

<u>Absorption</u>. Double alkali systems are frequently referred to as "sodium" ion scrubbing systems[3]. As there are other ion scrubbing systems as well, this is a misnomer. The absorption equations appropriate for a given sodium ion scrubbing process is shown in Table 8. Sodium or, for that matter, other ions are present only for maintaining electrical neutrality. In reality, the absorption reactions involve reaction of SO_2 with an aqueous

base such as OH^-, $SO_3^=$, HCO_3^- or $CO_3^=$ rather than Na^+. For example

$$2OH^- + SO_2 \rightarrow SO_3^= + H_2O$$

$$SO_3^= + SO_2 + H_2O \rightarrow 2HSO_3^-$$

Sodium associated with these anions is called "active".

<u>Oxidation</u>. Oxidation in a D/A system refers to the conversion of total oxidizable sulfur (TOS) to sulfate by one of the following equations:

$$SO_3^= + 1/2\ O_2 \rightarrow SO_4^=$$

$$HSO_3^- + 1/2\ O_2 \rightarrow SO_4^= + H^+$$

$$SO_2 + 1/2\ O_2 \rightarrow SO_3\ (SO_3 + H_2O \rightarrow H_2SO_4)$$

Oxidation in the system has the effect of changing active alkali to inactive alkali[3]. As was mentioned before this means that the SO_4^{-2} can not react with SO_2.

Oxidation can occur in the scrubber, reaction vessels, or in the regenerator. In general, the rate of the oxidation in the system is thought to be the function of rate of dissolution of oxygen, pH of the scrubbing solution, concentration of reactant, impurities present in the scrubber solution and residence time. Thus the oxidation rate is affected by the following factors: (1) The composition of the scrubbing liquor (liquor containing high concentration of dissolved salts may absorb oxygen more slowly); (2) the O_2 content in flue gas; (3) the presence of impurities in coal; (4) on lime or limestone; and (5) the design of equipment. The percent oxidation rate is defined by the following expression:

$$\text{Oxidation Rate, \%} = \frac{(SO_4^{=} \text{ leaving the system})}{(\text{Total Sulfur Collected})} \times 100$$

<u>Scrubber solution</u>. In the concentrated mode of operation, the pH of the solution is approximately 6.5. At higher pH values, above 7, carbon dioxide absorption becomes significant and can lead to $CaCO_3$ scaling. Below pH 6, the vapor pressure of SO_2 increases dramatically for concentrated systems and can lead to equilibrium limited scrubbing conditions. This is demonstrated in Fig. 2 in which SO_2 vapor pressure is plotted as a function of pH for a solution temperature of 130°F (a typical saturation temperature for a boiler flue gas stream)[5]. The vapor pressure of SO_2 over dilute solutions is not significant, as can be seen from the line in the figure calculated from the Henry's law constant for SO_2 and water. This calculation takes into account the first and second ionization constants for a sulfurous acid, for a solution with a total oxidizable sulfur (TOS) level of 0.03 gram moles/liter and an ionic strength of 0.3 gram moles/liter.

However, for concentrated solution, SO_2 vapor pressure at a pH 6 is approximately 100 ppm and increases rapidly with decreasing pH.

For this reason FMC[5] prefers to operate the scrubber operation at a pH range of 6 to 7 and probably at a set point of 6.5 where the sulfite/bisulfite system is highly buffered.

Regeneration. Regeneration processes involve the regeneration of sodium and other alkali from their inactive sulfate and bisulfite forms (no capability of absorbing SO_2) to active forms[3].

Regeneration chemistry is complicated because the Na_2SO_4 formed in the scrubber liquor via oxidation of sodium sulfite solution is not readily convertible to the active sodium form by reacting it with $Ca(OH)_2$ (lime) or $CaCO_3$ (limestone).*

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*One factor that complicates the regeneration chemistry is the difficulty of regenerating SO_4 associated with the sodium ion. The equilibrium data show that $CaSO_4$ is more soluble than $CaSO_3$ by two orders of magnitude. However, it has been reported that $CaSO_4$ precipitates under subsaturation conditions by forming a solid solution with $CaSO_3$ and when this occurs, it pulls out (purges) a large amount of sodiumsulfate with it. On one hand, the subsaturate precipitation of $CaSO_4$ is beneficial; however, the beneficial effect is offset by the simultaneous purge of Na_2SO_4. The reason is not clearly understood. Various theories [12,13] have been proposed and the area is the subject of active investigation by several groups.

In general, flue gas and solution composition controls the rate of sulfate formation[3]. An increase in the ionic strength, principally in the form of sulfate concentration, reduces the net soluble sulfate formation rate. The effect of increasing oxygen concentration and fly ash generally increases oxidation rates but no correlation has been developed to date. Residence time should be low as possible in all reactors, mixers and regenerators to minimize absorption of oxygen from air[5].

Phillips[4] has shown that Na_2SO_4 is not easily regenerable as NaOH in dilute system (dilute mode) using lime. This is because $CaSO_4 \cdot 2H_2O$ (gypsum) is considerably more soluble than $CaSO_3$; hence causticization of Na_2SO_4 becomes difficult in the presence of appreciable amounts of $SO_3^=$ or OH^-.

To provide for sulfate causticization, the recommended operating conditions are 0.1 molar OH^- and 0.5 molar $SO_4^=$ for design purpose. The equilibrium caustic formation in the $Ca(OH)_2$ - Na_2SO_4 solutions at 120°F is shown in a paper published by Phillips[15]. It again emphasizes the fact that gypsum precipitation occurs by sodium sulfate-lime reaction only at very dilute active sodium concentrations.

For the concentrated mode, causticization is not practiced in the USA. However, in Japan $CaSO_3$ use as a land refill is not allowed due to governmental regulations.

Two options exist. The first method adopts a procedure of precipitating gypsum by dissolving $CaSO_3$ in sulfuric acid solution (equation R VIII of Table 2). Efficiency is low, as sulfuric acid can be consumed by other species such as unreacted lime or limestone. The second technique involves diverting a part of the scrubber effluent into a holding tank containing $CaSO_3$ liquor and bubbling oxygen in the presence of acid.

Borgwardt[13] of EPA observed that the sulfate to sulfite ratio is a direct function of sulfate ion activity in the mother liquor. For a solution with no chloride and magnesium levels below 1000 ppm, the sulfate to sulfite molar ratio in the mixed crystal solids was found to reach a maximum level of 0.23. This is equivalent to a $[SO_4^{=}]$/total $[SO_x]$ ratio in the solids of 0.19. This was also observed by Arthur D. Little, Inc. (ADL) in their pilot work for a concentrated mode operation.

In Stone and Webster's ionic process, sulfate removal is effected electrolytically. Equation (RX) of Table 2 shows the stoichiometry and is the basis for Kureha/Kwawsaki Japanese pilot test unit. The process is supposed to be less expensive than sulfuric acid oxidation technique, and sodium losses are reported to be half the normal losses.

Dilute mode processes (Western low sulfur coals). For power plants that have high excess air and/or low flue gas SO_2 concentrations, the oxidation rate of the absorbed SO_2 changes the chemical equilibrium relationships in the system (Equation AI, AII and AIV of Table 1). The oxidation rate is not easily controllable due to high O_2 levels. The major alkali in the process is NaOH (sodium hydroxide) and not Na_2SO_3 (sodium sulfite) and the calcium ion concentration in the regenerated liquor is as high as 500 ppm. In order to control chemical scaling of the scrubber due to intrusion of calcium via the regenerated liquor return stream, a calcium softening step[2] by the addition of soda ash is utilized (Fig. 3). The liquor flow volumes is dictated by the concentration of NaOH.

Another way of distinguishing a dilute mode from concentrated mode is to examine the solubility parameters. For an ideal system, one can write

$$\frac{[Ca^{++}][SO_4^{=}]}{[Ca^{++}][SO_3^{=}]} = \frac{Ksp_1}{Ksp_2} \simeq 10^2$$

and cancelling Ca^{++} ion concentration

$$\frac{SO_4^{=}}{SO_3^{=}} = K \simeq 10^2$$

This indicates that for an ideal solution, based on theory, simultaneous precipitation of $SO_4^=$ and $SO_3^=$ is not possible when using relatively small quantities of lime slurry for regeneration. Thus, in theory if the ratio of sulfate to sulfite is higher than K, then calcium sulfate should precipitate and if the ratio is lower than the constant only calcium sulfite should precipitate.

However, such simplified criterion is clouded by nonideal behavior; a simultaneous precipitation of both as a mixed crystal or solid solution has been postulated by Borgwardt of EPA[13,16] and supported by ADL work[4].

Considering the nonideal behavior, a ratio of SO_4 to SO_3 can be determined for a given set of conditions and this ratio establishes a definition of 'dilute' or 'concentrated' double alkali systems. If the ratio is such that when either gypsum or gypsum and calcium sulfite coprecipitates with the addition of lime, then the system is 'dilute'. Normal ionic concentrations for the dilute mode operation is 1 molar Na[2]. This variation of the basic double alkali systems provides scale control and process reliability but the capital cost is higher than a comparable concentrated mode due to the equipment for control of the soluble calcium and the higher volume of liquor that must be handled by the post precipitation system.

Concentrated mode (high sulfur Eastern coals). For power plants that have high flue gas SO_2 levels and/or low minimum air, the oxidation rate of the absorbed SO_2 changes the chemical equilibrium relationship to predominantly bisulfite and sulfite. The flue gas is scrubbed with a concentrated sodium bisulfite/sulfite solution to remove SO_2. A bleed stream of spent scrubbing liquor at pH near 6 is reacted with lime to precipitate $CaSO_3$ (calcium sulfite) and the limited amount of $CaSO_4$ that has been formed due to oxidation in the scrubber[2].

The normal ionic concentration for this system is approximately 2 molar Na[2]. In contrast to the dilute mode operation, no softening step is required to control gypsum scaling; in the concentrated mode there is a "built in" softening since the high sulfite concentration keeps the Ca^{++} ion low (sulfite softening) and maintains the scrubber solution unsaturated with respect to the gypsum. Fig. 4 and 5 show the concentrated mode operation as depicted by two different companies (Buell, FMC) and they are essentially the same. Fig. 6 is a schematic for the high chloride process. As indicated, filter cake washing is employed to wash out and recycle the soluble sodium salt to the process. When chloride is absorbed into the scrubbing liquor the sodium chloride concentration builds up.

Washing and recovering the soluble salts from the filter cake to the scrubber reduces the scrubber efficiency as Na is not in the active form. In such cases, a pretreatment of the flue gas via water scrubbing is desirable to absorb chlorine and, to some extent SO_2, thus restoring a stable operation by preventing the depletion of active Na.

In some cases, accumulated sodium chloride concentration as high as 1.5 to 2.0 molar may result, causing sodium sulfate insolubility problems as well as increased usage of soda ash, with higher sodium content in the filter cake. In order to eliminate these problems, a separate precooler section upstream from the scrubber is incorporated. The chlorides and other secondary coal contaminants are removed in a low scrubbing liquor. A slip stream of the resulting acidic solution is neutralized with lime/limestone to produce calcium chloride solution which is used as a final wash on a horizontal filter of the Eimco-Extractor type (Fig. 6). This wash is so designed that the filter cake absorbs the chlorides.

In a further refinement of this process, a fly ash thickener is added to the precooler loop, and can be used as a back-up to the electrostatic precipitators. Primary function of this refinement is to accommodate temporary malfunctions of the electrostatic precipitators. This is the basis for the Newton Station of Central Illinois Public Service Company, scheduled to operate this year.

Softening. This term refers to various techniques used to lower the dissolved calcium ion concentration in regeneration solutions. The purpose of developing the double alkali processes was to prevent scaling and constant plugging of scrubbers due to calcium deposits. Calcium deposits usually occur as sulfate or carbonate or both, depending upon the scrubber conditions. As $CaSO_4$ is more soluble than $CaSO_3$ (0.25% vs. .0025%), the regenerated liquor can have sufficient calcium ion concentration for it to precipitate in the scrubber itself. Softening in essence assures the regenerated scrubber liquor to be subsaturated with respect to gypsum. For the dilute mode operation, an external softening step using soda ash (Na_2CO_3) is usually adopted and the stochiometry of softening reactions is shown below:

$$Ca^{++} + Na_2CO_3 \rightarrow 2Na^{+} + CaCO_3\downarrow \qquad S\text{-}1$$

$$Ca^{++} + NaSO_3 + 1/2H_2O \rightarrow 2Na^{+} + CaSO_3 \cdot 1/2H_2O\downarrow \qquad S\text{-}2$$

$$Ca^{++} + CO_2 + H_2O \rightarrow 2H^{+} + CaCO_3\downarrow \qquad S\text{-}3$$

Reactions S-1 and S-3 are referred to as carbonate softening and Reaction S-2 is considered sulfite softening.

Generally, carbonate softening is needed for the diluted mode of operation; for the concentrated mode, carbonate softening is not needed.

Scaling. The fact that the double alkali process employs a clear solution rather than a slurry, does not mean that the system is scale proof. Though the phenomena of scaling is markedly less than in the lime scrubbing process, scaling does occur due to either carbonate or sulfate scaling; carbonate scaling occurs as a result of localized high pH scrubbing liquor (above 9) in the scrubber in which CO_2 absorption by the scrubber solution results in producing the carbonate ion. Interaction with the dissolved calcium results in the precipitation of calcium carbonate[14]. The reaction summary for this type of scaling is shown below:

$$CO_2 + 2OH^- \rightarrow CO_3^= + H_2O \qquad \text{SC-1}$$

$$Ca^{++} + CO_3^= \rightarrow CaCO_3\downarrow \qquad \text{SC-2}$$

Below pH 9

$$CO_3^= + H^+ \rightleftarrows HCO_3^- \qquad \text{SC-3}$$

At a low pH, the bicarbonate/carbonate equilibrium tends to limit the free carbonate ion and thus limit the carbonate scaling.

As discussed under the section softening, the "sulfate" scaling results due to interaction between the sulfate ion and the soluble calcium ion in the recycled scrubber liquor, i.e.:

$$Ca^{++} + SO_4^{=} + 2H_2O \rightarrow CaSO_4 \cdot 2H_2O\downarrow$$

In dilute systems, gypsum ($CaSO_4 \cdot 2H_2O$) scaling is controlled by softening the liquor prior to recycling. For concentrated systems gypsum is not a problem since the high sulfite concentration keeps the Ca^{++} ion low. This built in sulfite softening step eliminates the need of an external softening step.

Other data reported in this area is interesting in that gypsum has been found to supersaturate easily to about 130% saturation; thus, even if sulfate formation is higher, gypsum precipitation will not occur in the scrubber till it surpasses this supersaturation level. Essentially, this non-ideal phenomena is a built in safety for the double alkali process. Also, the formation of pentasalts, glaubirites, mixed crystals or solids solutions have the effect of minimizing the scaling phenomenan.

Settling characteristics of regenerated solids. The settling characteristics of the waste product solids is influenced by the following:

(1) The concentration of soluble sulfates[3].

(2) The concentration of soluble magnesium and iron in the liquor[3].

(3) The concentration of suspended solids in reaction[3].

(4) The reactor configuration[4] and kinetics[4,5].

(5) The system being employed (limestone/lime).

The work performed by Arthur D. Little, Inc. (ADL)[4], indicates that poor settling characteristics were observed for dilute systems utilizing limestone at sulfate levels above 0.5M. For concentrated systems, similar degradation of solids settling was observed at magnesium levels of 120 ppm (at 0.45M TOS, 5.4 pH, 0.6M sulfate) and virtually no settling at 200 ppm magnesium levels. At higher sulfate level (1M) poor settling was observed at about 20 ppm Mg levels.

Envirotech[16] advocates the recycle of precipitated solids from thickner underflow to the reaction zone in order to agglomerate the crystals (crystal growth) so as to produce a better settling filterable waste.

The work of Arthur D. Little[17] also cites reactor configuration as being important for producing a filterable fast settling cake, but again reaction kinetics is not specified.

Selmeczi and Knight[18] have ascribed the thixotropic nature of $CaSO_3$ crystals to its morphology. The crystals are highly open, porous or spongy. A considerable amount of water is retained within the cluster, which is released under pressure giving if fluidity.

Ellison's work[19] for dilute systems has shown that the proportion of gypsum in the sludge can be increased by aeration of the scrubbing liquor. Japan has included a separate oxidation reactor at the tail end of the system to oxidize the calcium sulfite to calcium sulfate.

FMC's[5] procedure indicates regeneration using lime at 120°F requires few minutes. This high temperature regeneration may be beneficial kinetic-wise; however, it may result in promoting scrubber scaling by increasing calcium solubility in liquor. (The anhydrites and hemihydrate salts of $CaSO_4$ show typical inverted solubility curves at all temperature levels, where as gypsum solubilities go through a maximum at a temperature of 75°F and then decrease with increasing temperatures up to 212°F.)

Comparison of dilute and concentrated modes. The comparison of the dilute and the concentrated modes, in terms of major variables is shown on the following page.

Mode of Operation	Concentrated	Diluted
SO_2 level:	High	Low
SO_4 level:	Little	High
Scrubber mode:	SO_3^{-2}	OH^-
Scaling:	Not a problem, because even if Ca^{+2} is high, $CaSO_3$ precipitates in preference to $CaSO_4$ & is relatively insoluble.	A problem; $CaSO_4$ precipitation must have low Ca^{+2} level or use a softening step with CO_3^{-2}.
Filteration characteristic	Poor, since $CaSO_3$ has a tendency to be thixotropic.	$CaSO_4$ is a better product because contrast to $CaSO_3$, it is not thixotropic.

Process flow sheets and reaction schemes. The reaction schemes, chemistry process flow sheets and a summary of significant operating and planned full scale for various double alkali process is shown in Tables 1 to 9 and Figures 1 to 11. The general description of the processes has been covered in Chapter I.

Project R/D justifications. The Literature Survey on the double alkali process has indicated that the evolution of D/A process was mainly aimed at providing a highly efficient scale free scrubber desulfurization processes. Two modes of operation, namely, the dilute mode and concentrated mode were developed to desulfurize two kinds of flue gas.

Flue gas composition from a power plant varies depending on the source of coal - eastern or western types. Both of them are subjected to air burning under equivalent amounts, which is slightly in excess of the stoichiometric amounts.

The eastern type of coal usually contains a higher sulfur content than its counterpart, the western type, and it is the presence of sulfur that has led to the two modes of operations. For high sulfur content coal, the ratio of HSO_3^-/HSO_4^- in the effluent scrubber liquid is generally larger; SO_2 absorption occurs at about pH 8 (Na_2SO_3 mode) and an external softening step is not needed.

For low sulfur content coal, the ratio of HSO_3^-/HSO_4^- is significantly less and requires a higher pH to effect SO_2 absorption and necessitates the use of an external softening step.

While the Literature Survey has documented process parameters and scrubber conditions with a degree of certainty for a successful scrubber operation, the regeneration of the scrubber liquor is yet to be fully understood and has been a topic of "controversial", but interesting discussion. It is the presence of Ca^{++} ions in the regenerated scrubber liquor that has constantly led to process upsets and scaling in the scrubber operation. Thermodynamic aspects and solubility criteria for sulfate systems can explain the sulfite-sulfate precipitation phenomena only to a certain degree as these phenomena are clouded by non-ideal system behavior. Very often, one observes simultaneous precipitation of sulfite-sulfate, simultaneous precipitation of sodium-calcium salts, etc. Several theories such as the Blinding Theory which suggests that a diffusional barrier due to the presence of H^+ dictates whether $CaSO_3 \cdot CaSO_4$ precipitates; the mixed crystal or solution theory of Borgwardt suggests a $CaSO_3 \cdot CaSO_4$ precipitation on account of morphology behavior of $CaSO_3$.

Lime-D/A process has replaced the limestone-D/A process mainly because of its high reactivity rates but actual data in this area is very limited.

The object of this undertaking is to investigate these aspects in some detail. The concentrated mode was selected as it is applicable to eastern coal and is a topic of deep concern to Envirotech/Chemico as a full scale plant is under construction which will utilize this mode and can operate successfully if the sulfates are removed continuously as they are formed. Both lime/limestone regeneration system will be examined.

TABLE 1

SODIUM/CALCIUM BASED DOUBLE ALKALI PROCESS
(ZURN, BUELL & EIMCO - ENVIROTECHS, EPA, CEX/ADL OF GULF POWER/SOUTHERN SERVICES, FMC)

Absorption of SO_2

Reactions:

$$2NaOH + SO_2 \rightarrow Na_2SO_3 + H_2O \qquad \text{-AI}$$

$$2NaOH + SO_2 + H_2O \rightarrow Na_2SO_3 + 2H_2O \qquad \text{AII}$$

$$Na_2SO_3 + SO_2 + H_2O \rightarrow 2NaHSO_3 \qquad \text{-AIII}$$

$$\left\{ \begin{array}{c} SO_2 + H_2O \rightarrow H_2SO_3 \\ Na_2SO_3 + H_2SO_3 \rightarrow 2NaHSO_3 \end{array} \right\}$$

$$Na_2SO_3 + 1/2O_2 \rightarrow Na_2SO_4 \qquad \text{-AIV}$$

$$Na_2CO_3 + SO_2 \rightarrow Na_2SO_3 + CO_2\uparrow \qquad \text{-AV}$$

$$Na_2CO_3 + 2SO_2 + H_2O \rightarrow 2NaHSO_3 + CO_2\uparrow \qquad \text{-AVI}$$

TABLE 2

SODIUM/CALCIUM BASED ALKALI PROCESS (ZURN, BUELL & EIMCO - ENVIROTECH, EPA, CEA/ADL OF GULF POWER/SOUTHERN SERVICES, FMC)

Regeneration/Lime

$$Na_2SO_3 + Ca(OH)_2 \rightarrow CaSO_3\downarrow + 2NaOH \qquad \text{-RO}$$

$$Na_2SO_3 + Ca(OH)_2 + 1/2H_2O \rightarrow CaSO_3 \cdot 5H_2O\downarrow + 2NaOH \qquad \text{-RI}$$

$$NaHSO_3 + Ca(OH)_2 \rightarrow CaSO_3\downarrow + NaOH + H_2O \qquad \text{-RII}$$

$$2NaHSO_3 + Ca(OH)_2 \rightarrow CaSO_3\downarrow + Na_2SO_3 + 2H_2O \qquad \text{-RIII}$$

$$2NaHSO_3 + Ca(OH)_2 \rightarrow CaSO_3 \cdot 5H_2O\downarrow + Na_2SO_3 + 1.5H_2O \qquad \text{-RIV}$$

$$Na_2SO_4 + Ca(OH)_2 \rightarrow CaSO_4\downarrow + 2NaOH \qquad \text{-RV}$$

$$Na_2SO_4 + Ca(OH)_2 + 2H_2O \rightleftarrows CaSO_4 \cdot 2H_2O\downarrow + 2NaOH \qquad \text{-RVI}$$

$$Na_2SO_4 + Ca(OH)_2 + H_2O \rightarrow CaSO_4 \cdot H_2O\downarrow + 2NaOH \qquad \text{-RVII}$$

$$Na_2SO_4 + 2CaSO_3 \cdot 5H_2O + H_2SO_4 + H_2O \rightarrow -$$
$$2CaSO_4 \cdot 2H_2O\downarrow + 2NaHSO_3 \qquad \text{-RVIII}$$

$$yNa_2SO_4 + xNaHSO_3 + (x + y)Ca(OH)_2 + (z - x)H_2O \rightarrow$$
$$xCaSO_3yCaSO_4zH_2O\downarrow + (x + 2y)NaOH \qquad \text{-RIX}$$

$$Na_2SO_4 + 3H_2O \xrightarrow{\text{EL CELL}} 2NaOH + H_2SO_4 + H_2 + 1/2O_2\uparrow \qquad \text{-RX}$$

$$Na_2CO_3 + Ca(OH)_2 \rightarrow CaCO_3\downarrow + 2NaOH \qquad \text{-RXI}$$

Regeneration/Limestone

$$2NaHSO_3 + CaCO_3 + 0.5H_2O \rightarrow CaSO_3 \cdot 5H_2O\downarrow + Na_2SO_3 +$$
$$CO_2\uparrow + H_2O \qquad \text{-RXII}$$

TABLE 3

DOUBLE ALKALI PROCESS OTHER THAN Na/Ca

Kureha's Sodium Acetate-Gypsum Process

Absorption:

$2CH_3COONa + SO_2 + H_2O \rightarrow Na_2SO_3 + 2CH_3COOH$ A VIII

Oxidation:

$Na_2SO_3 + 1/2O_2 \rightarrow Na_2SO_4$ A III

Regeneration:

$2CH_3COOH + CaCO_3 \rightarrow Ca(CH_3COO)_2 + CO_2\uparrow + H_2O$ R XIV

$Ca(CH_3COO)_2 + Na_2SO_4 \rightarrow CaSO_4\downarrow + 2CH_3COONa$ R V

TABLE 4

DOUBLE ALKALI PROCESS OTHER THAN Na/Ca

Dowa's Process

Absorption:

$$Al_2(SO_4)_3 \cdot Al_2O_3 + SO_2 \rightarrow Al_2(SO_4)_3 \cdot Al_2(SO_3)_3 \qquad \text{A-VI}$$

Oxidation:

$$Al_2(SO_4)_3 \cdot Al_2(SO_3)_3 + 3/2O_2 \rightarrow 2Al_2(SO_4)_3 \qquad \text{A-VII}$$

Regeneration:

$$2Al_2(SO_4)_3 + CaCO_3 + 6H_2O \rightarrow$$
$$3CaSO_4 \cdot 2H_2O\downarrow + Al_2(SO_4)_3 \cdot Al_2O_3 + 3CO_2\uparrow \qquad \text{R XIII}$$

TABLE 5

DOUBLE ALKALI PROCESS OTHER THAN Na/Ca

Mg Base Process

Absorption:

$$MgO\ (aq) + SO_2 \rightarrow MgSO_3$$

Regeneration:

$$MgSO_3 \rightarrow MgO + SO_2$$

TABLE 6

DOUBLE ALKALI PROCESS OTHER THAN Na/Ca

Comparison of Significant Features of SO2 Removal Processes for Treating Gas Streams Containing Less Than 1% SO2

PROCESS	APPROACH	NORMAL SO_2 REMOVAL CAPABILITY	BY-PRODUCT	UNIQUE OPERATING REQUIREMENTS
Cat-Ox	Oxidation of SO_2 to SO_3 and collection as H_2SO_4	90%	78% H_2SO_4	None
CALSOX	Water soluble alkaline scrub with lime regeneration	To 50 ppm SO_2	$CaSO_3/CaSO_4$	Absorbent, Lime
NOSOX	Water soluble alkaline scrub with thermal regeneration	To 200 ppm SO_2	Pure gaseous or liquid SO_2 saturated with water	Absorbent, Steam
AMMSOX*	Water soluble alkaline scrub with by-product that can be thermally decomposed to SO_2	To 100 ppm SO_2	$(NH_4)_2SO_3/(NH_4)_2SO_4$ solution	Absorbent, Thermal Energy

*Potential for pollution by the highly volatile ammonium compounds

TABLE 7

SODIUM/CALCIUM BASED DOUBLE ALKALI PROCESSES

PROCESS	ZURN	BUELL	EPA REVIEW KAPLAN	CEA/ADL	FMC
Reaction Chemistry	DM* Softening	CM* & DM	CM & DM	CM, Solid Solution	CM
Absorption of SO_2 (EQS/Final Alkali)	A I A III A IV	A II(AI) A III	A I A III	A I A III A V A IV	A III
Regeneration (EQS/Ppted Spieces)	R II R O R V R XI	R IV R VIII	R IV R I R VI	R IV R II R V	R IV
(Sulfate Removal)			R VI R VIII R IX R X		
Limestone			R XII		

*DM - Dilute Mode; CM - Concentrated Mode.

TABLE 8

SUMMARY OF SIGNIFICANT OPERATING AND PLANNED FULL SCALE DOUBLE ALKALI SYSTEMS

System Operator	System Application	Vendor or Developer	Size (Mw, Equivalent)	Active Alkali	Calcium Sources	Start-Up Date[a]
FMC Modesto, Ca Plant	Reduction kilns	FMC	10 (Gas Rate) 30 (Regen.)	Conc.	Lime	12/71
Showa Denko KK Chiba, Japan	Oil-fired elec. power boiler	Showa Denko	150	Conc.	Limestone	6/73
Tohoku Electric Shinsendai Sta., Japan	Oil-fired utility boiler	Kawasaki/ Kureha	150	Conc.	Limestone	1/74
General Motors Parma, Ohio Plant	4 coal-fired industrial boilers	General Motors	40 (Regen) 32 (Gas Rate)	Dilute	Lime	3/74
Catepillar Tractor Co. Joliet, Illinois	2 coal-fired industrial boilers	Zurn Industries	20-30	Dilute	Lime	10/74
Showa Pet. Chem. Kawasaki, Japan	Oil-fired industrial boiler	Showa Denko	62	Conc.	Limestone	1974
Kanegafuchi Chem. Takasago, Japan	Oil-fired industrial boiler	Showa Denko	93	Conc.	Limestone	1974
Poly Plastic Fuji, Japan	Oil-fired industrial boiler	Showa Denko/Ebara	65	Conc.	Limestone	1974
Kyowa Pet. Chem. Yokkaichi, Japan	Oil-fired industrial boiler	Showa Denko/Ebara	46	Conc.	Limestone	1974

TABLE 8 (Cont'd.)

System Operator	System Application	Vendor or Developer	Size (Mw, Equivalent)	Active Alkali	Calcium Sources	Start-Up Date[a]
Kinuura Utility Nagoya, Japan	Oil-fired industrial boiler	Tsukishima	63	Conc.	Lime	1974
Daishuwa Paper Fuji, Japan	Oil-fired boiler	Tsukishima	85	Conc.	Lime	1974
Firestone Pottstown, Pa.	Coal & oil-fired industrial boiler-demonstration	FMC	3	Conc.	Lime	1/75
Gulf Power Company Scholz Plant (Southern Services)	Coal-fired utility boiler-prototype	A.D. Little/ Combust. Equip. Associates	20	Conc.	Lime	2/75
Caterpillar Tractor Co. Mossville, Illinois	Coal-fired industrial boiler system	FMC	45-55	Conc.	Lime	10/75
Sikoku Electric Power Anan, Japan	Oil-fired utility boiler	Kawasaki/ Kureha	450	Conc.	Limestone	1975
Sikoku Electric Power Sakaide, Japan	Oil-fired utility boiler	Kawasaki/ Kureha	450	Conc.	Limestone	1975
Kyushu Electric Power Buzen, Japan	2 oil-fired utility boilers	Kawasaki/ Kureha	(2-450) 900	Conc.	Limestone	(5/77)
Caterpillar Tractor East Peoria, Illinois	Coal-fired industrial boiler	FMC	100	Conc.	Lime	(1977)

TABLE 8 (Cont'd.)

System Operator	System Application	Vendor or Developer	Size (Mw, Equivalent)	Active Alkali	Calcium Sources	Start-Up Date[a]
Central Illinois Public[b] Service-Newton #1	Coal-fired utility	Envirotech	575	Conc.	Lime	(77-78)
Louisville Gas & Electric[b] Cane Run #6 Louisville, Kentucky	Coal-fired utility	CEA/ADL	280	Conc.	Lime	(77-78)
Springfield Water Light[b] & Power-Dallman #3 Springfield, Illinois	Coal-fired utility	FMC	192	Conc.	Lime	(77-78)
Caterpillar Tractor Mapleton, Illinois	Coal-fired industrial boiler	FMC	100	Conc.	Lime	(1978)

[a] Dates in parentheses are projected start-up dates.

[b] These units were proposed in response to the RFP for a full scale utility demonstration.

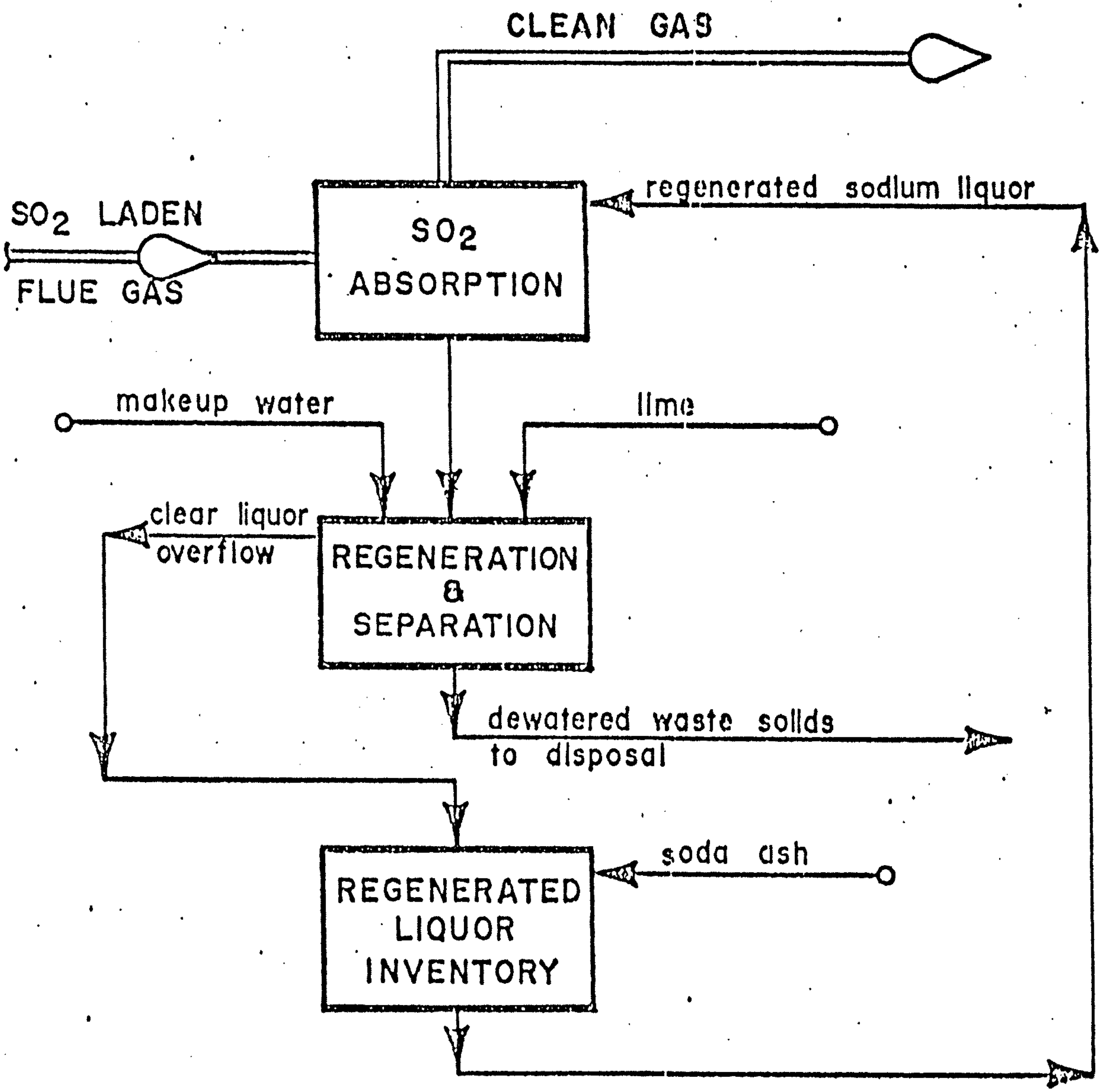


FIGURE 1. Basic Scheme

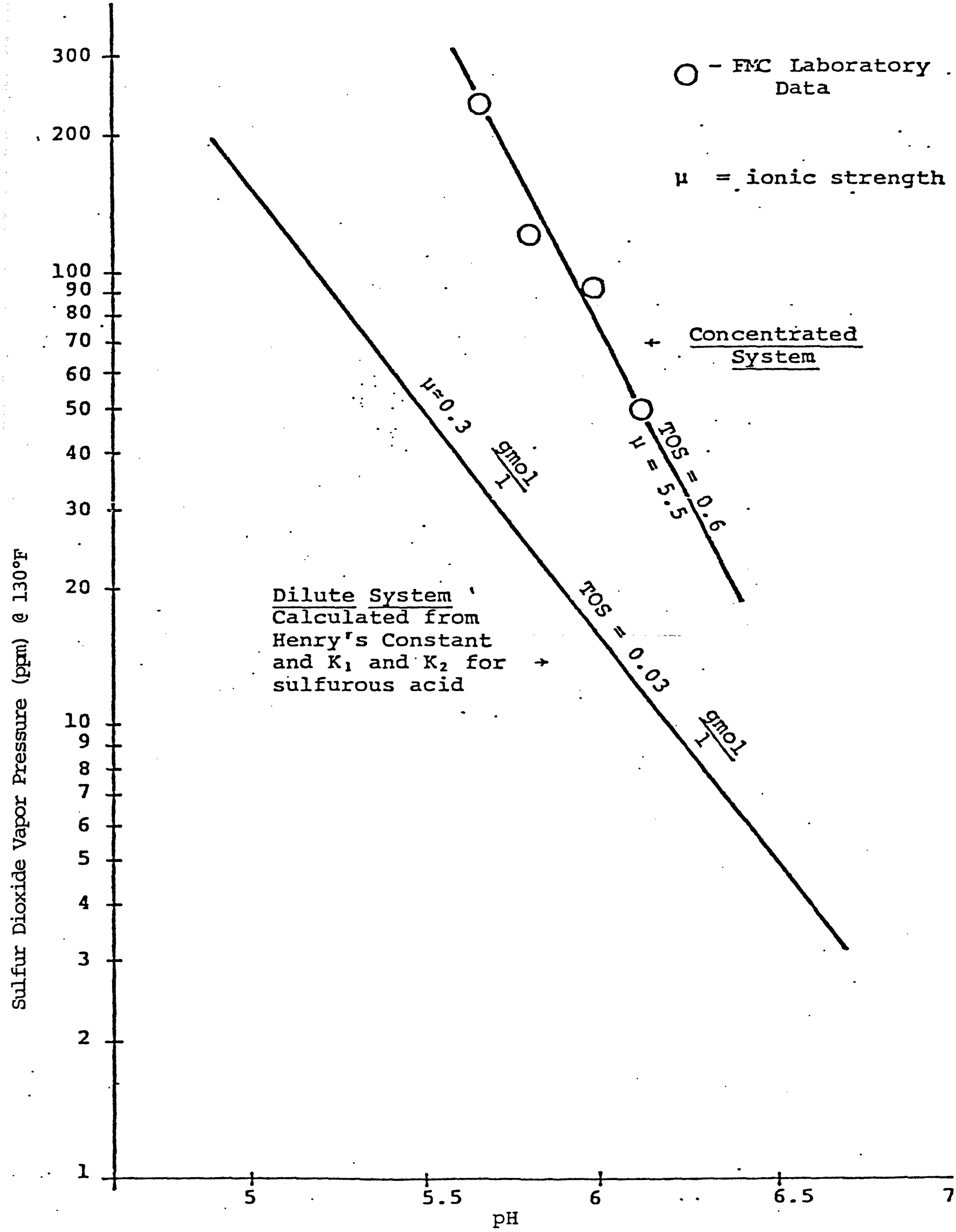
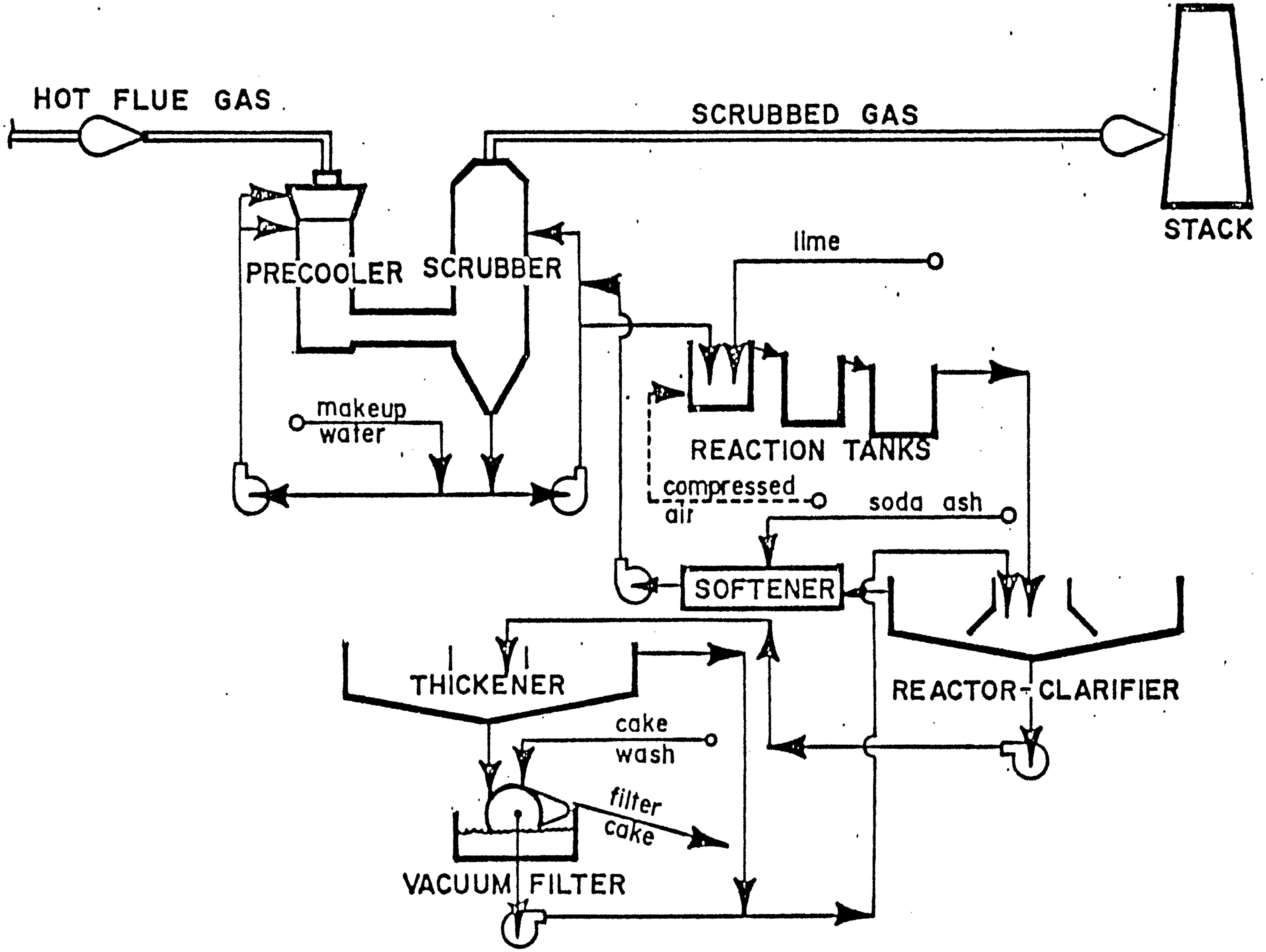


FIGURE 2. SO_2 Vapor Pressure Data as a Function of pH

FIGURE 3. Dilute Mode



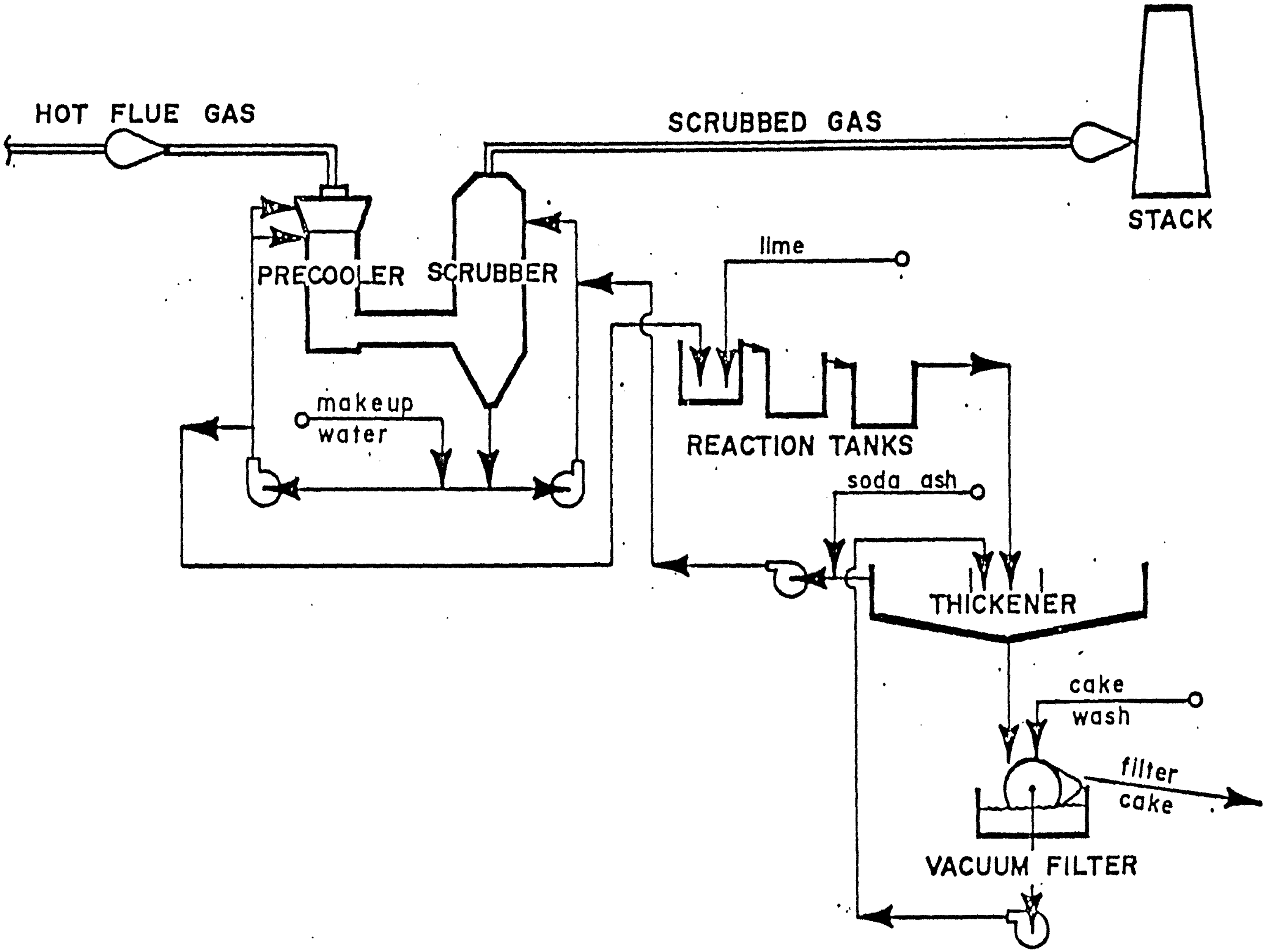
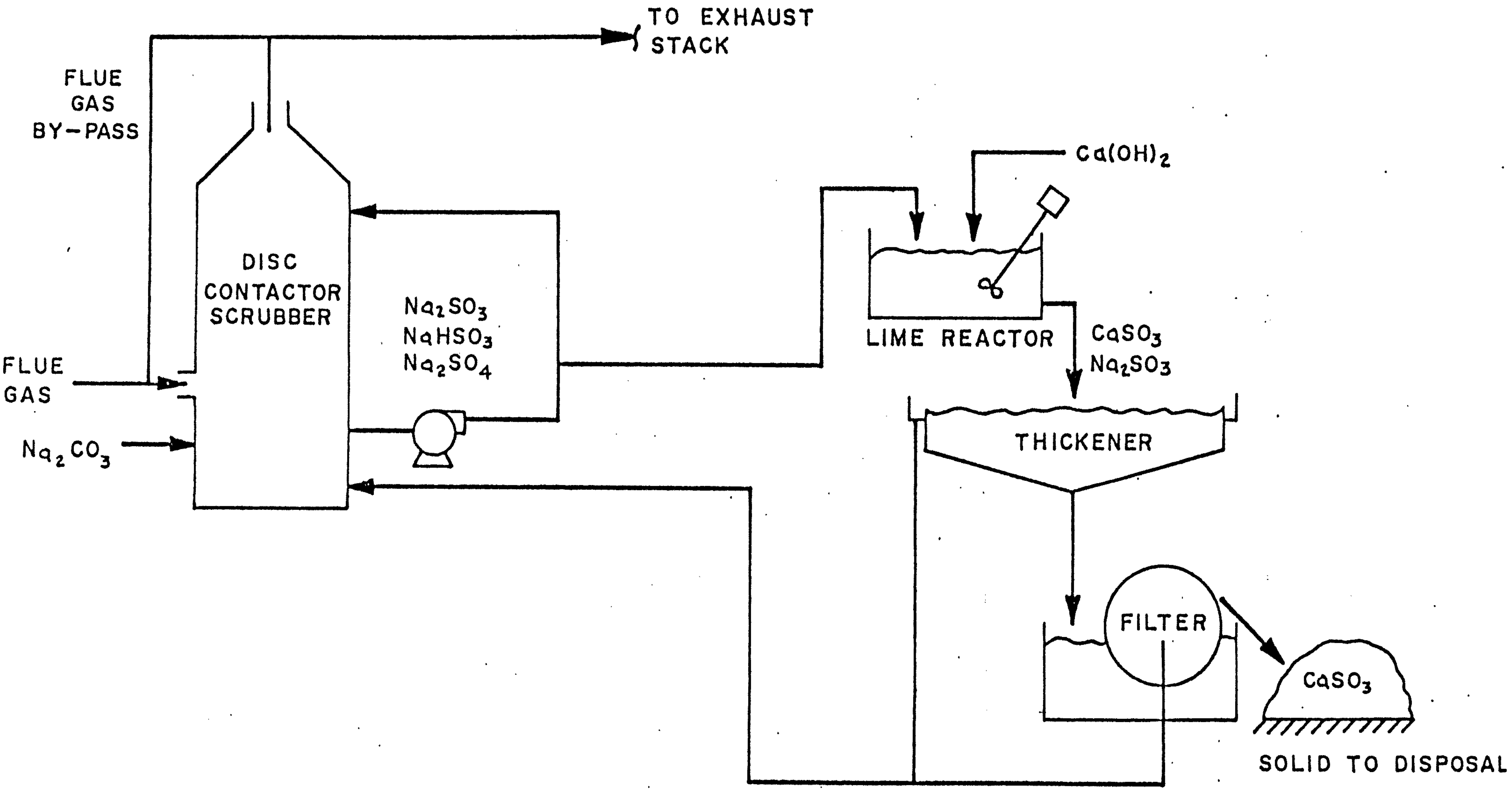


FIGURE 4. Concentrated Mode



SCRUBBING

$$SO_2 + Na_2SO_3 + H_2O \rightarrow 2NaHSO_3$$

REGENERATION

$$Ca(OH)_2 + 2NaHSO_3 \rightarrow CaSO_3\downarrow + Na_2SO_3 + 2H_2O$$

FIGURE 5. Schematic of FMC's Concentrated Double Alkali Process

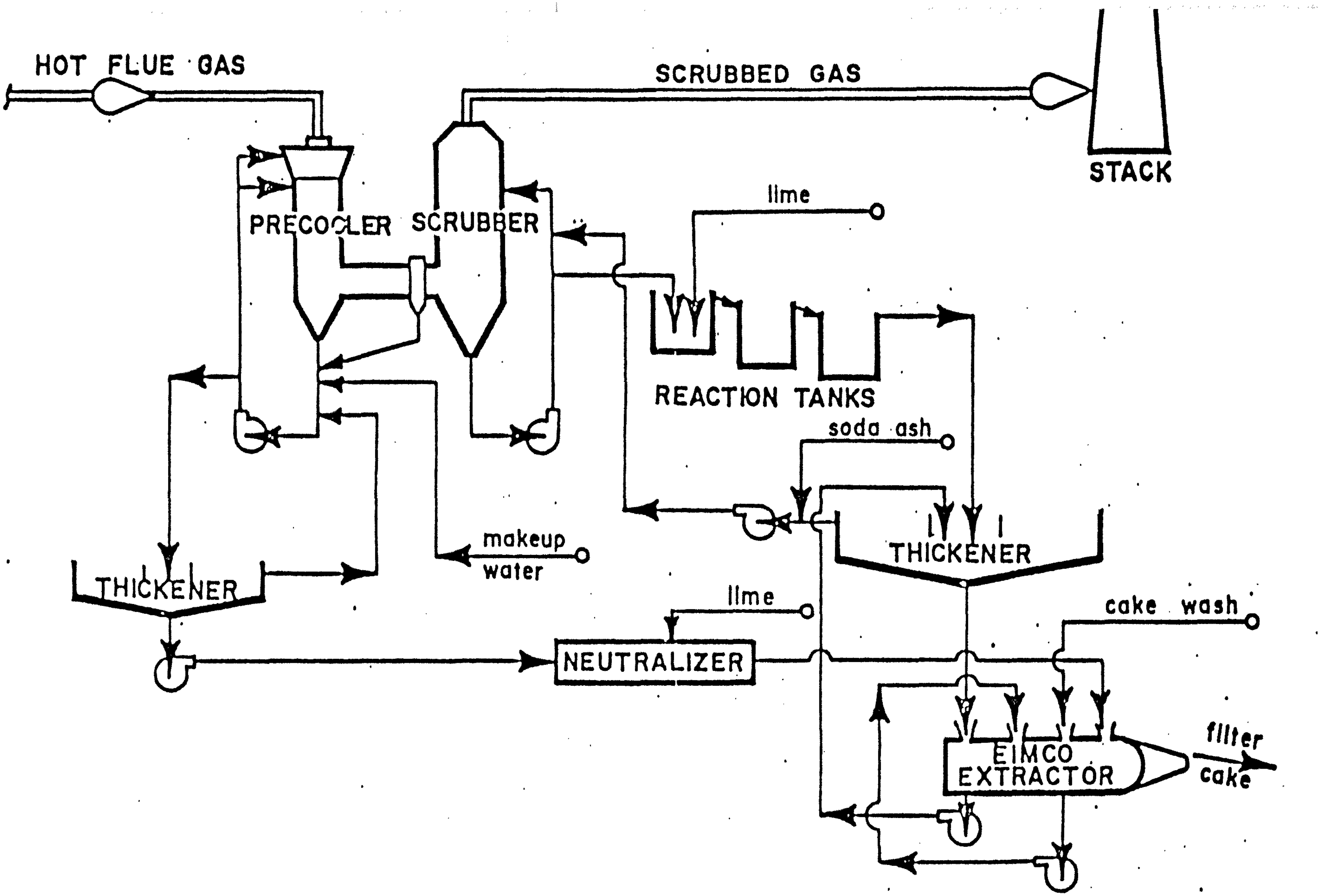


FIGURE 6. High Chloride Mode

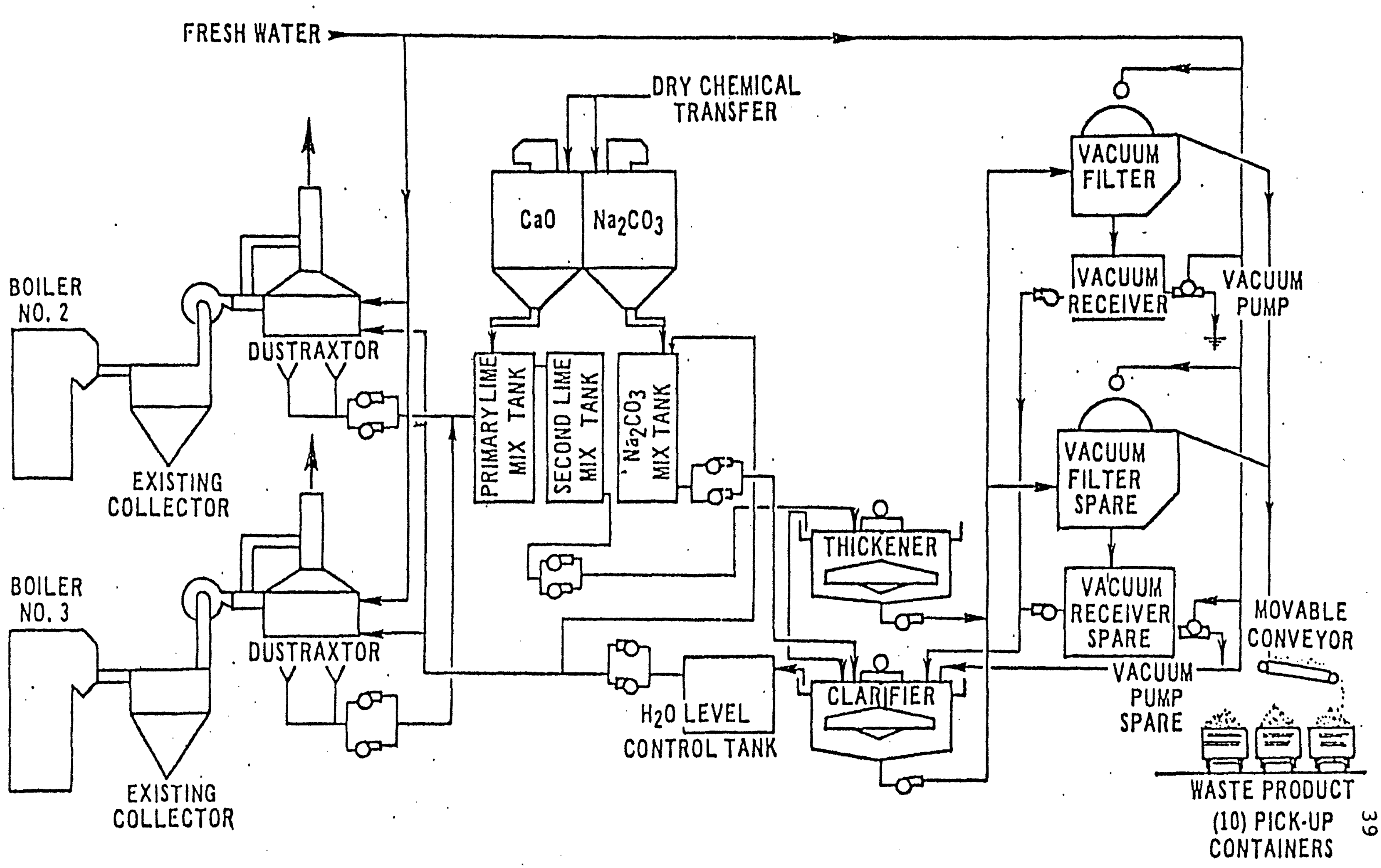


FIGURE 7. Zurn Double Alkali System

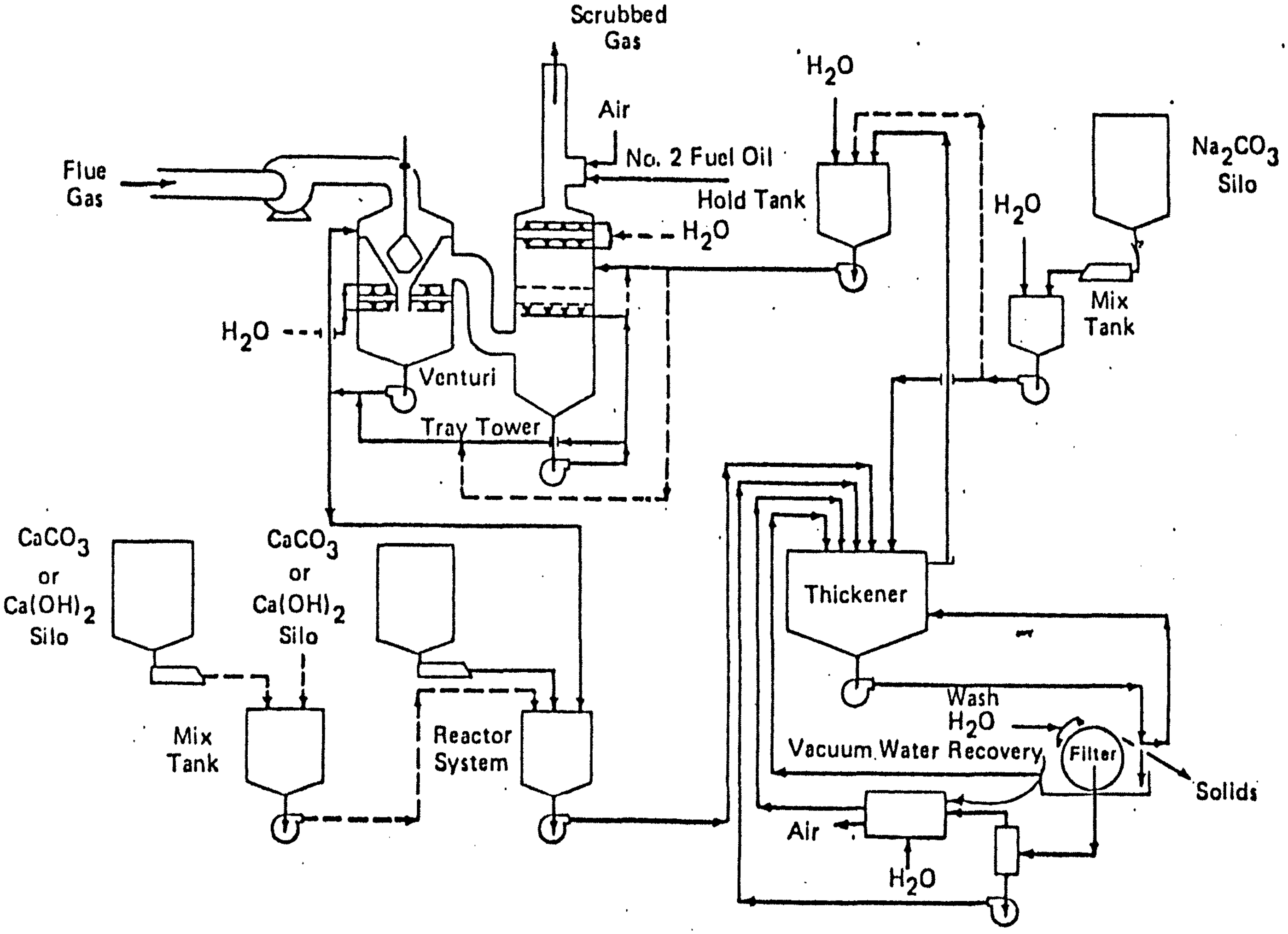


FIGURE 8. CEA/ADL Dual Alkali Process Flow Diagram - Scholz Station

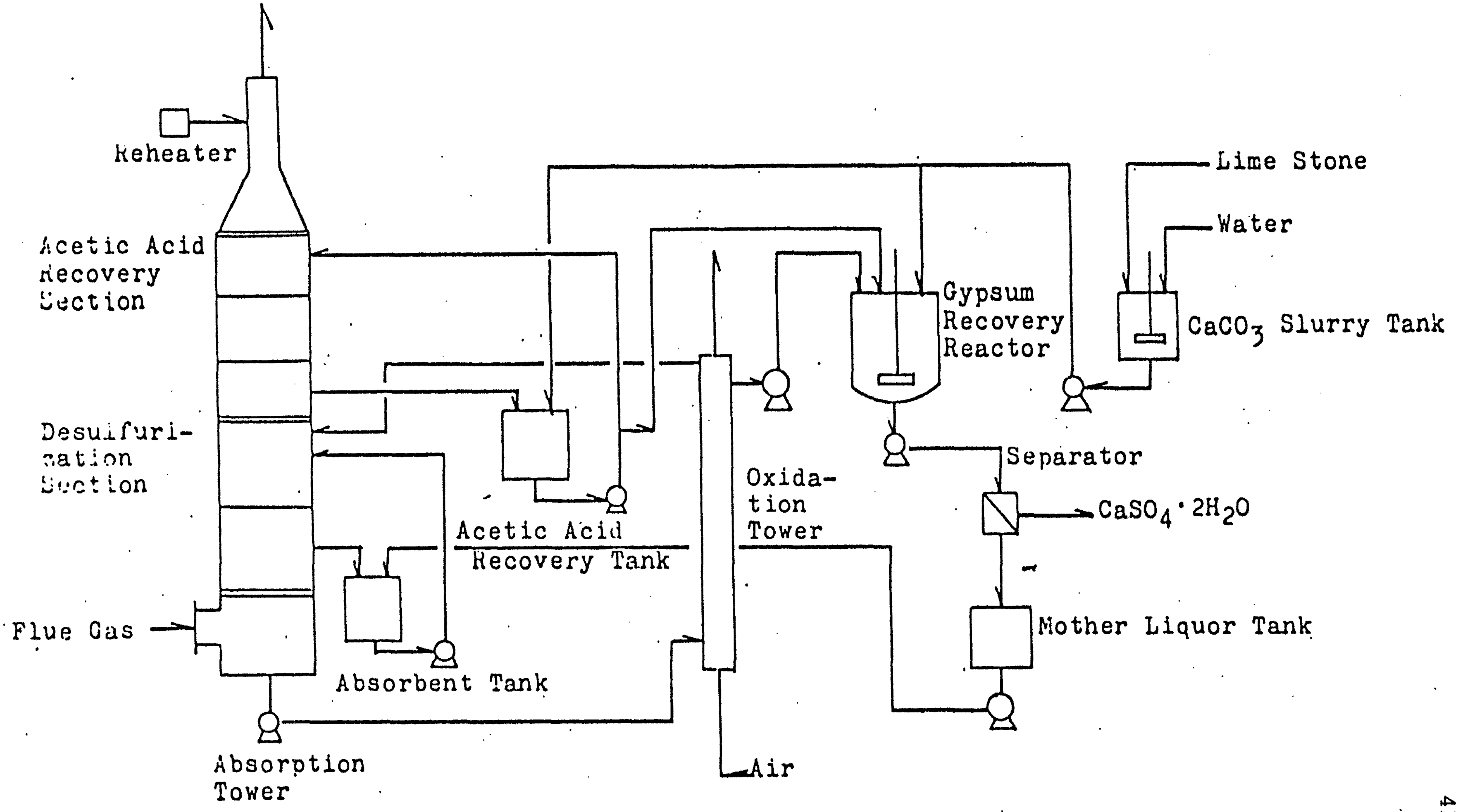


FIGURE 9. Schematic Flow Diagram of Limestone Desulfurization Process

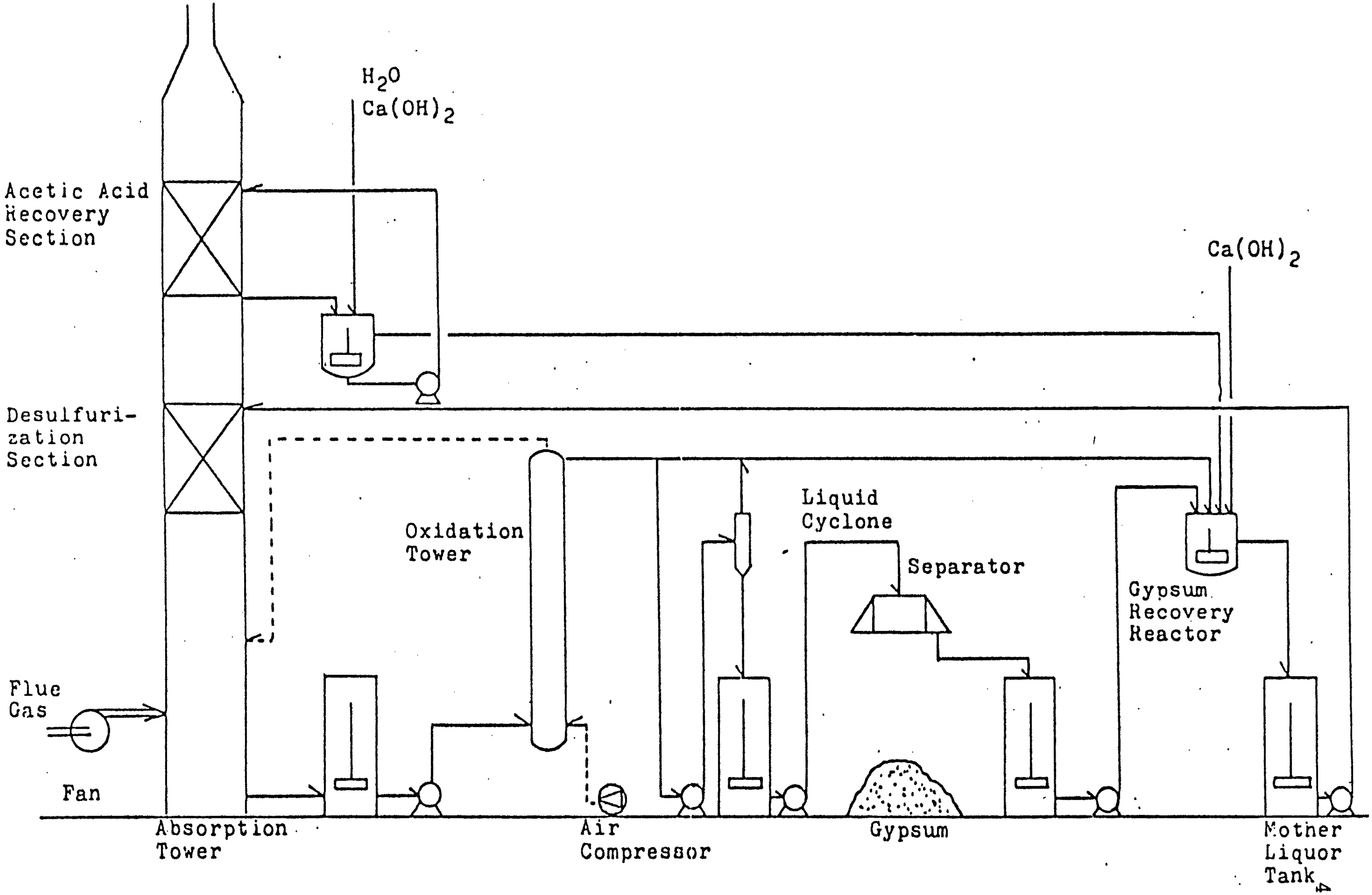


FIGURE 10. Lime Desulfurization Process

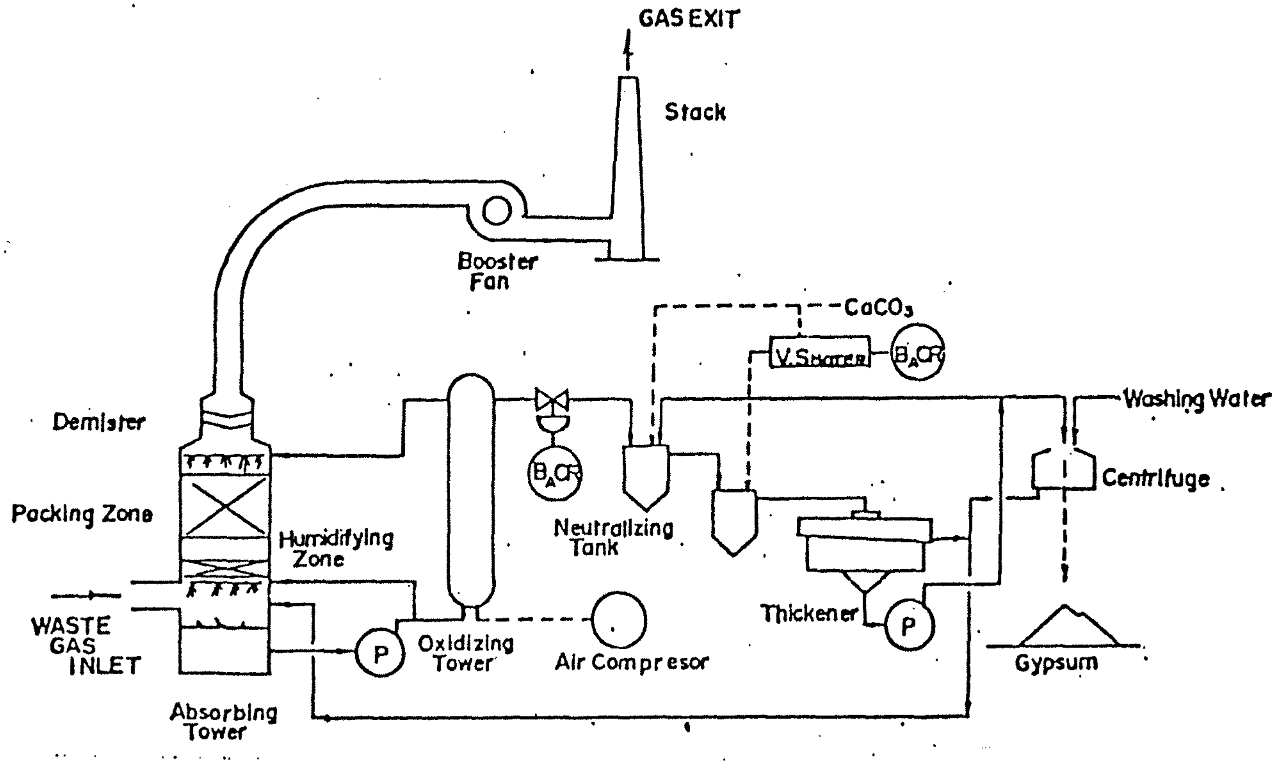


FIGURE 11. Flow Diagram of Dowa's Alumina Sulfate/Gypsum Process

CHAPTER III

Experimental Plan

The literature review in the flue gas desulfirization (FGD) area indicated that this field expanded so rapidly that data especially in the regeneration aspects is very limited.

The current energy programs and energy outlook demands suggest that energy from coal will be one of the principal sources of energy developed to meet the energy challenge, which almost mandates a more fundamental and in depth outlook into all aspects of FGD technology.

A survey of viable processes indicates the following similarities:

1. All such processes make an univalent claim that the double alkali processes provide an almost "fool proof" non scaling scrubbing operation as against a troublesome "scaling scrubber operation" experienced with its percursor, namely "single alkali processes".
2. The regeneration scheme depicted does not differentiate between a lime regeneration or limestone regeneration operation. Process schemes depict this aspect as being carried out in a series of jacketed backmix reactors.

However, the data reported by a few clearly indicates the lime regeneration system is indeed different from limestone processes in that the former is more active and requires less regeneration time. In fact, FMC[5] depicts the regeneration for lime systems to be carried out at 120°F in a backmix reactor with residence time of a few minutes. This high temperature regeneration, at first, may seem logical kinetic wise, but may, in reality, be detrimental to the overall efficiency in that calcium entrainment (for example, anhydrite and hemihydrate salts of $CaSO_4$ show typical inverted solubility curves at all temperature levels, whereas gypsum solubilities go through a maximum and then decrease with increasing temperatures up to 100°C)[20] in the regenerated liquor via solubilization may occur and could be detrimental for a smooth scrubber operation. The work of ADL[17], FMC[5] and others also indicates pH reactor geometry as critical for this step, but again data is very limited.

It may be interesting to note that even with the knowledge that the lime systems require much shorter regeneration cycles than limestone systems, the backmix reactor was envisioned for the lime system on pure deduction that the regeneration chemistry for both is similar.

However, the reaction chemistry may indeed be different. For example, let us examine the reaction chemistry for a "virgin" sodium bisulfite system using lime/limestone.

For lime regeneration systems, the applicable equations are:

$$2NaHSO_3\ (\ell) + Ca(OH)_2\ (s) \rightarrow CaSO_3 \cdot 1/2H_2O\ (s)\downarrow - \\ + Na_2SO_3\ (\ell) + 3/2H_2O$$

$$NaHSO_3\ (\ell) + Ca(OH)_2\ (s) \rightarrow CaSO_3 \cdot 1/2H_2O\ (s)\downarrow - \\ + NaOH\ (\ell) + 1/2H_2O$$

and for limestone regeneration systems, the reaction chemistry is governed by

$$2NaHSO_3\ (\ell) + CaCO_3\ (s) + 1/2H_2O\ (\ell) \rightarrow \\ CaSO_3 \cdot 1/2H_2O\ (s)\downarrow + CO_2\ (g)\uparrow + Na_2SO_3\ (\ell) + H_2O$$

$$NaHSO_3\ (\ell) + CaCO_3\ (s) + 1/2H_2O\ (\ell) \rightarrow \\ CaSO_3 \cdot 1/2H_2O\ (s)\downarrow + CO_2\ (g)\uparrow + NaOH\ (\ell)$$

An examination of the applicable equations reveal that lime regeneration chemistry is fundamentally different from the limestone processes in that the system is itself different; the former involving a solid-liquid reaction system, whereas the latter depicts a solid-liquid-gas reaction system.

Secondly, the existence of reported data and the very nature of the system suggests that the reaction, in principle will also be governed by the solubility characteristics and again lime and limestone differ from one another in this respect.

Thirdly, the fact that the applicable reactions involve solid-liquid systems suggests that the reactivity rates can be governed by "agglomeration phenemona." The presence of water, and reaction conditions such as pH, temperature, degree of mixing and others can significantly contribute to the above phenemona and may produce a slurry of poor settling and filterable characteristics.

One of the objects of this research program was to conduct a literature survey on FGD technology; the second objective and yet of utmost importance was to cite areas worth R/D efforts and to execute a part of the program itself.

The experimental plan pursued in this study was multifold and are cited below:

(1) Analytical techniques to evaluate and test any hypothesis is critical. A considerable amount of time was expended to develop reliable methods to analyze sulfites, calcium both in the liquor and solid phases. Infrared technique and sample preparation technique to study the morphology of the regenerated cake was

perfected to assure repeatability.

(2) Systems selected for this study were essentially a sodium bisulfite-lime, sodium bisulfite-limestone.

(3) Reactor configuration varied; a backmix reactor system, pipe line tubular reactors were set up on cite with a continuous filtering system. Both pH and flow characteristics were varied with reactant ratios and pumps.

(4) The final phase of this work will address itself to the importance of this work, its impact on current practices and its value for the future.

CHAPTER IV

Experimental Set Up

Essentially two types of reactor configurations were considered for this regeneration study and are shown in Figures 12 and 13.

Figure 12 depicts a backmix reactor set up. The reactor was jacketed and had a temperature controller hook up to study regeneration aspects at high temperatures. Pumps as shown were used to feed the sodium bisulfite liquor and lime/limestone slurries. The set up also indicates feeding both streams at one inlet with a 'Y' port-connection or at separate inlet ports.

Figure 13 is essentially a tubular reactor, not jacketed with the same feed systems as before. Minor modifications not shown included reactors of different dimensions and a 'venturi' type reactor where in flow of one stream controlled the flow of the other and resembled somewhat an "aspirator-vacuum system".

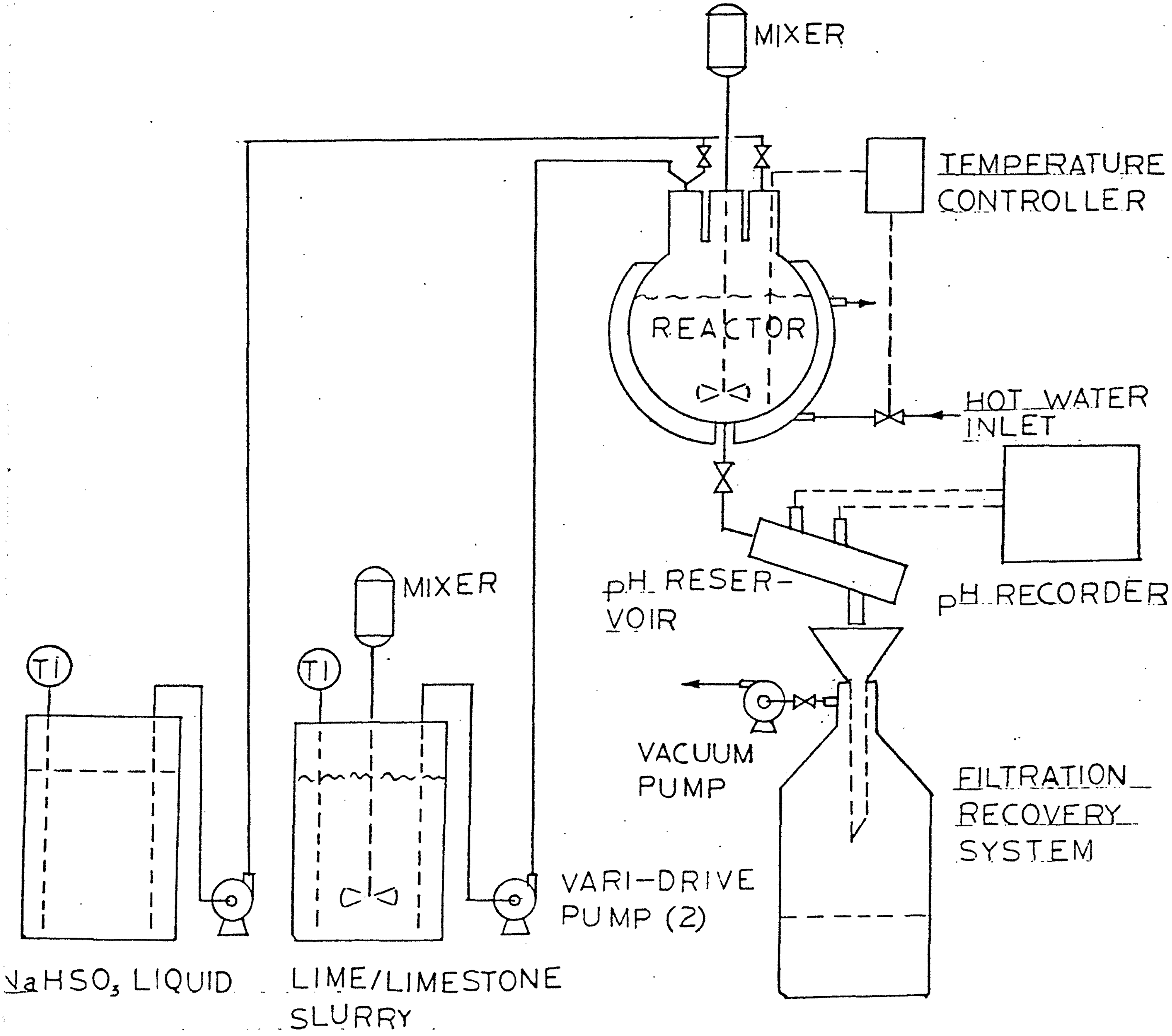
Common to both these systems were the following:

(1) A 'pH chamber' wherein the pH of the system was either displayed or recorded continously.

(2) A filtration set up to continously filter the regenerated reactant system and to evaluate filtration characteristics and rates.

FIGURE 12.

PROCESS SETUP FOR REGENERATION STUDIES: BACKMIX REACTOR



PROCESS SETUP FOR REGENERATION STUDIES: TUBULAR REACTOR

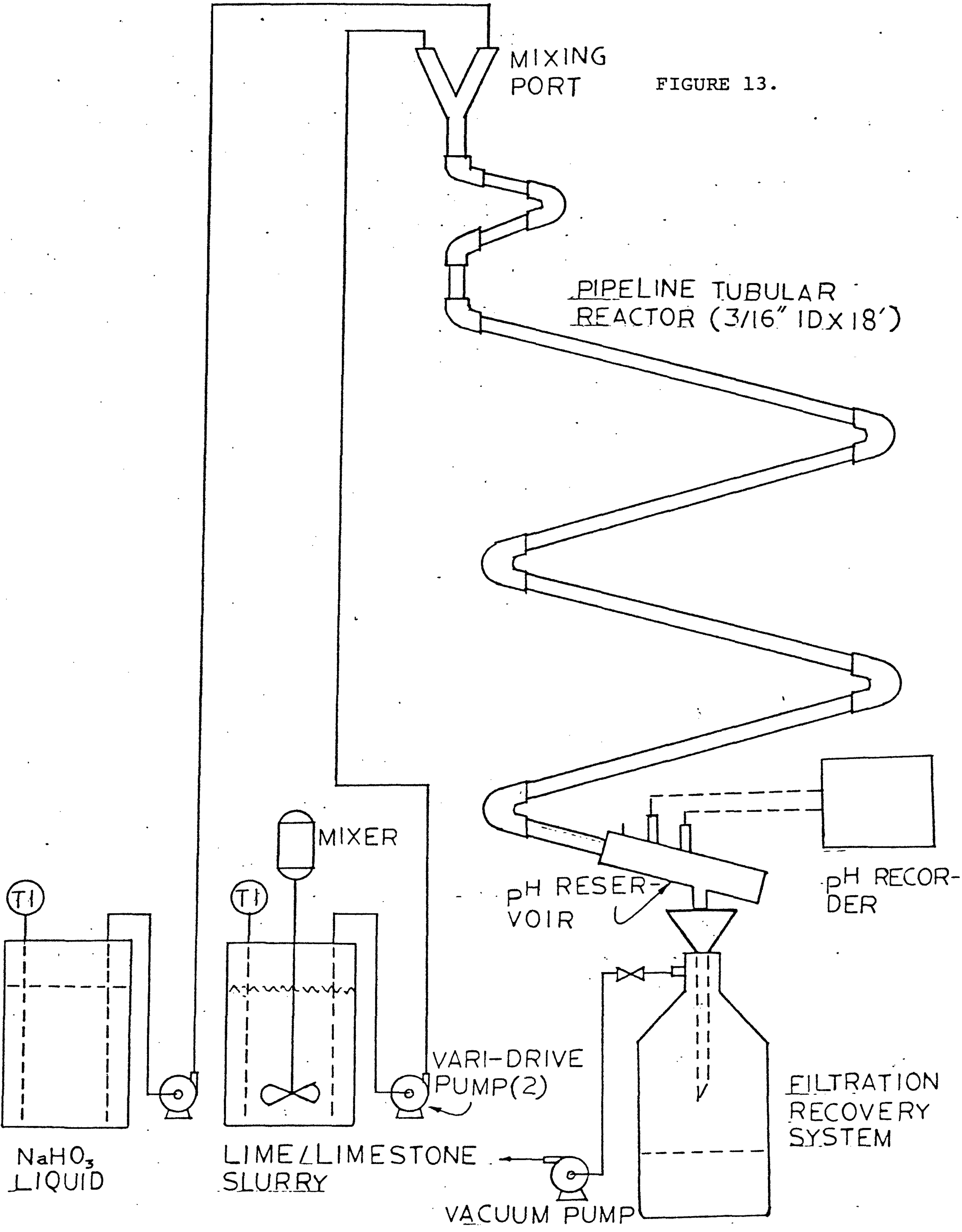


FIGURE 13.

CHAPTER V

Iodometric Determination of Sulfite, $SO_3^{=}$ in an Insoluble Sample or Liquid Sample

Procedure. Accurately weigh 100-150 mg of insoluble sample (dry cake) or pipet 10 ml of liquid sample into a 250 ml Erlenmeyer flask. Add 50 ml of distilled water and then add 25 to 50 ml of standard (≃0.1 N) iodine solution. Slowly feed 10 ml of 1.1 HCl and let solution stir for two minutes.

Back titrate the unreacted iodine with standard (≃0.1 N) sodium thiosulfate solution until the iodine color almost disappears (a faint yellow tint is present). Add 2-5 ml of starch indicator and continue titration until one drop of sodium thiosulfate removes all blue color that is present. This is the end point.

Standardization of solutions.

(a) Standardize sodium thiosulfate solution by titrating with a standard solution of potassium dichromate of known normality. No 'external' indicator is needed as the end point is reached when system color changes from orange to colorless.

(b) Similarly, standardize iodine solution by titrating against the 'normalized' sodium thiosulfate.

Add starch indicator and continue titration till blue color disappears.

Sample calculations.

(a) Normality of sodium thiosulfate:

$N_{K_2Cr_2O_7}$ normality of potassium Dichromate = 0.2165/gms/liter x

$\frac{1}{49.04}$/gm equivalents/liter = .004415

$V_{K_2Cr_2O_7}$, volume of potassium Dichromate solution = 1000 ml

$V_{Na_2S_2O_3}$, volume of sodium thiosulfate consumed = 43.95 ml

$$\text{Normality of sodium thiosulfate, } N_{Na_2S_2O_3} = \frac{N_{K_2Cr_2O_7} \cdot V_{K_2Cr_2O_7}}{V_{Na_2S_2O_3}}$$

$$= 0.004415 \times \frac{1000}{43.95}$$

$$= 0.10046$$

(b) Normality of iodine solution:

$N_{Na_2S_2O_3}$, Normality of sodium thiosulfate solution = 0.10046

$V_{Na_2S_2O_3}$ = Volume of sodium thiosulfate consumed = 24.1 ml

V_{I_2} = Volume of iodine solution = 25 ml

$$\text{Normality of iodine solution, } N_{I_2} = \frac{N_{Na_2S_2O_3} \cdot V_{Na_2S_2O_3}}{V_{I_2}}$$

$$= \frac{0.10046 \times 24.1}{25}$$

$$= .09684$$

(c) Determination % $SO_3^=$ by weight in a sample:

Run No. 35-3

S_W, Sample wt: 0.1492 grams

N_{I_2} - Normality of iodine = .09684

V_{I_2} - Volume of iodine solution = 25 ml

$N_{Na_2S_2O_3}$ - Normality of sodium thiosulfate = .10046

$V_{Na_2S_2O_3}$ - Volume of sodium thiosulfate = 24.08 ml

$$\% \ SO_3^= \text{ in sample by weight} = \frac{[N_{I_2}V_{I_2} - N_{Na_2S_2O_3}V_{Na_2S_2O_3}]\text{x}40.03\text{x}100}{S_W}$$

where 40.03 gms $SO_3^=$ represents 1 equivalent per liter solution for a normal solution.

$$= \frac{[.09684\text{x}25 - .10046\text{x}2408] \text{ x } 40.03 \text{ x } 100}{0.1492}$$

$$= 51.60$$

Calcium Analysis

Preparation and standardization of EDTA solution. Prepare an approximately 0.015 M EDTA solution by adding 4 g of the disodium salt of EDTA, 20 ml of 1% $MgCl_2$ solution, and 3 ml of 6 M NH_3 to about 750 ml of water.* In

---

*The disodium salt of EDTA, $Na_2H_2Y \cdot 2H_2O$, is the most commonly used form, being easier to prepare commercially and more soluble in water than the acid, H_4Y. It is somewhat slow to go into solution, however, requiring 10 to 15 minutes for comple dissolution. Occasional shaking speeds the process, as does gentle warming.

this experiment use only distilled water purified by passage through a column containing either a cation-exchange resin or a mixture of cation- and anion-exchange resins. Prepare a buffer solution of 3 g NH_4Cl in 50 ml of 6M NH_3.

Weigh to the nearest 0.1 mg approximately 0.5 g of dry $CaCO_3$ on a sheet of glazed weighing paper. Transfer quantitatively to a funnel inserted in the top of a 100 ml volumetric flask, using a camel-hair brush to aid in transfer of the last particles. Rinse the material into the flask with a ml or two of 12 M HCl, then add 10 more ml of 12 M HCl by rapid dropwise addition.* Warm if necessary to complete the dissolution.** When dissolution is complete, remove the funnel, rinsing inside and out with deionized water from a wash bottle. Fill the flask to the mark and mix well. Using a calibrated 10-ml pipet, measure aliquots of the standard calcium solution into each of three or four 200-ml conical flasks. Immediately before

---

*Alternatively the sample may be weighed into a 100-ml beaker and dissolved before transfer. Cover the beaker with a watch glass during the acid addition to avoid loss of spray, and swirl the solution gently after each addition. When dissolution is complete, rinse the undersurface of the watch glass into the beaker with a little deionized water from a wash bottle before quantitative transfer of the solution to the volumetric flask.

**Heating of volumetric flasks to moderate temperatures on a hot plate does not affect calibration, as the original volume is regained upon cooling to room temperature.

each titration add 50 mg of ascorbic acid, 10 ml of NH_3-NH_4Cl buffer, and 10 ml of a solution 0.4 M in NaCN (Caution: Poison) and 0.75 M in triethanolamine, mixing after each addition.* Then add 4 to 5 drops of Calmagite indicator solution. Titrate with EDTA solution until the indicator changes from red to pure sky blue with no tint of red.

Titration of sample. In a 100-ml beaker weigh 0.5 g of sample to the nearest 0.1 mg. Dissolve as for the standard.** A small residue of insoluble silicate minerals may be ignored. Dilute to 100 ml in a volumetric flask, pipet 10-ml aliquots into 200-ml flasks, and titrate in the same way as the standard.*** Report the percentage of calcium in the sample.****

Calculations. The concentration of the EDTA solution is found by

$$\text{molarity of EDTA} = \frac{(\text{gCaCO}_3)(V_{10}/100)}{(\text{mol wt CaCO}_3)(\text{ml EDTA}/1000)}$$

---

*The cyanide solution may be dispensed by following the directions for disposal carefully, as contact with acid produces poisonous HCN gas.

**For limestone samples, heating for 1/2 to 1 hour at 80 to 90° usually is necessary for dissolution.

***Most difficulties with indistinct end points arise from incorrect pH adjustment.

****The result could be reported in a number of ways, such as % $CaCO_3$, % $MgCO_3$, or % Mg. Here it is reported on the basis that all the material titrated is calcium. This is the common reporting practice.

where V_{10} is the calibrated volume of the 10-ml pipet. The percentage of calcium in the sample is then calculated by

$$\% \text{ Ca} = \text{wt Ca}(100)/\text{wt sample}$$

$$\text{wt Ca} = (\text{ml EDTA}/1000)(\text{molarity EDTA})(\text{mol wt Ca})$$

$$\text{wt sample} = (\text{initial wt of unknown})(V_{10}/100)$$

<u>Sample calculations</u>.

(a) For estimating molarity of EDTA:

$$\text{gms } CaCO_3 = 0.5$$

$$\text{M wt } CaCO_3 = 100.09$$

$$\text{Volume, EDTA} = 34.25 \text{ ml}$$

$$V_{10}, \text{ Volume of sample} = 10 \text{ ml}$$

$$M_{EDTA} = \frac{(\text{g } CaCO_3)(V_{10}/100)}{(\text{M } CaCO_3)(\text{ml EDTA}/1000)}$$

$$= \frac{0.5 \times (10/100)}{(100.09)(34.25/1000)}$$

$$= 0.014575$$

(b) For estimating % calcium:

Run no: 34-1

Sample wt: 0.5 grams

Volume of EDTA = 28.50 (average of 3 values)

$$\text{Wt. } Ca^{+} \text{ present} = \frac{(\text{ml EDTA})}{1000} (\text{MEDTA})(\text{M.W. Ca})$$

$$= \frac{28.50}{1000} \times .014575 \times 40.08 = .0165$$

$$\% \text{ Ca, by wt} = (\text{Wt Ca}^{+} \text{ present})100/\text{Wt sample}$$

$$\doteq \frac{.0165 \times 100}{.5}$$

$$= 33.30$$

Infrared Analysis of Dried Regenerated Cake

Preparation of samples. 200 mg infrared grade Potassium Bromide was weighed and 1-2 mg sample was added to it. The mixture was ground together and placed in Perkin-Elmer Pellet die. The die is placed in a press and pressed from 2 to 3 minutes at 20,000 psi. The pellet is removed from the die and is placed in the I.R. Spectrometer.

Operational procedure.

(a) Each pellet was scanned over the instrument's entire range (2.5-50 microns, 200-400 cm^{-1}(wave number)).

(b) The data obtained was used for qualitative information only as no exact correlation between concentration and transmittance was developed.

(c) The scan produced a graph on which the presence of different chemical species can be observed. The identifying characteristic is the wave number at which a certain species absorbs infrared radiation. The extent to which it absorbs is related to the concentration of the species present.

Several different compounds could be observed easily:

Species	Wave Number
sulphates (SO_4)	1130 cm^{-1}
sulphites (SO_3)	980 cm^{-1}
carbonates (CO_3)	1500-1400 cm^{-1}

Note: A hydrated compound may cause a shift in wave number (i.e. $CaSO_4 \cdot 1/2H_2O$, etc.) but was not observed during this work.

Specification. The following specification refers to the full range scan mode of operation of the Model 457 Spectrophotometer; the figures quoted correspond to the maximum tolerance limits permitted in the manufacture of the instrument. The performance of each instrument will be equal to or better than that specified. Measurements and calibration are effected at an ambient temperature of approximately 20°C.

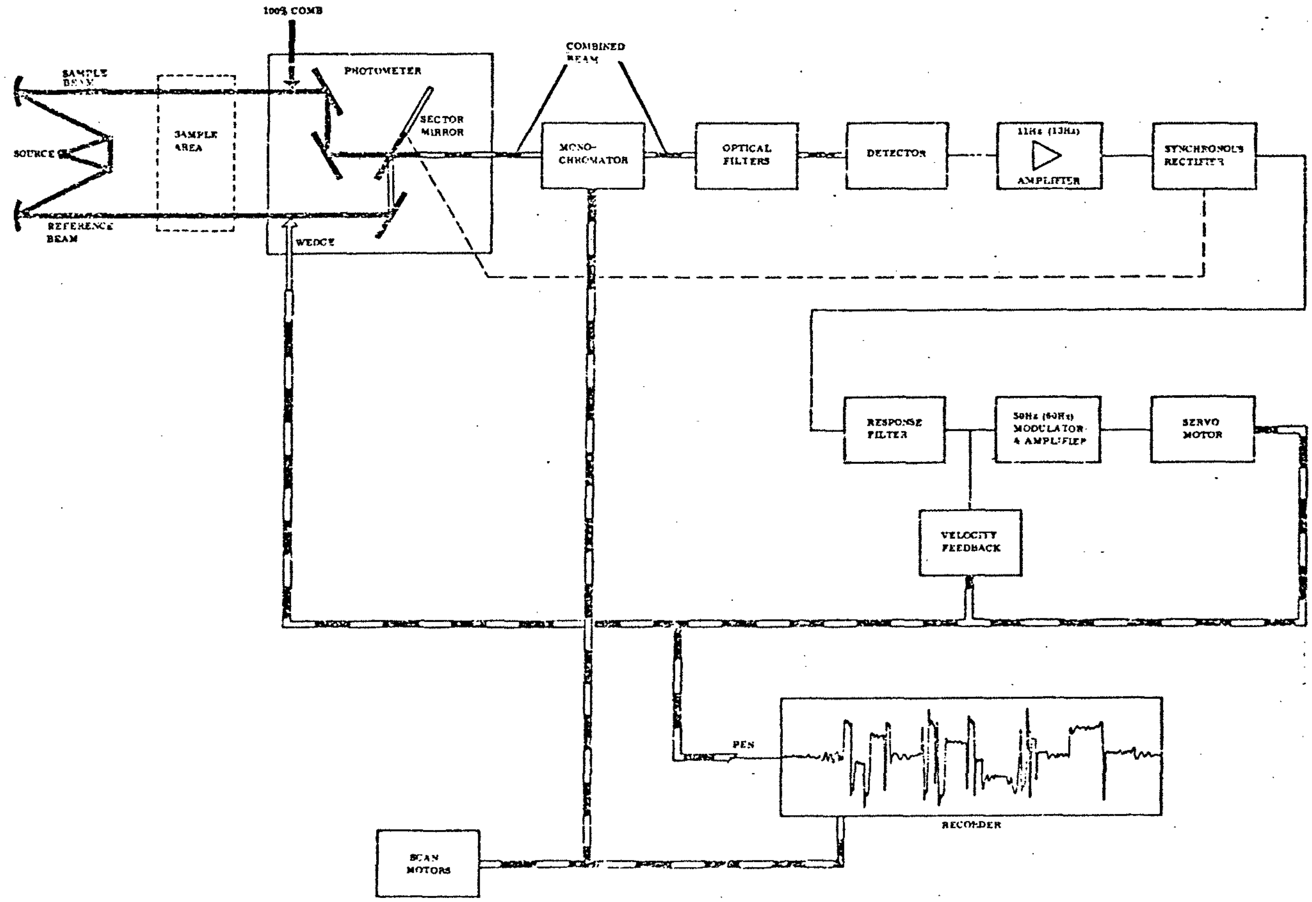
Principle	Double beam, optical null, linear transmittance versus linear wavenumber recording.
Optics	f/5 monochromator, two gratings, reflecting optical system employing planar and aspheric mirrors.

Chart Presentation	Chart size 21-1/2 x 60 cm with a grid size 15 cm ordinate and 55 cm abscissa and 2:1 scale change at 2000 cm^{-1}.
Abscissa Range	4000 to 250 cm^{-1}.
Abscissa Accuracy	Better than ±4 cm^{-1} from 4000 to 2000 cm^{-1} Better than ±2 cm^{-1} from 2000 to 250 cm^{-1}.
Abscissa Repeatability	2 cm^{-1} from 4000 to 2000 cm^{-1} 1 cm^{-1} from 2000 to 250 cm^{-1}.
Ordinate Range	0 to 100% Linear in Transmission
Ordinate Accuracy	±1% of full scale
Ordinate Repeatability	Within 1% of full scale
Double Beam I_0	Flat within 4% of full scale. I_0 change at 2000 and 600 cm^{-1} not more than 2% of full scale.
Noise	Peak to peak noise not greater than 1% of full scale for 90% of the time on normal slit programme.
Resolution: Normal Slit Programme	4 cm^{-1} at 3000 cm^{-1} 2 cm^{-1} at 1000 cm^{-1}
Narrow Slit Programme	2 cm^{-1} at 3000 cm^{-1} 1 cm^{-1} at 1000 cm^{-1}
Slit Control	The slit programme gives approximately constant energy over the

Slit Control (Cont'd.)	complete wavenumber range and allows operation at energy levels differing by a factor of approximately 8.
Stray Light	Less than 1/2% over 90% of the range 4000 to 420 cm^{-1}, and never more than 1%. Less than 2% from 420 to 280 cm^{-1}. Less than 3% at 250 cm^{-1}.
Scan Times	2-3/4 (5-1/2), 13-3/4 and 55 minutes corresponding to scan speeds of 2000 (1000), 400 and 100 cm^{-1}/minute in the range 4000 to 2000 cm^{-1} and 1000 (500), 200 and 50 cm^{-1}/minute in the range 2000 to 250 cm^{-1}.
Pen Servo Response	Full scale deflection of the pen in 0.8 seconds with maximum signal to the servo motor.
Supply Requirements	210 to 250V, 50 Hz, 150W. 115V, 60 Hz, 150W.

<u>Brief description</u>. The Model 457 Spectrophotometer provides a continuous record of the infrared transmittance of a sample as a function of frequency (expressed in wavenumber units). A chart is driven in synchronism with the

monochromator so that a pen moving laterally across the chart records the sample transmittance as a function of wavenumber.



As shown above,the wavenumber scan motor drives both the recorder and the grating monochromator scan mechanism, both of which are directly coupled, thus maintaining an accurate reproducibility of wavenumber setting.

The radiation emitted by the source is divided into two beams. One beam passes through the sample, which absorbs radiation of wavenumber corresponding to its characteristic molecular vibrational frequencies, whilst the other serves as a reference. In the sample beam there is a wedge-shaped comb attenuator, which is mechanically controlled by the 100% knob on the front panel, whilst in the reference beam there is a similar attenuator controlled by a servo motor. In the photometer section the two beams are combined by a rotating semicircular sector mirror to form a single beam consisting of alternate pulses of radiation from the sample and reference beams. This combined beam passes into the monochromator where it is dispersed by the grating into its spectral components. Rotation of the grating results in the dispersed spectrum being scanned across the monochromator exit slit. The mechanical width of the monochromator slit determines the width of the wavenumber band emerging from the monochromator. Thus decreasing the slit width decreases both this bandwidth, (i.e. improves the resolution) and the intensity of the emerging radiation (i.e. decreases the signal to noise ratio). The slit width is adjusted by the slit control on the front panel. After leaving the monochromator the radiation passes through one of a set of optical filters, the correct filter being automatically selected for the spectral region being scanned. This filter absorbs unwanted radiation diffracted from the grating at the same angle as the component of the desired wavenumber. Finally the transmitted radiation is focussed onto a thermocouple detector.

An alternating signal on the detector is amplified and fed to a servo-motor which moves the reference beam attenuator to equalize the intensity of the sample and reference beams. The alternating signal is thereby reduced to zero, producing a state of equilibrium.

When, at the characteristic absorption frequencies of the sample, the intensity of the sample beam changes, the two beams become unequal and the combined beam flickers at 11 Hz (13 Hz)(the rotational frequency of the sector mirror). An alternating signal called the ERROR signal is then generated by the detector, the amplitude of this signal being proportional to the error between the true transmittance and the indicated transmittance.

The error signal is amplified by the 11 Hz (13 Hz) amplifier, rectified by the synchronous rectifier, smoothed and modulated to give a 50 Hz (60 Hz) signal the phase of which is dependant on which beam is the more intense. After further amplification by the main amplifier this signal is used to drive the servo motor in a direction depending on the phase of the 50 Hz (60 Hz) signal so that the reference beam attenuator is moved to equalize the intensity of the sample and reference beams, thus reducing the error signal to zero. Since the recorder pen is mechanically linked to the attenuator, the pen will be displaced by an amount proportional to the change in sample transmittance.

Viscosities of Lime, Limestone and Sodium Bisulfite Solutions

Procedure. Shear stress-viscosity measurements were made using a Brookfield Model LVF 4-speed rotational viscometer. The instrument was calibrated against Cannon Instrument Company's Certified Viscosity Standards S60 and S200. Each slurry sample was stirred vigorously immediately before taking measurements at both increasing and decreasing shear rates in order to minimize settling effects. The average value was used to calculate viscosity. All measurements were performed at ambient temperature (~30°C). Each viscosity value represents an average of 4 individual readings.

Data. Viscosity data for sodium bisulfite, limestone and lime systems at varying solid levels is shown below.

SYSTEM	% SOLIDS	TEMPERATURE °C	RPM	VISCOSITY VALUES cps	AVERAGE VISCOSITY cp	SYSTEM VISCOSITY cp
Sodium Bisulfite	2.5	29.5	30	2.2 2.4 2.0 2.2	2.2	
		↓	60	3.0 3.0 3.0 3.0	3.0	
						2.6
	50		30	2.8 2.6 2.8 2.9	2.77	
			60	3.3 3.4 3.4 3.45	3.39	
						3.08

SYSTEM	% SOLIDS	TEMPERATURE °C	RPM	VISCOSITY VALUES cps	AVERAGE VISCOSITY cp	SYSTEM VISCOSITY cp
Sodium Bisulfite (Cont'd.)	10.0	29.5	30	3.0 2.9 2.8 3.0	2.93	
			60	3.4 3.43 3.45 3.45	3.42	
						3.17
	15.0		30	3.0 3.1 3.0 3.2	3.08	
			60	3.9 3.9 3.95 4.0	3.93	
						3.50
Limestone	1.5	30.0	60	5.0 4.5 4.5 5.0	4.75	4.75
	2.5		60	6.25 6.5 7.0 6.5	6.56	6.56
	10.0		60	10.0 10.5 9.5 10.0	10.0	10.0
Lime	2.5		30	3.0 3.0 2.9 3.0	3.0	
			60	3.3 3.4 3.6 3.7	3.5	
						3.25
	5.0		30	7.0 7.0 7.6 7.4	7.25	
			60	8.0 8.1 8.1 7.9	8.0	
						7.63
	15.0		30	14.0 15.0 16.0 15.0	15.0	
			60	12.5 12.0 12.5 12.5	12.4	
			60	11.6 12.5 12.5 13.0	12.4	
						13.26

CHAPTER VI

Experimental Data

Lime systems. Data gathered during this study are documented in the form of tables and figures. In order to differentiate and understand the regeneration systems, this section will deal with the lime-sodium Bisulfite system, and discuss the experiments conducted to acquire such data.

(a) Table 9 shows the particle size distribution of lime used for this study. The screen analysis was obtained by conventional technique.

(b) Table 10 documents pH and conversion data obtained in a tubular reactor. The procedure involved in feeding the two reactants at varying concentrations into the tubular reactor. The system was run for sufficient length of time to ensure steady states (steady pH value, not transient) after which a sample was drawn, filtered, dried and analyzed for conversion. Assumptions involved in estimating conversion is discussed under the section "analysis of data".

(c) Table 11 shows conversion data obtained in a backmix reactor and Figures 14 and 15 are plots of conversion data as functions of pH for tubular and backmix reactor.

(d) Table 12 shows backmix reactor data. Flow rates, molar ratios of reactants, conversion data, pH, reaction time are tabulated. Also, to the type of "feed" port entry whether single or separate port is indicated. A sample calculation is also included to indicate how conversion data was obtained.

(e) Table 13 shows tubular reactor data with detailed reaction parameters. Reactant concentrations, flow rates, residence time, sample time, material balances, pH, etc. are documented in this table. The procedure involved in running the tubular reactor system at steady states (pH of system steady not transient) and then continuously filtering the sample for a specific length of time (sample time), weighing the filtrate and cake, and analyzing them in the standard manner as discussed in the analytical section. Table 14 documents overall material balance, calcium and sulfite accountability and conversion data. Sample calculations for runs at different reactant ratios is also included as part of experimental documentation. Figure 16 essentially plots the conversion data as a function of residence time (vol. of reactor/vol. flow rates)(at varying Reynolds No.) with molar ratio of reactant ratio as parameters. Figures 17, 18 and 19 plot conversion, material balance data as a function of residence time for a given reactant ratio.

(f) Tables 15 and 16 present the same data obtained in a larger length tubular reactor and Figure 20 represents conversion plots as a function of residence time at same flow rates (same Reynolds Number).

CHAPTER VII

Data - Discussion & Results Lime-Sodium Bisulfite Systems

Particle size. The screen analysis of lime indicates 96.2% of the material weight to be in the -80 to +300 range. Finer particles less than -400 mesh amount to 2.85 wt % and above 80 mesh range to be 0.95% (Table 9).

The average particle size, "dp" was estimated by using the equation

$$dp = \frac{\sum_{i=1}^{n} (Wt)_i\% \ (dp)_i}{\sum_{i}^{n} (Wt)_i\%}$$

is found to be .0041" (105 μ).

pH conversion data. pH conversion data is tabulated in Tables 10 and 11. Both tubular reactor and backmix reactor were used for this study. All told, 10 runs were done in the 1/4" x 15" tubular reactor, (Runs 6A to 6E, 7A to 7E of Table 10) and 3 runs in the backmix reactor (Runs 8A to 8C of Table 11).

For the tubular reactor studies, the molar concentration of sodium bisulfite was 1 and the calcium hydroxide solid levels were varied between 2.5% (Runs 7A to 7E of

TABLE 9

SIEVE ANALYSIS OF LIME

Mesh	Wt %	Opening, Inches (Diameter)
50	-	.0117
60	-	.0098
70	-	.0083
80	.95	.0070
100	16.6	.0059
120	28.5	.0049
140	27.15	.0041
170	10.45	.0035
325	10.10	.0017
400	2.3	.0015
>400	2.85	-

Table 10) to 5% (Runs 6A to 6E of Table 10).

For the backmix reactor study, only one concentration level of sodium bisulfite and calcium hydroxide was investigated (Runs 8A to 8E of Table 11).

The conversion data for each case was investigated by varying pH which in turn was varied by varying reactant flow rates (volumes).

Conversion values varied between 88.4 to 92.7% (pH varied between 7.6 to 9.5) for Runs 6A to 6E of Table 10, 90.7 to 97.2% (pH varied between 6.8 to 8.6) for Runs 7A to 7E of Table 10 and 89.5 to 91.8% (pH varied between 6.8 to 8.5) for Runs 8A to 8C of Table 11.

Figures 14 and 15 are plots of above data with the reactant ratios and reactor type specified.

In plotting the conversion data as a function of pH, the following assumptions were made. An examination of Tables 10 and 11 show no material balances. Hence for estimating conversion, it was assumed that the system worked with no excess lime and Equation 1 or 2 is applicable indicating the system to be in the "sodium sulfite" or "sodium hydroxide" modes. The sulfite content in pure calcium sulfite hemihydrate is 62%. Therefore, the sulfite analysis of the precipitated dried cake divided by above value gave directly the conversion values. This simplified assumption was eventually verified to be valid with later experiments where actual material balances were made.

For the backmix reactor, similar calculations were made though the procedure of experimental running was slightly different. The exit port of the backmix reactor was closed so as to build up the batch level to reach the agitator. Then the exit port was opened to maintain a constant level of batch in the reactor. At steady state conditions, the batch was filtered, dried and analyzed as before.

Data from this study indicates the following:

(1) For all cases, conversion increases with decreasing pH (Figures 14 and 15).

(2) At the same reactant concentration, i.e., at 1 Molar Sodium bisulfite and at 5% (weight) calcium hydroxide levels, the tubular reactor regeneration gives higher conversion than backmix reactor (Figure 14) [Runs 6A to 6E vs 8A to 8C] conversion level of 94.5% at pH 7 for tubular reactor versus a value of 92.5% at pH 7 for backmix reactor.

(3) For the same reactor configuration, a tubular reactor, higher conversion is obtained for a

given pH by reducing the solid concentration level. Notice conversion levels as high as 96% a5 2.5 wt % solid concentration at pH 7 versus 94.5% at 5% solid level at the same pH (upper curve of Figure 15 versus Figure 14; Runs 7A to 7E versus 6A to 6E).

An analysis of the data shows two interesting features. Both reactor geometry and solid concentration level are critical. Better conversion is obtainable in a tubular reactor because of better mixing; in a backmix reactor, the conversion depends upon the ability of the agitator to keep the system well dispersed. Also, higher conversion is obtainable when the system becomes dilute. This indicates, then, to achieve higher conversions, one has to control the "agglomeration phenomena" which increases with poor mixing and increased solid levels. By agglomeration it is meant that lime in the absence of good mixing can cluster together to form a large mass (less surface area) or can be coated by the $CaSO_3$ formed in the regeneration. Note that in this system, a solid phase reactant is transformed to a solid phase product. When the system efficiency drops reactant agglomeration occurs, dramatically.

TABLE 10

CONVERSION DATA AS A FUNCTION OF pH

Reactor: Tubular Reactor, 1/4" I.D. x 15" Length

System: Sodium Bisulfite - Lime

Run No.	$NaHSO_3$ M(Molarity)	$Ca(OH)_2$ Wt %	pH of System	$SO_3^=$ Concn.	Conversion	IR Taken
6A	1	5	9.5	56.9	91.8	Yes
6B	DO	DO	8-9	54.8	88.4	DO
6C	DO	DO	8.6-8.9	57.5	92.7	DO
6D	DO	DO	8.5	56.9	91.8	DO
6E	DO	DO	7.6-8.2	56.7	91.5	DO
7A	DO	2.5	8.4-8.6	56.2	90.7	DO
7B	DO	DO	7.9	56.2	90.7	DO
7C	DO	DO	7.2-7.4	56.9	91.8	DO
7D	DO	DO	DO	59.5	96.0	DO
7E	DO	DO	6.8-7.0	60.2	97.2	DO

TABLE 11

CONVERSION DATA AS A FUNCTION OF pH

Reactor: Backmix Reactor, Separate Port Entries for Reactants

System: Sodium Bisulfite - Lime

Run No.	$NaHSO_3$ M(Molarity)	$Ca(OH)_2$ Wt %	pH of System	$SO_3^{=}$ Concn.	Conversion	IR Taken
8A	1	5	8.5	55.5	89.5	Yes
8B	DO	DO	7.0-7.5	56.9	91.8	DO
8C	DO	DO	6.8-7.0	57.4	92.6	DO

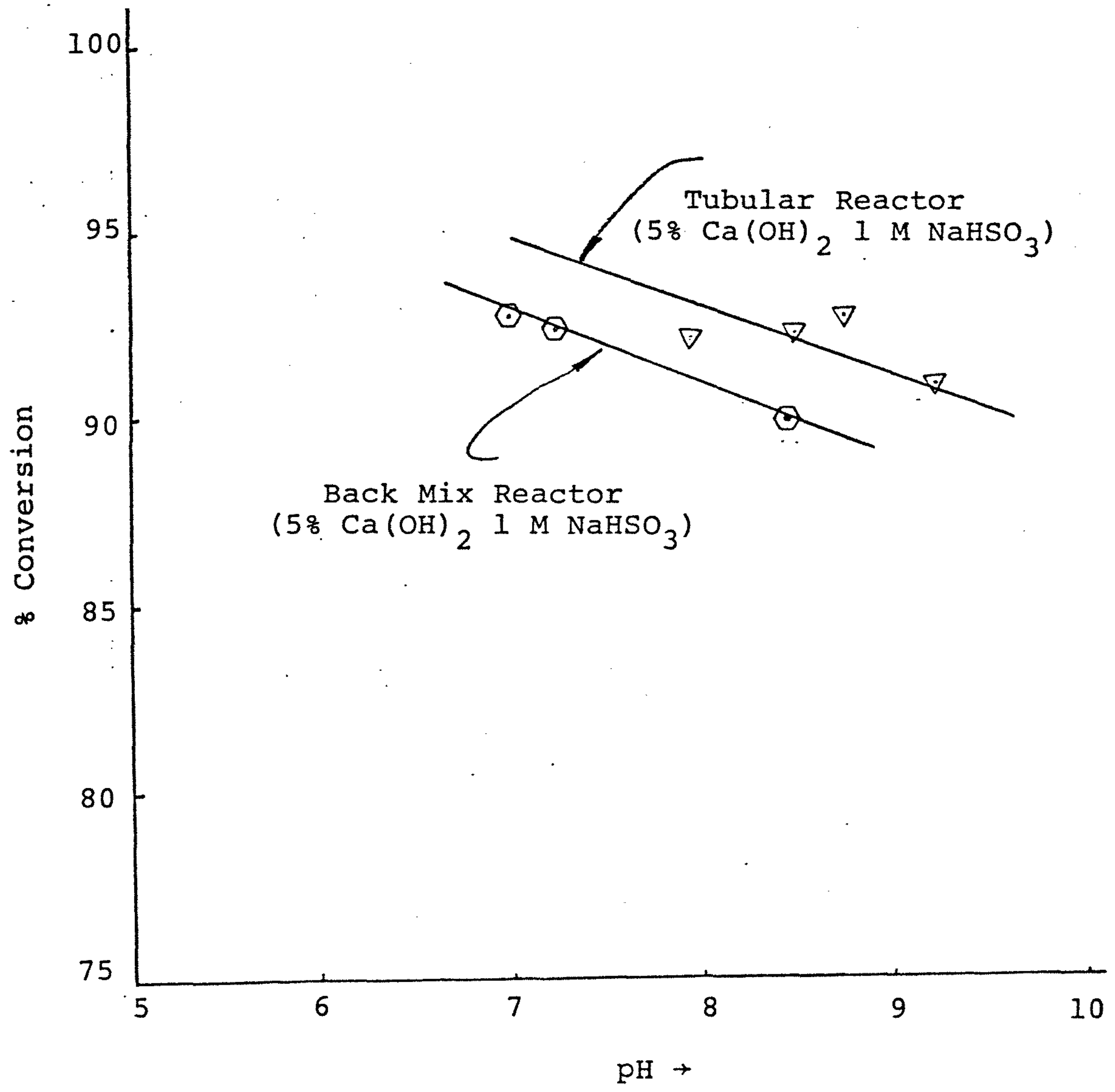


FIGURE 14. Conversion Data as a Function of pH

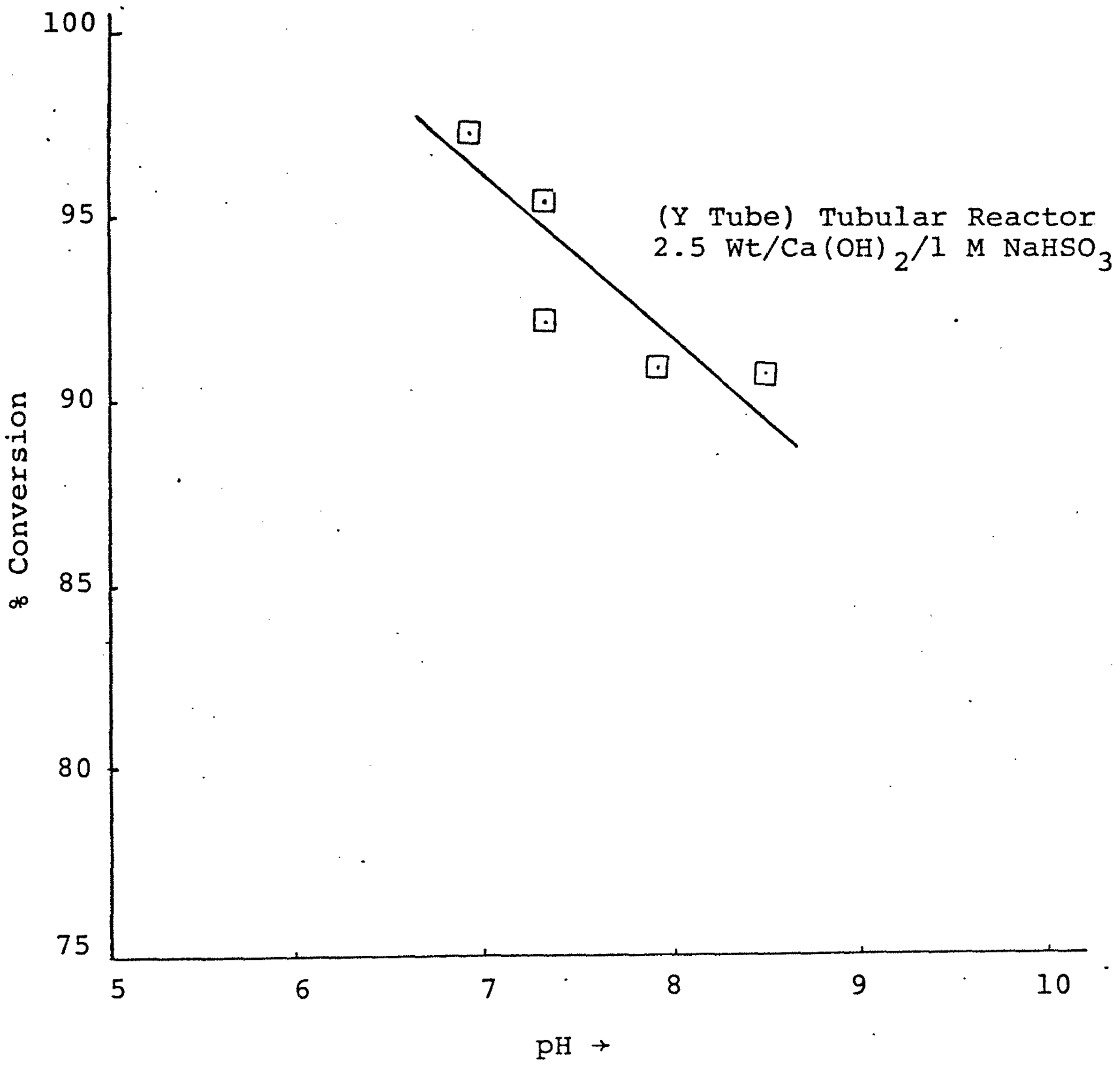


FIGURE 15. Conversion Data as a Function of pH

Backmix Reactor Data

The backmix reactor system has been depicted for scale up in various reports. Hence, regeneration aspects in a backmix reactor was initially examined. The two reactants were fed at separate entry ports or at single entry ports. The reactants were fed at different flow rates into the reactor and in some cases, were subjected to extended mixing in the reactor itself. Regeneration temperature was set at 104°F. Table 11 documents the results obtained. A total of six runs were made and the following results can be noted.

(1) A conversion of 69% was obtained, when the molar ratio of sodium bisulfite to $Ca(OH)_2$ was 0.1953 (excess lime) concentration of reactants and flow rates being 15 wt % lime at 0.22 liters/min and 0.6 Molar $NaHSO_3$ at 0.145 liters/min and reactants being fed at separate ports (Run 4A). A sample calculation is included to indicate how these values were calculated.

(2) When the above batch was further agitated for 15 minutes, calculated conversion was 64% and continued mixing for hours (equilibrium conversion) gave a conversion of 108% (Runs 4AE, 4AF).

(3) Repetition of run 1 at slightly different flow rates, at nearly the same molar ratio, with reac-

tants being fed together at a single entry port gave the following results.

(a) For runs 3A, with reactants entering at single port at flow rate of .166 liters per minute of sodium bisulfite at the same reactant concentration (15% wt lime, 0.6 M $NaHSO_3$), a conversion of 91% was obtained (Run 3A).

(b) Repeat of Run 4A, but using single port entry a conversion of 97% was obtained (Runs 3B, 3C) vs. 69% obtained for separate port entry (Run 4A).

Results of this study indicate the following:

(1) Conversion values of over 90% and close to 100% are obtainable by feeding the reactants together at one single port entry (Runs 3A, 3B & 3B).

(2) Conversion value of about 70% is obtained at equivalent flow rates and reactant ratio when regeneration is carried out in a back mix reactor with reactants entering at two separate ports (Run 4A). Additional mixing did help to bring conversion to 100% (Runs 4AF).

Data from this study as well as from earlier pH-conversion studies reveal that tubular or pipe line reactor systems are ideal for this regeneration step. A simple unsophisticated change of feeding reactants in the back mix reactor set up brought about a significant change in conversion values. This again points out that this drop in conversion values may be due to agglomeration of lime or due to the precipitation of calcium sulfite over lime thus rendering it unavailable for further reaction. Additional mixing presumably breaks these clusters and makes it available for further reaction.

Whatever is the actual phenomenon, these preliminary runs pointed out that the back mix reactor depicted for such regeneration schemes may indeed be not the reactor of choice, but rather pinpointed that regeneration should be carried in a "pipeline" or "tubular reactor system.

Sample calculation.

$$R = NaHSO_3/Ca(OH)_2 = \frac{1}{5.12} = 0.1953$$

Since pH >12, Equation I applicable (i.e., NaOH instead of Na_2SO_3).

$$\therefore \text{ Max } CaSO_3 \cdot 1/2H_2O \text{ obtainable} = .1953 \times 129 = 25.2 \text{ grams}$$

$$\text{Excess } Ca(OH)_2 \text{ in system} = (1-.1953) \times 74 = \underline{59.6} \text{ grams}$$

$$\text{Total } \underline{84.8}$$

$$\therefore SO_3^{=} \text{ concentration at 100\% conversion} = \frac{25.2 \text{x} .62}{84.8} = 18\%$$

$$\therefore \text{ For Run 4A; conversion} = \frac{SO_3^{=} \text{ in actual dry cake}}{SO_3^{=} \text{ theory}}$$

TABLE 12

BACKMIX REACTOR, $NaHSO_3$ - $Ca(OH)_2$ SYSTEM, REGEN TEMP-104°F, SEPARATE OR SINGLE PORT ENTRY VOLUME

Run #	Entry	$Ca(OH)_2$		$NaHSO_3$		Moles/Minute		R	pH System	Cake Analysis		
		Wt %	Ltrs/Min	M	Ltrs/Mt	$Ca(OH)_2$	$NaHSO_3$	$\frac{NaHSO_3}{Ca(OH)_2}$		$SO_3^=$ Concn	$SO_3^=$ Conc*Theor	% Conversion
4A	Separate	15	0.22	0.6	0.145	0.445	.0870	.1953	12.4	12.5	18	69
4AE	Separate & external mix -15mts	↓	↓	↓	↓	↓	↓	↓	↓	11.5	18	64
4AF	Separate but with external mix (batch)	↓	↓	↓	↓	↓	↓	↓	↓	19.5	18	100 (108)
3A	Single	↓	0.166	↓	0.111	0.336	.0666	.1980	-	16.9	18.6	91
3B	Single	↓	0.22	↓	0.145	0.445	.0870	.1953	-	17.6	18	97
3C	Repeat DO	↓	↓	↓	↓	↓	↓	↓	-	17.6	18	97

*$SO_3^=$ concentration in dry cake at 100% conversion.

$$= \frac{12.5}{18} = 69\%$$

Similar calculations for other runs.

Tubular Reactor Data

The object of this study was multifold. Earlier results had indicated that this type of system was ideal for regeneration but did not establish conversion data, calcium and material balances as a function of various parameters such as residence time, molar ratio of reactants reactant flows.

In this part of the experimental work, the following studies were undertaken:

I. Evaluate conversion as a function of flow rates, residence times and reactant ratios; this aspect was carried out at

   A. Three levels of reactant ratio, molar ratio of $NaHSO_3$/Lime being about 0.5, 1 and 2.

   B. The concentration of lime was kept the same at 2.5 wt % solids and the molar concentration of sodium bisulfite was varied between 0.24 to 0.94 molar to vary the molar ratio.

   C. Flow rate of lime varied between 130 to 385 cc/minute; and for sodium bisulfite solution between 100 to 300 cc/minute.

D. Tubular reactor length was 2 feet or 20 feet of same diameter (1/4"). Such variations in length were needed to investigate the effect of residence time at varying flow (varying Reynold's Number) and at same flow parameters (same Reynold's Number).

E. Residence time varied between 1 to 3.2 seconds (at varying Reynold's Number) and up to 32 seconds when constant flow conditions were desired (i.e., when constant flow conditions were desired, residence time varied between 1 to 10 seconds, 3.2 to 32 seconds respectively).

F. For a given run, the following parameters were recorded.

1. Reactor configuration
2. Reactant concentrations, pH and specific gravity.
3. Reactor flow.
4. Sample time.
5. Weights of filtrate, wet cake.
6. pH of filtrate and system.
7. Weight of dried cake.
8. Filtration time.

G. For the same run the following functions were calculated.

1. Residence time.
2. Material balance.
3. Calcium balance.
4. Conversion based on sulfite analysis of dried cake.
5. Conversion corrected to 100% material balance.
6. Infrared spectra of dried cake.
7. Sulfite analysis of filtrate.

Evaluating process data. Before analyzing actual data, method adopted to estimate various functions along with sample calculations will be discussed.

(1) Calculate residence time, Q_R, which is defined by the expression

$$Q_R = \frac{VR}{\Sigma(F_{V,NaHSO_3} + F_{\nu,Ca(OH)_2})} = \frac{VR}{F_{T_\nu}} \times 60$$

where VR = volume of reactor, cc

$F_{\nu NaHSO_3}$ = Flow of sodium bisulfite solution, cc/minute

$F_{\nu Ca(OH)_2}$ = Flow of lime solution, cc/minute

F_{T_ν} = Total flow of reactants, cc/minute

Q_R = Residence time, in seconds

(2) Estimate dry cake weight, $S_{D_{act,t}}$ by dividing dry cake weight S_D obtained for a given run by

sample time in minutes

$$S_{D_{act,t}} = \frac{S_D}{S_t}$$

where

S_D = dry cake weight

S_t = sample time, minutes

$S_{D_{act,t}}$ = dry cake weight per minute

(3) Obtain calcium and sulfite accountabilities per unit time $Ca^{++}_{act,t}$, $SO^{=}_{3_{act,t}}$ as follows

$$Ca^{++}_{act,t} = S_{D_{act,t}} \times Ca^{++}$$

$$SO^{=}_{3_{act,t}} = S_{D_{act,t}} \times SO_3^{=}$$

where Ca^{++}, $SO_3^{=}$ are calcium and sulfite analysis of dried cake.

(4) Estimate from flow conditions, the following

(a) Reactant molar ratio

$$R = \frac{F_{M_{NaHSO_3}}}{F_{M_{Ca(OH)_2}}} = \frac{F_{\nu_{NaHSO_3}} \times S_{NaHSO_3} \times Wt\%_{NaHSO_3} \times \frac{1}{M_{NaHSO_3}}}{F_{V_{Ca(OH)_2}} \times S_{Ca(OH)_2} \times Wt\%_{Ca(OH)_2} \times \frac{1}{M_{Ca(OH)_2}}}$$

where F_M, S, Wt%, M represents molar flow/

minute, density of soln, wt% of a reactant in solution and molecular wt of a reactant species.

(b) If $R \geq 1$, then such systems does not have excess lime. However, depending on the value of R, either sodium sulfite or sodium hydroxide can prevail in the system (equations 1 or 2). If $R < 1$, system suggests having excess lime and sodium is regenerated in the sodium hydroxide form (equation 2). Calcium and sulfite accountabilities at 100% conversion is evaluated by the following expressions.

$$Ca^{++}_{theor,t} = F_{M_{Ca(OH)_2}} \times M_{Ca}, \text{ for all values of R where } M_{Ca} = 40 \text{ (at. wt of Ca)}$$

$$SO_{3\,theor,t}^{=} = F_{M_{Ca(OH)_2}} \times M_{SO_3^=}, \text{ For } R \geq 1$$

$$= F_{M_{Ca(OH)_2}} \times R \times M_{SO_3^=}, \text{ For } R < 1$$

where $M_{SO_3^=} = 80$ (mol. wt of sulfite species)

(c) To estimate theoretical dry cake weight at 100% conversion for a given run, the following expression is used

$$S_{D_{theor,t}} = F_{M_{Ca(OH)_2}} \times M_{CaSO_3 \cdot 1/2H_2O} \text{ For } R \geq 1$$

where $M_{CaSO_3 \cdot 1/2H_2O} = 129$

$$= F_{M_{Ca(OH)_2}} [R \times M_{CaSO_3 \cdot 1/2H_2O} + [1-R] \, M_{Ca(OH)_2}] \text{ For } R < 1$$

where $M_{Ca(OH)_2} = 74$

(d) Sulfite analysis of liquor: Operating at $R \geq 2$, i.e. for systems which are operated under "starved" conditions of lime. Usually, its presence is indicated by reaction conditions and pH.

$$L\ SO_{3_{act,t}} = F_T \times SO_{3_L}^{=}$$

where $SO_{3_L}^{=}$ = sulfite analysis of liquor in gms/1000cc.

$$L\ SO_{3_{theor,t}} = \frac{(F_{M_{Ca(OH)_2}} \times M_{Na_2SO_3})}{(F_T \times S_T)}$$

where $M_{Na_2SO_3} = 126$

S_T = density of final solution (filtrate).

(5) With the various functions calculated from section (4) estimate the following material balance factor.

(a) % material balance on solids =

$$\frac{S_{D,act,t}}{S_{D,theor,t}} \times 100$$

(b) % calcium balance =

$$\frac{Ca^{++}_{act,t}}{Ca^{++}_{theor,t}} \times 100$$

(c) % conversion =

$$\frac{SO_3^{=}{}_{act,t}}{SO_3^{=}{}_{theor,t}} \times 100$$

(d) % conversion at 100% material balance =

$$\frac{SO_3^{=}{}_{act,\ t}}{SO_3^{=}{}_{theor,t}} \times \frac{S_{D,theor,t}}{S_{D,act,t}} \times 100$$

(e) % $SO_3^{=}$ balance in filtrate =

$$\frac{L\ SO_3^{=}{}_{act,t}}{L\ SO_3^{=}{}_{theor,t}} \times 100$$

<u>Sample calculations</u>. For Run 36-4

(1) Residence time, $Q_R = \frac{V_R}{F_T} = \frac{\frac{\pi D^2}{4} \times L}{(300+385)} \times 60 =$

$$\frac{\frac{\pi}{4} \times \frac{3}{16} \times \frac{3}{16} \times 26 \times (2.54)^3}{685} \times 60$$

$= 1.03$ seconds, where $F_{V_{NaHSO_3^=}} = 300$ cc/min

$F_{V_{Ca(OH)_2}} = 385$ cc/min

$D = 3/16"$

$L = 26"$

(2) Calculate $S_{D_{act,t}}$ = dry cake wt/minute

$$S_{D_{act,t}} = \frac{S_D}{S_t} = \frac{14.4}{(60/60)} = 14.4$$

where $S_D = 14.4$ gms (dry cake wt)

S_t = sample time (60 secs)

(3) Estimate calcium and sulfite accountability

$$Ca^{++}_{act,t} = S_{D_{act,t}} \times Ca^{++} = 14.4 \times .3836 = 5.523 \text{ grams}$$

(Ca^{++} - average of 3 values)

$$SO^=_{3_{act,t}} = S_{D_{act,t}} \times SO_3^= = 14.4 \times .383 = 5.52 \text{ grams}$$

(SO_3^{++} - average of 3 values)

(4) Evaluate

(a) $$R_M = \frac{F_{M,NaHSO_3}}{F_{M,Ca(OH)_2}} = \frac{(300 \times 1.014 \times \frac{2.48}{100} \times \frac{1}{104})}{(385 \times 1.0135 \times \frac{2.5}{100} \times \frac{1}{74})} =$$

$$\frac{.07254}{.13182} = 0.551$$

Since $R < 1$, excess lime present.

(b) $Ca^{++}_{theor,t} = F_{M_{Ca(OH)_2}} \times M_{Ca} = .13182 \times 40 =$

5.272 grams

$SO^{=}_{3\,theor,t} = F_{M_{Ca(OH)_2}} [R \times M_{SO_3^{=}}] =$

$.13182 \times .551 \times 80 = 5.81$ grams

$S_{D_{theor,t}} = F_{M_{Ca(OH)_2}} [R \times M_{CaSO_3 \cdot 1/2H_2O} +$

$(1-R) M_{Ca(OH)_2}] = .13182 \; [.551 \times 129 + (.449)74]$

$= 13.749$ grams

(c) Since $R < 1$, pH >> 8 (12.84), Sodium hydroxide mode (Eq. RI applicable)

$L\; SO^{=}_{3\,theor,t} = 0$

$L\; SO^{=}_{3\,act,t} = (F_T)[SO_3^{=}]_{\ell} = [685][4/1000] =$

2.74 grams

(5) Material balances

$$\% \text{ material balance on solids} = \frac{S_{D,act,t}}{S_{D,theor,t}} \times 100 =$$

$$\frac{14.4}{13.75} \times 100 = 104.7$$

$$\% \text{ calcium balance} = \frac{Ca^{++}_{act,t}}{Ca^{++}_{theor,t}} \times 100 = \frac{5.52}{5.27} \times 100 = 104.7$$

$$\% \text{ conversion} = \frac{SO^{=}_{3act,t}}{SO^{=}_{3theor,t}} \times 100 = \frac{5.52}{5.81} \times 100 = 95.00$$

% conversion @ 100% material balance =

$$\frac{SO^{=}_{3act,t}}{SO^{=}_{3theor,t}} \times \frac{S_{D,theor,t}}{S_{D,act,t}} \times 100 = (0.95) \times (\frac{1}{1.047})$$

$\times\ 100 = 90.74\%$

Sample calculations for Run 35-4

(1) $Q_R = \frac{V_R}{F_T} = 1.03$ seconds, (same flow conditions as 36-4).

(2) $S_{D_{act,t}} = \frac{S_D}{S_T} = 15.75$ grams/min

(3) $Ca^{++}_{act,t} = S_{D_{act,t}} \times Ca^{++} = 15.75 \times .3161 = 4.98$

(Ca^{++} - average of 3 values).

$SO^{=}_{3_{act,t}} = S_{D_{act,t}} \times SO^{=}_{3} = 15.75 \times .589 = 9.28$

($SO^{=}_{3}$ - average of 3 values).

(4) (a) $$R_M = \frac{F_{M_{NaHSO_3}}}{F_{M_{Ca(OH)_2}}} = \frac{300 \times 1.0365 \times \frac{4.95}{100} \times \frac{1}{104}}{385 \times 1.0135 \times \frac{2.5}{100} \times \frac{1}{74}}$$

$= 1.128$

Since $R \geq 1$, no excess lime present, since pH = 12.9, it suggests systems present in the 'NaOH' mode.

(b) $Ca^{++}_{theor,t} = F_{M_{Ca(OH)_2}} \times M_{Ca} = .13182 \times 40 =$ 5.272 grams

$$SO_{3\,theor,t}^{=} = F_{M_{Ca(OH)_2}} \times M_{SO_3^=} = 10.55 \text{ grams}$$

$$S_{D_{theor,\,t}} = F_{M_{Ca(OH)_2}} \times M_{CaSO_3 \cdot 1/2H_2O} =$$

17.00 grams

(c) Since pH >> 8 and R = 1.128,

$$L\ SO_{3\,theor,t}^{=} = 0$$

$$L\ SO_{3\,act,t}^{=} = [F_T \times SO_3^= L] = 685 \times \frac{4.8}{1000} =$$

3.28 grams

(5) Material balances

% material balance on solids =

$$\frac{S_{D,act,t}}{S_{D,theor,t}} \times 100 = \frac{15.75}{17.00} \times 100 = 92.65\%$$

% calcium balance =

$$\frac{Ca^{++}_{act,t}}{Ca^{++}_{theor,t}} \times 100 = \frac{4.98}{5.27} \times 100 = 94.5\%$$

% conversion =

$$\frac{SO_{3\,act,t}^{=}}{SO_{3\,theor,t}^{=}} \times 100 = \frac{9.28}{10.55} \times 100 = 87.96\%$$

% conversion at 100% material balance =

$$\frac{SO_{3\,act,t}^{=}}{SO_{3\,theor,t}^{=}} \times \frac{S_{D_{theor,t}}}{S_{D_{act,t}}} \times 100 = (.8796) \times (\frac{1}{.9265}) \times 100$$

= 94.94%

Sample calculations for Run 34-4

(1) $Q_R = \frac{V_R}{F_T}$ = 1.03 seconds (same flow conditions as 34-4)

(2) $S_{D_{act,t}} = \frac{S_D}{S_T} = \frac{8.5}{(30/60)} = 17.0$ grams/mt

$S_D = 8.5$ grams, $S_T = 30$ secs.

(3) $Ca^{++}_{act,t} = S_{D_{act,t}} \times Ca^{++} = 17.0 \times .3183 = 5.41$ grams

$SO_3^{=}{}_{act,t} = S_{D_{act,t}} \times SO_3^{=} = 17.0 \times .587 = 10.10$ grams

(4) (a) $$R_M = \frac{F_{M_{NaHSO_3}}}{F_{M_{Ca(OH)_2}}} = \frac{300 \times 1.069 \times \frac{9.4}{100} \times \frac{1}{104}}{385 \times 1.0135 \times \frac{2.5}{100} \times \frac{1}{74}}$$

= 2.12

Since R > 1, pH = 6.9, < 8 suggests that equation 1 applicable (i.e. sodium sulfite mode).

(b) $Ca^{++}_{theor,t} = F_{M_{Ca(OH)_{2,t}}} \times M_{Ca} = .13182 \times 40$

= 5.272 grams, R > 1

$SO_3^{=}{}_{theor,t} = F_{M_{Ca(OH)_2}} \times M_{SO_3^{=}} = .13182 \times 80$

= 10.55 grams, R > 1

$S_{D_{theor,t}} = F_{M_{Ca(OH)_2}} \times M_{CaSO_3 \cdot 1/2H_2O} =$

.13182 x 129 = 17.00 grams, R > 1

(c) pH << 8,

$$L\ SO_{3\ \text{theor},t}^{=} = \frac{F_{M_{Ca(OH)_2}} \times M_{Na_2SO_3}}{F_T \times S_T} =$$

$$\left(\frac{.13182 \times 126}{685}\right) \times 1000 = \frac{24.24\ \text{grams}}{\text{liter}}$$

$$L\ SO_{3\ \text{act},t}^{=} = 17.10\ \text{grams/liter}$$

(5) Material balance

% material balance on solids =

$$\frac{S_{D_{\text{act},t}}}{S_{D_{\text{theor},t}}} \times 100 = \frac{17.0}{17.0} = 100$$

$$\%\ Ca^{++}\ \text{balance} = \frac{Ca^{++}_{\text{act},t}}{Ca^{++}_{\text{theor},t}} \times 100 = \frac{5.41}{5.27} = 102$$

% conversion =

$$\frac{SO_{3\ \text{act},t}^{=}}{SO_{3\ \text{theor},t}^{=}} \times 100 = \frac{10.10}{10.53} \times 100 = 95.9$$

% conversion at 100% material balance =

$$\frac{SO_{3\ \text{act},t}^{=}}{SO_{3\ \text{theor},t}^{=}} \times \frac{S_{D_{\text{theor},t}}}{S_{D_{\text{act},t}}} \times 100 = 95.9$$

In a manner illustrated above, data for other runs were calculated and Tables 14 and 15 tabulate the results. Figure 16 plots conversion data at 100% material balance versus residence time with reactant ratios as a parameter.

Tables 15 and 16 are summaries of conversion data as a function of residence time at constant flow conditions. Altogether four sets of data (2 data point for each set) is shown. For estimating conversion, only sulfite analysis were made and compared.

Data. Detailed documentation of various functions of process data is shown in Tables 13, 14, 15 and 16. However, in order to discuss and scrutinize data, certain aspects of process data will be redocumented and is shown below.

From Tables 13 and 14 the following can be noted:

Run #	R_M	Q_R(sec)	%Overall Mat Bal	%Calcium Balance	% Conv.	%Conversion @ 100% M.B.
36-4	0.55	1.03	104.7	104.7	95	90.7
36-1	0.55	1.60	99.0	96.0	88.5	90.0
36-3	0.56	2.10	98.0	102.0	70.1	71.5
36-2	0.54	3.20	90.0	86.0	64.9	72.0
35-4	1.12	1.03	92.7	95.0	88.0	94.9
35-3	1.14	2.10	91.2	98.2	84.6	92.0
35-2	1.11	3.20	86.8	86.0	78.0	90.7
35-2 (Rep)	1.11	3.20	-	-	-	85.0
34-4	2.12	1.03	100	102	95.8	95.9
34-3	2.17	1.60	85	85	76.0	90

Run #	R_M	Q_R(sec)	%Overall Mat Bal	%Calcium Balance	%Conv.	%Conversion @ 100% M.B.
34-2	2.22	2.10	63	67	53.0	84
34-1	2.1	3.20	74	76	59.0	80

From Tables 15 and 16 one can note the following:

R_M	Run #	Q_R(sec)	Conversion	Run #	Q_R(sec)	Conversion
2.0-2.2	40-3	3.2	84	40-1	32	84.8
2.0-2.2	40-4	1.0	86.7	40-2	10	88.2
1.0-1.1	41-3	1.0	95.3	41-2	10	95.3
0.5-0.55	42-3	1.0	92.3	42-2	10	94.1

TABLE 13

EFFECT OF REACTOR RATIOS AND RESIDENCE TIME ON LIME-$NaHSO_3$ SYSTEM (REACTOR GEOMETRY)

Run	System	$NaHSO_3$				$Ca(OH)_2$				Moles Flow Rates			QR (Secs)	Total Wt	Run Time (Min)	pH of System	Filtrate			Cake			
		M	Wt %	pH	S.G.	Wt %	pH	S.G.	Grnd	$\frac{NaHSO_3}{Ca(OH)_2}$	$NaHSO_3$	$Ca(OH)_2$					Wt	pH	$SO_3^=$ Anal g/liter	Wet Wt	Dr Wt	$SO_3^=$	Ca^{++}/IR
36-4	Tubular	.24	2.48	4.47	1.014	2.5	12.7	1.0135	No	.551	.300	.385	1.03	709.8	60	12.3	682.2	12.84	4.0	27.6	14.4	38.3	38.36
36-1										.548	.198	.255	1.60	112.4	150	12.35	1072.2	12.05	4.08	40.2	22.4	37.8	37.59
36-3										.558	.150	.190	2.10	531.3	100	11.65	510.1	12.81	3.4	21.2	11.1	30.8	39.79
36-2										.543	.100	.130	3.30	1051.4	250	12.55	1013.8	12.88	4.2	37.6	20.85	41.8	36.48
35-4		.495	4.95		1.0365	2.5	12.7	1.0135	No	1.123	.300	.385	1.03	707.7	60	12.9	681.2	12.87	4.8	26.5	15.75	58.9	31.61
35-3										1.1385	.150	.190	2.10	352	60	12.15	337.4	12.84	3.85	14.6	8.1	56.9	33.08
35-2										1.109	.100	.130	3.2	1201.6	306	8	1156.1	6.99	13.5	45.5	25.4	55.4	30.69
34-4		.94	9.4		1.069	2.5	12.7	1.0135	No	2.117	.300	.385	1.03	367.5	30	7.8-8.4	352.8	6.79	17.10	14.7	8.5	58.7	31.83
34-3										2.173	.150	.190	2.10	392.2	68	7-7.4	318.6	6.89	16.74	13.6	8.1	55.1	30.86
34-2										2.216	.106	.135	3.2	144.8	35	6.6	140.3	6.75	8.08	4.5	2.2	51.5	32.59
34-1										2.203	.198	.255	1.6	200.8	26	6.75	193.9	6.87	14.4	6.9	3.6	50.4	33.3
34-1R															-	8.6-8.7	-	-		-	-	49.4	
34-1RR															-	7.65	-	-		-	-	47.7	

TABLE 14

MATERIAL BALANCE FOR CALCIUM, SOLIDS AND CONVERSION DATA FOR LIME-$NaHSO_3$ SYSTEMS (BASIS: PER MINUTE)

Run #	R = $\frac{NaHSO_3}{Ca(OH)_2}$	Q_R, Res. Time (Sec)	Material Balance For Solids			Calcium Analysis			$SO_3^=$ Analysis			pH	% Conversion at 100% Material Balance on Solids
			Dry Wt.	Expected Weight	% M B	Ca^{++} in Cake	Ca^{++} by Theory	% Ca^{++}, M B	$SO_3^=$ in Cake	$SO_3^=$ for 100% Conv	% Conv		
36-4	.551	1.03	14.40	13.74	104.0	5.523	5.27	104.0	5.52	5.80	94.9	12.9	91.2
36-1	.548	1.60	8.96	9.10	99.0	3.370	3.49	96.0	3.39	3.83	88.5	12.8	90.0
36-3	.558	2.10	6.66	6.808	98.0	2.650	2.60	102.0	2.05	2.90	70.1	12.8	71.5
36-2	.543	3.20	4.98	5.500	90.0	1.530	1.78	86.0	2.09	3.21	64.9	12.9	72.0
35-4	1.123	1.55	15.75	17.00	92.7	4.980	5.27	95.0	9.28	10.55	88.0	12.9	94.9
35-3	1.139	2.10	8.10	8.88	91.2	2.680	2.73	98.2	4.62	5.456	84.6	12.9	92.0
35-2*	1.109	3.20	4.98	5.74	86.8	1.53	1.78	86.0	2.76	3.56	78.0	8	90.7
35-2R	1.109	3.20										12.6	85.0
34-4	2.117	1.55	17.0	17.0	100	5.41	5.27	102	10.1	10.54	95.8	7.8-8.4	95.9
34-3	2.173	1.60	7.15	8.38	85	2.21	2.60	85	3.94	5.20	76.0	7-7.4	90
34-2	2.216	2.10	3.8	5.96	63	1.23	1.85	67	1.95	3.70	53.0	6.6	84
34-1	2.203	3.20	8.3	11.26	74	2.76	3.49	76	4.19	6.98	59.0	6.8	80

*Suspect Analysis since pH = 8

TABLE 15

CONVERSION DATA FOR LIME-SODIUM BISULFITE SYSTEM AS A FUNCTION OF RESIDENCE TIME AT CONSTANT FLOW CONDITIONS (SAME REYNOLDS NUMBER)

Reactant	Flow Rate cc/minute
Lime Slurry	385
Sodium Bisulfite Solution	300

RUN NO	40-4	40-2	41-3	41-2	42-3	42-2
Reactant Ratio, R_M	← 2-2.2 →		← 1.0-1.1 →		← 0.5-0.55 →	
Residence Time, Q_R, Seconds	1	10	1	10	1	10
Sulfite($SO_3^=$) Analysis of Cake	53.7	54.7	55.1	55.2	42.2	43.3
% Conversion	86.7	88.2	95.3	95.3	92.3	94.1

TABLE 16

CONVERSION DATA FOR LIME-SODIUM BISULFITE SYSTEM AS A FUNCTION OF RESIDENCE TIME AT CONSTANT FLOW CONDITIONS (SAME REYNOLDS NUMBER)

Reactant	Flow Rate cc/minute
Lime Slurry	150
Sodium Bisulfite Solution	100

RUN NO	40-3	40-1
Reactant Ratio, R_M	2.1	2.2
Residence Time, Q_R, Seconds	3.2	32
Sulfite$(SO_3^=)$ Analysis of Cake	51.5	52.0
% Conversion	84.0	84.8

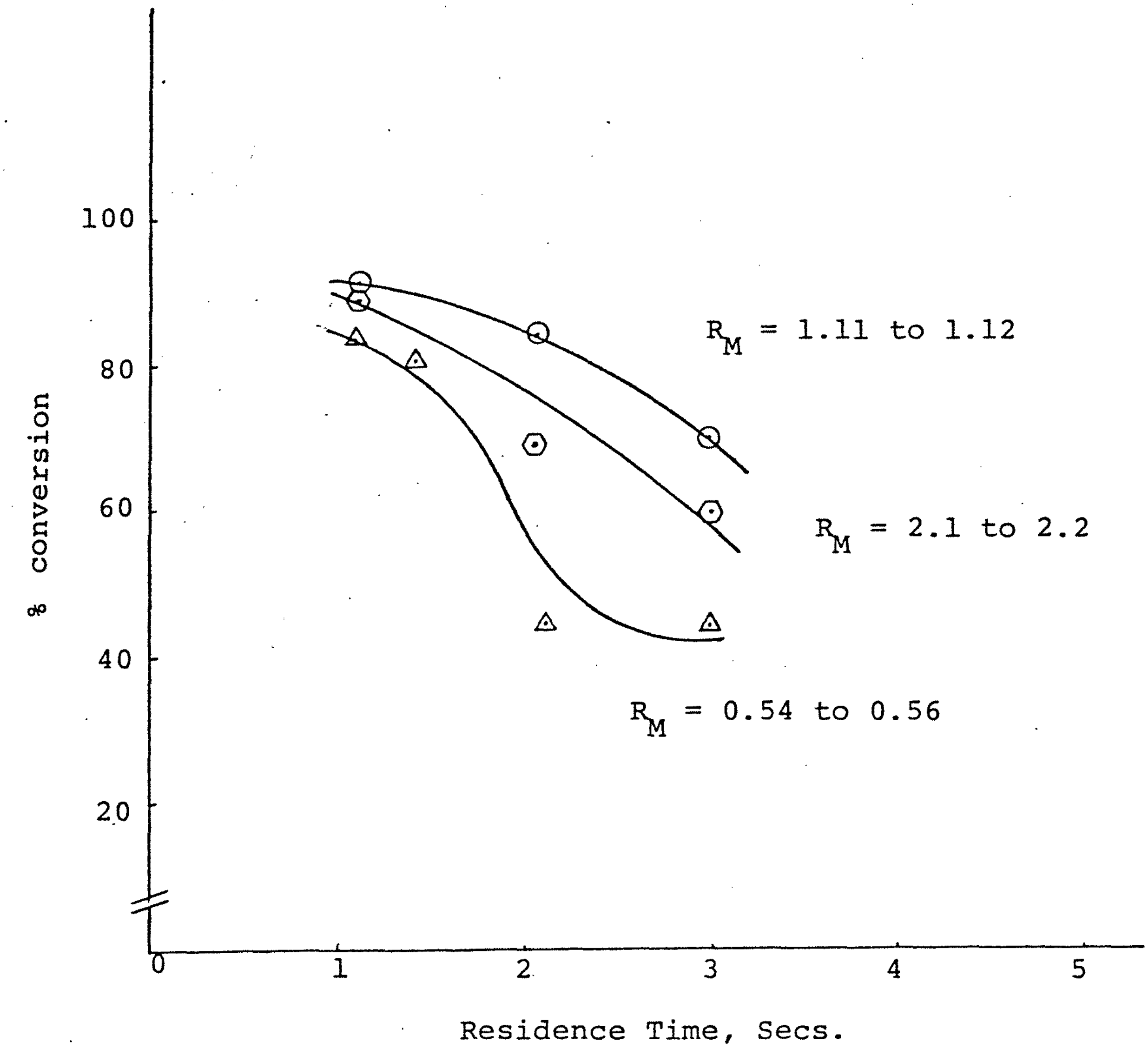


FIGURE 16. % Conversion at 100% Material Balance
Lime-Sodium Bisulfite Systems

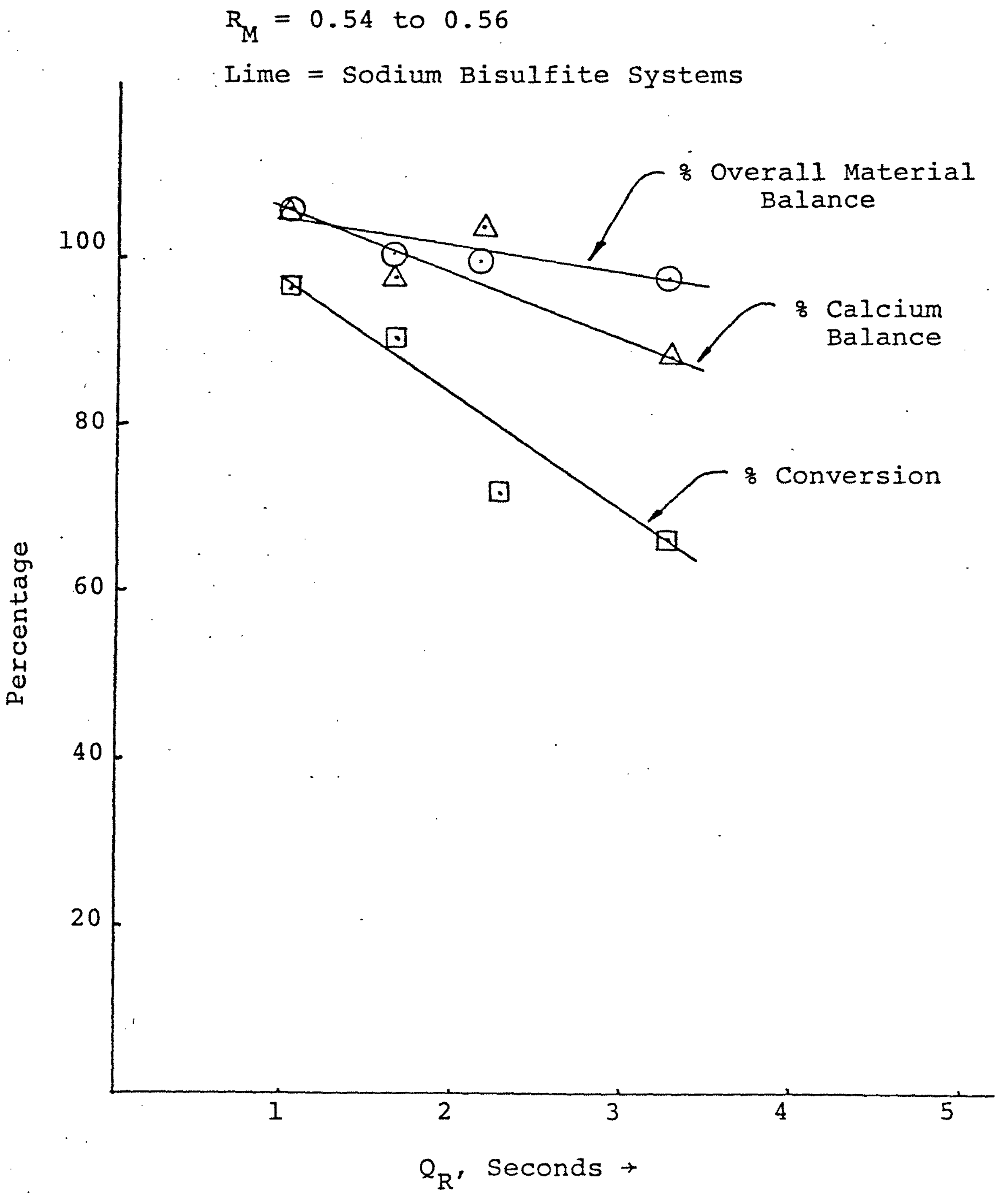


FIGURE 17.

Conversion, Calcium and Overall Material Balance for Lime-Sodium Bisulfite System at Reactant Ratio of 0.54 to 0.56.

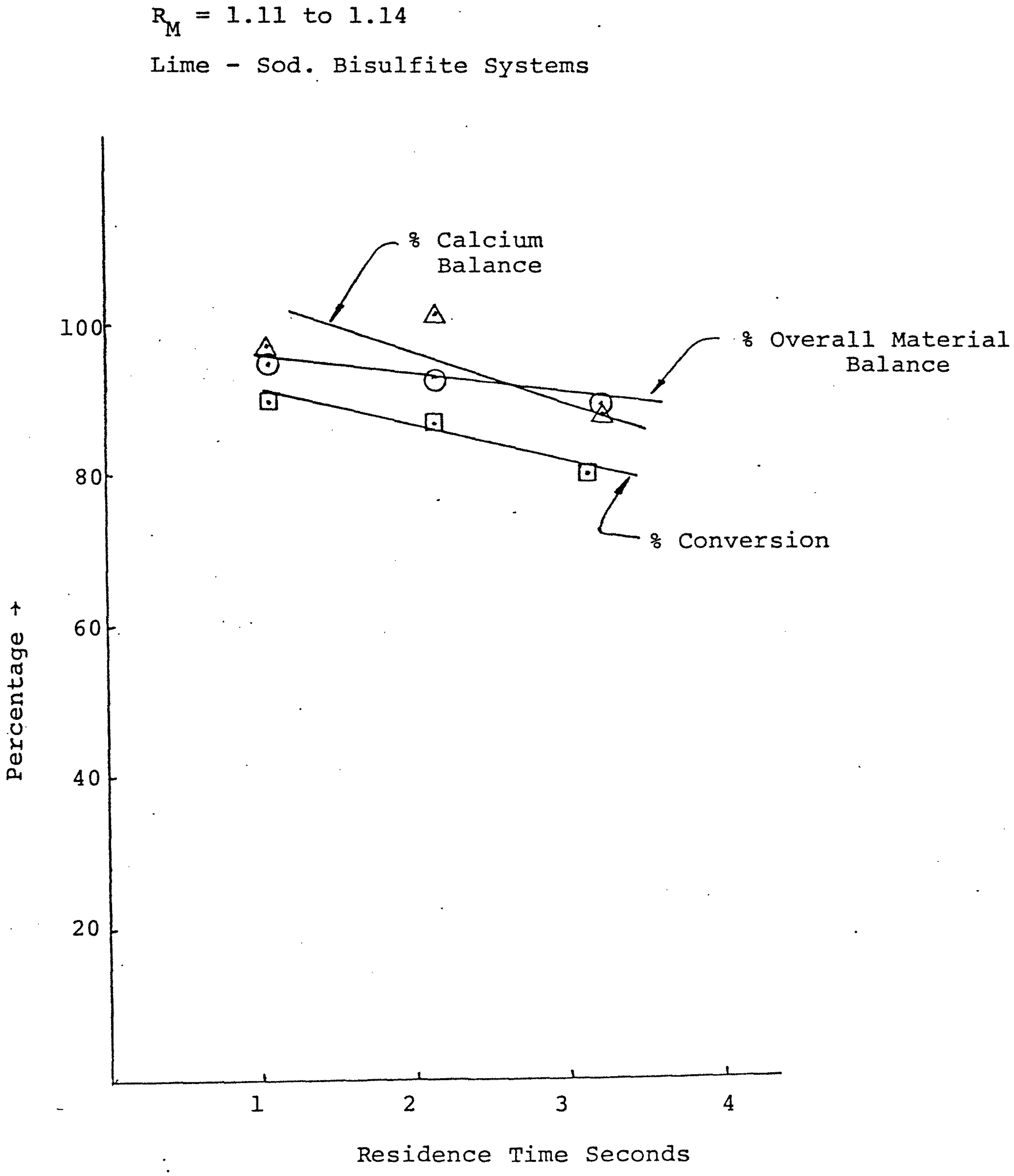


FIGURE 18.

Conversion, Calcium and Overall Material Balance for Lime-Sodium Bisulfite System at Reactant Ratio of 1.1 to 1.14

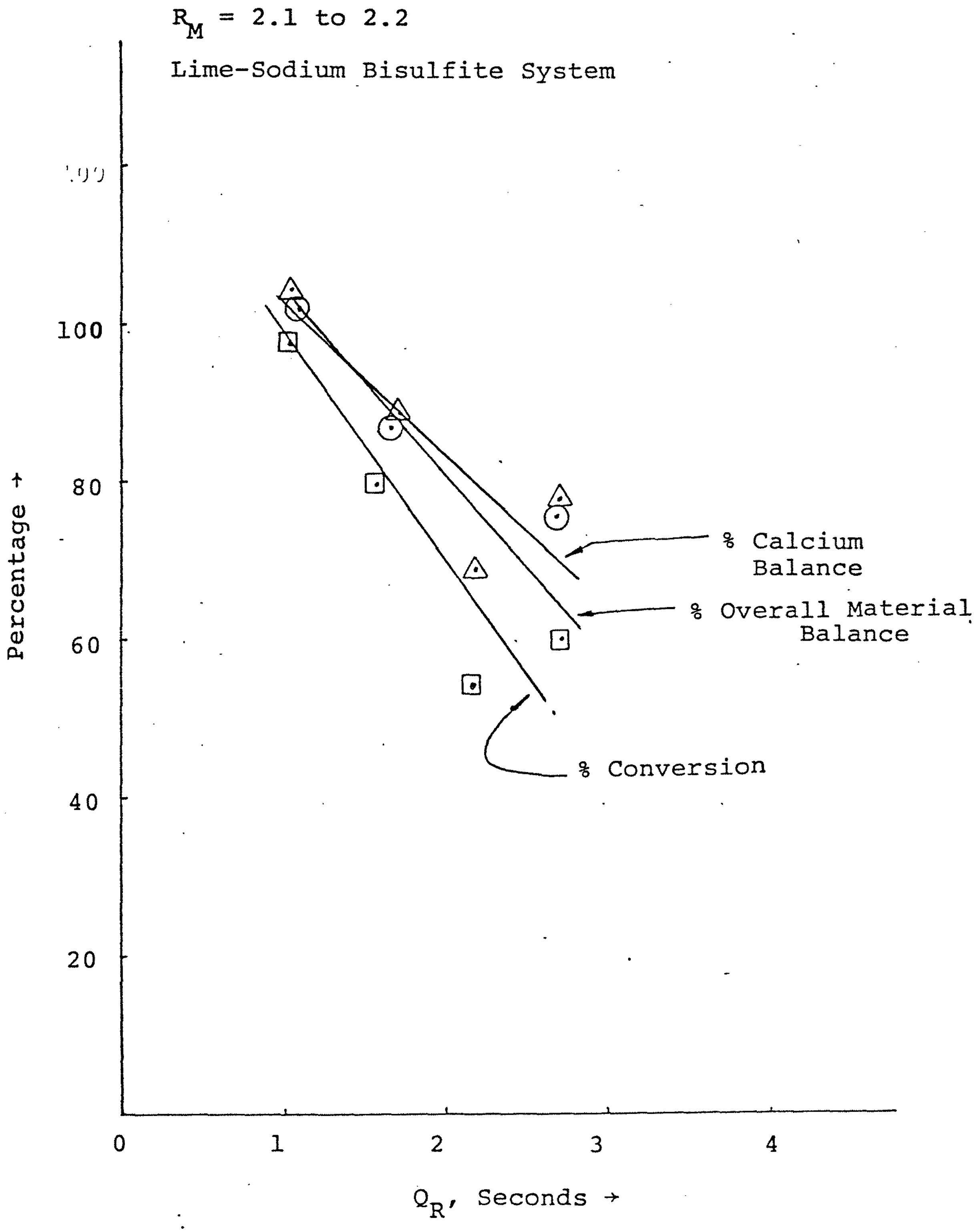
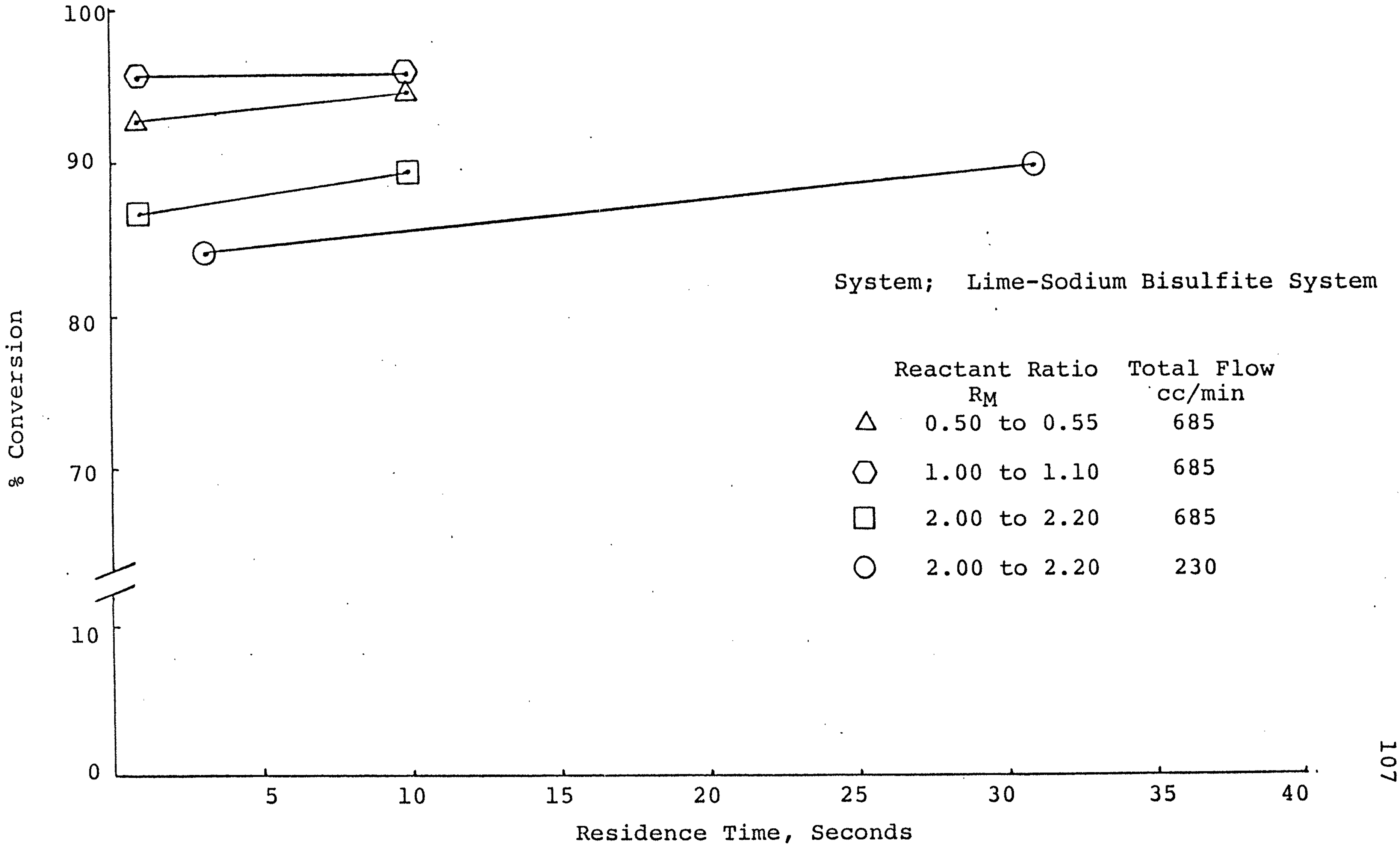


FIGURE 19.

Conversion, Calcium and Overall Material Balance for Lime-Sodium Bisulfite System at Reactant Ratio of 2.1 to 2.2.

FIGURE 20. Conversion Data as a Function of Residence Time (At Same Flow Conditions).



Data Analysis

An analysis of documented data reveals the following:

(1) For a given reactant molar ratio in general, the overall material balance, the calcium balance, the conversion decreases as the flow in the reactor (residence time) decreases. For example, $R_M = 0.55$, the overall material balance varied between 104.7 (1.03 seconds) to 90.0 (3.2 seconds), the % calcium balance varied between 104.7 (1.03 seconds) to 86.0 (3.2 seconds), % conversion varied between 95 (1.03 seconds) to 64.9 (3.2 seconds).

Similarly, for $R_M = 1.1$, the appropriate functions were 92.7 vs. 86.8, 95.0 vs. 86.0, 88.0 vs. 78 respectively, and for $R_M = 2.1$ to 2.2, the equivalent functions were 100 vs. 74, 102 vs. 76, 95.8 vs. 59.0.

All of these effects can be seen more vividly from Figures 16, 17 and 18. Though the above trend is clear, anomalies do exist, for example % calcium balance of 102 (2.10 secs)(36-3) vs. 96 (1.6 seconds)(36-1); % overall material balance of 63 (2.10 seconds)(34-2) vs. 74 (3.2 seconds)(34-1); % calcium balance of 67 (2.10 seconds)(34-2) vs. 76 (3.2 seconds)(34-1).

(2) The overall material balance is poor with decreasing flow rates and one probable cause for this is the settling of solids observed in the reactor, pH chamber, etc. Assuming that this did not occur, the calculated conversion values were reestimated for 100% material balance and plotted in Figure 16, and again show a drop in conversion as residence time (flow volumes) decreased.

At residence time of 1.0 seconds, conversion for all values of R_M were above 90% (90.7% at R_M = 0.55 (36-4); 94.9 for R_M = 1.12 (35-4); and 95.9% at R_M = 2.12 (34-4).

At residence time of 3.2 seconds, conversions dropped considerably (72.0% at R_M = 0.54 (36-2), 85.0% at R_M = 1.12 (35-2R) and 80% at R_M = 2.10 (34-1)).

(3) Conversion, in general, from Figure 16 increases with decreasing residence time or with increasing Reynold's number.

(4) Increasing lime, i.e. decreasing Reactant Ratio R_M has interesting effect on conversion. At very high flow rates, (Q_R = 1.0 seconds) conversions at R_M = 0.55, 1.12 and 2.12 are 90.7, 94.9 and 95.9%, respectively (36-4, 35-4 and 34-4).

At low through put rates, say at Q_R = 3.2 seconds for the approximately equal values of R_M, conversion values of 72.0, 85.0 and 80 are obtained.

(5) An insignificant, but slight increase in conversion values is noted when residence time is increased for the same flow conditions (Table 15). For example,

  (a) Increasing residence time for 3.2 to 32 seconds at R_M = 2.0 to 2.2 results in conversion values of 84% (Run 40-3) to 84.8% (Run 40-1).

  (b) Increasing residence time for 1.0 to 10 seconds at R_M = 2.02 to 2.2, conversion values of 86.7% (Run 40-4) and 88% (Run 40-2) were obtained respectively.

(6) Filtration rates were very rapid though actual data was not recorded. In almost all cases, the filteration time was equivalent to "sample time".

Final Comments

As a final note, this work has demonstrated the importance of mixing for effective regeneration; the Reynold's number, which is a measure of inertial to viscous forces, ultimately governs the degree of mixing. This work has shown the following:

(1) Reynold's number is the most significant variable that controls conversion and agglomeration. At high through put rates, conversions are quite high (over 90%) irregardless of reactant molar ratio. However, at low through put rates (increasing residence time) in the same reactor, agglomeration seems to increase with increasing amount of lime, resulting in low conversion values.

(2) Increasing residence time at same through put rates has the affect of slightly increasing conversion. A few seconds is sufficient for regeneration.

(3) Filtration characteristics of regenerated cake suggests rapid filterability rates and may be carried out in a rotary or similar filter.

(4) Data clearly supports that the jacketed back mix reactor envisioned for scale up may be determental and a pipeline mixing in its place is desirable. This eliminates the need of back mix reactor, temperature controls, etc. and provides the direct feed of two reactants in a single transfer line to the clarifier, bypassing the need of regenerator.

CHAPTER VIII

Experimental Data: Limestone-Sodium Bisulfite System

Data gathered for this system is summarized in the following tables and figures:

(A) Table 17 presents screen analysis for limestone.

(B) Table 18 documents pH data obtained in a tubular reactor by varying reactant ratio and flow rates.

(C) Table 19 summarizes Back-Mix Reactor data (Batch data)

Figure 21 is a plot of pH data versus reaction time.

Figure 22 is a plot of conversion data versus batch reaction time, for a given particle size.

(D) Table 20 shows pH and conversion data obtained at two different flow rates with filtration time as a variable.

Figure 23 is a plot of conversion data versus total flow rate with reactant molar ratio and filtration time as parameter.

Figure 24 is a plot of conversion data as a function of filtration time for a given flow and reactant molar ratio.

CHAPTER IX

Data-Discussion and Results

System-Limestone-Sodium Bisulfite.

(1) Particle size - The screen analysis of limestone indicates 76.75% of the material weight to be in the -20 to +50 mesh range and 98.15% in the range -20 to +100 mesh range (Table 17). The average particle size "dp" estimated by the equation

$$dp = \frac{\Sigma(\text{Wt }\%)_i (dp)_i}{\Sigma(\text{Wt }\%)}$$

is found to be .0120 inches.

(2) pH and Conversion Data in a Tubular Reactor - Initial experimental approach adopted to investigate was similar to the technique applied to study the lime-sodium bisulfite system. Nineteen experimental data points are recorded in Table 18 (Runs 15 to 32C).

For runs 15 to 21, a tubular reactor of 3/16 inch diameter and 9 inches length was used. The molar ratio of sodium bisulfite to limestone varied between 1.1 and 3.66, molar concentration of limestone varied between 0.15 M to 0.25 M,

TABLE 17

SIEVE ANALYSIS OF LIMESTONE

MESH SIZE	WT %	OPENING, INCHES
20	.15	.0331
40	23.3	.0165
50	53.3	.0117
60	5.8	.0098
70	9.8	.0083
80	3.3	.0070
100	2.5	.0059
120	0.5	.0049
140	0.8	.0041
170	0.15	.0035
325	0.30	.0017
>325	0.10	<.0017

$$\text{Average particle size} = \frac{\Sigma(\text{Wt }\%)_i(dp)_i}{\Sigma(\text{Wt }\%)_i}$$

$$= \frac{\Sigma(\text{Wt }\%)_i(dp)_i}{100}$$

$$= .0120 \text{ inches}$$

and for sodium bisulfite between 1 M to 2 M. Flow rates of reactants were varied so as to achieve high pH values. However, the pH of the system did not increase significantly and varied between 4.7 to 5.4 (Runs 15 to 20). No conversion data was obtained for these runs, as at the time of experimentation the main objectivity of the experimental goal was to achieve higher pH values. Considerable time may have been saved, as will be shown later, had the applicable equations been critically reviewed. However, this was not done, and attention was focused on reactor geometry. Two types of reactors were considered. A venturi type reactor (3/16 inch Inlet diameter and 3/8 inch outlet port by 10 inches length) was used for Runs 21 to 25. Both the reactant concentration and flow rates were varied and the pH values were slightly higher (5.3 to 5.75). However, an analysis of dried cake showed about 0.8% conversion (Run 25). At this point, the venturi reactor was replaced by a tubular reactor of longer length (3/16 inch diameter by 26 inches length). Data obtained in this reactor is shown in Runs 26 to 30. The molar reactant ratio of sodium bisulfite to limestone varied between 0.17 to

0.80 (excess limestone), the molar concentrations of sodium bisulfite solution varied between .025 M to .125 M, and for limestone between .05 M to .15 M. Flow rates for sodium bisulfite solution varied between .137 to .205 liters/minute and for limestone slurry between .155 to .341 liters/minutes. pH of the system did increase to 6.0 to 6.3 levels. For Run 28, the molar reactant ratio was 0.187, pH was 6.3, yet conversion was only 3.5%. For Run 29, initial pH recorded was 6.3 and molar reactant ratio was 0.230. This particular batch was further externally agitated. The pH of the system was continuously recorded, and from this recorded value it was found that the batch equilibrated to a pH of 7.7 over nineteen hours. A conversion estimate at this high pH showed conversion less than 5%. This then suggested that the solubilization of limestone may be rate limiting factor and emphasis was shifted to investigate this effect. Runs 32A to 32C show regeneration data using limestone of 50 mesh size (dp = .0117 inch). Conversions of 7.1 to 14.2% were obtained which were considerably higher than the values of previous runs and suggested this indeed may be the rate limiting factor.

It can be noted from these experiments that considerable amounts of time were expended in trying to increase the pH of the system, which was not successful. This, at first, seemed surprising but an examination of the applicable equations did justify the experimental results. As shown in an earlier section, the limestone regeneration schemes involve a solid-liquid gas reaction in which carbon dioxide gas is evolved. Secondly, as the experimental studies were conducted at extremely dilute concentrations, it is conceivable that the carbon dioxide evolved from reaction is immediately absorbed forming bicarbonate, i.e.

$$CO_2 + H_2O \rightarrow HCO_3^- + H^+$$

which being acidic tends to keep the system buffered irregardless of the mode of operation (sulfite or hydroxide mode) and conversion levels.

Hence, attempts to increase pH by variation of reactant ratio and flow rates which seemed possible based on lime regeneration analogy is virtually impossible for this system because of its buffering nature.

Secondly, the second aspect of this work which showed increase in conversion level with decreasing particle size indicated the rate limiting step for this reaction is the solubilization rate of limestone in the buffered system.

(3) Batch Reactor Data - Earlier work had demonstrated that the importance of particle size on regeneration. This section deals with limestone regeneration in a batch reactor at room temperature. Six experimental runs were made. For Runs 29F and 30F, the limestone of varying particle size (average particle size .012 inch) were used. The pH of the system was continuously recorded and Figure 21 is a plot of data for Run 30. Conversion for Runs 29F and 30F were 5 and 1% and equilibration time from plot was about five hours.

Runs 31 to 47 represent regeneration data for particle size between 50 to 100 mesh. For runs 31 and 32, the reactant molar ratio of sodium bisulfite to limestone was 2. Only the particle size of limestone was varied between 50 mesh to 100 mesh. After an hour of agitation, the con-

TABLE 18

TUBULAR REACTOR DATA: LIMESTONE-SODIUM BISULFITE SYSTEM

	Sodium Bisulfite		Limestone							
Run No	Molar	Liter/Min	Molar	Liter/Min	R = $\frac{NaHSO_3}{CaCO_3}$	Reactor	pH	% $SO_3^=$ in Dry Cake	% $SO_3^=$ Theory for 100% Conv	Conversion
15	1	0.137	.25	0.5	1.1	Tubular, $\frac{3}{16}$" x 9"	5	-	-	-
16	1	0.137	.15	0.5	1.83	DO	5	-	-	-
17	1	-	.15	-	-	DO	5.4	-	-	-
18	2	-	.15	-	3.66	DO	4.7	-	-	-
19	2	-	.5	-		DO	5.4	-	-	-
20	1	-	.5	-	-	DO	5.2	-	-	-
21	1	.120	.15	.42	1.90	Venturi Type 3/16" inlet port 3/8" outlet port by 10" length	5.4	-	-	-
22	2		.25			DO	5.3	-	-	-
23	1	-	.50	-	-	DO	5.5	-	-	-
24	0.75	-	.75	-	-	DO	5.75	-	-	-
25	0.75	-	.150	-	-	DO	5.5	0.5	62.0	0.8

TABLE 18 (Cont'd.)

Run No	Molar	Liter/Min	Molar	Liter/Min	R = $\frac{NaHSO_3}{CaCO_3}$	Reactor	pH	% $SO_3^=$ in Dry Cake	% $SO_3^=$ Theory for 100% Conv	Conversion
26	.125	0.137	.150	.155	0.74	Tubular, $\frac{3}{16}$" x 26"	6.0	-	-	-
27	.0625	.152	.150	.362	0.17	DO	6.1	-	-	-
28	.0500	.137	.100	.365	0.187	DO	6.3	0.5	14.2	3.5
29	.025	.152	.050	.341	.230	Tubular, $\frac{3}{16}$" x 26"	6.3		-	< 5
						At Equil (19 hrs)	7.7	0.4	-	-
30	.050	.205	.050	.255	0.80	DO	6.0	-	-	-
						At Equil (19 hrs)	7.2			
32A 50 Mesh Part. Size	2	.28	1	.28	2		6.1	8.8	62	14.2
32B	1	.15	1	.30	.5		6.0	4.4	34.9	12.6
32C	1	.28	1	.28	1		5.7	4.4	62	7.1

versions were 30% and 27.3% for the 50 mesh and 100 mesh particle size range, indicating no significant difference in reaction rates at these two particle size ranges.

Run 33 operated at excess limestone, as Reactant molar ratio of 0.5 and particle size at 50 mesh. Sulfite analysis of cake after two hours agitation showed 57.30% versus 34.90% (theoretical value, for 100% conversion), and the dried cake is suspected to be not homogeneous. Hence, a conversion of 100% is recorded as the experimental value.

Run 47 presents conversion data obtained in a batch reactor. Reactant molar ratio was 4.00 indicating a depleted limestone system. Particle size of limestone was 50 mesh. The regenerated cake was analyzed at various time intervals for sulfite content and from these sulfite values, conversions were computed. Figure 22 is a plot of conversion data versus batch reaction time, and indicates 94% conversion in about 30 minutes.

(4) Conversion Data in a Tubular Reactor - An earlier section had shown that about 94% conversion is achievable in a back mix reactor if batch residence time is held to about 30 minutes for a

TABLE 19

BATCH REACTOR DATA (BACK MIX REACTOR)

Run No	Sod.Bisulfite Molar	Limestone Molar	Ratio $\frac{NaHSO_3}{CaCO_3}$	Particle Size	pH of System	Hours Agitation	$SO_3^=$ Conc in Cake	$SO_3^=$ Conc for 100% Conv	% Conv	Calcium Analysis
29F	0.040	0.40	.10	Not Screen	7.7	18.0	0.4	7.7	5	-
30F	0.050	0.60	.804	Not Screen	7.2	19.0	0.43	52.1	< 1	-
31	0.20	0.1	2.0	50 Mesh		1.0	18.40	62.0	30.0	37.5
32	0.20	0.1	2.0	100 Mesh		1.0	16.90	62.0	27.3	38.4
33	0.05	0.1	0.5	50 Mesh		2.0	57.30*	34.90	100.0	-
47-1	1	0.25	4.00	50 Mesh		0.017	11.7	62.0	18.9	
	2					0.083	29.0	↓	46.7	
	3					0.250	52.4		84.5	
	4					0.500	57.9		93.4	
	5					0.750	58.3		94.0	
	6					1.000	58.1		93.7	

*Suspect dried cake not homogeneous

$R = \frac{NaHSO_3}{CaCO_3} = 0.804$, Room Temp, Particle Size

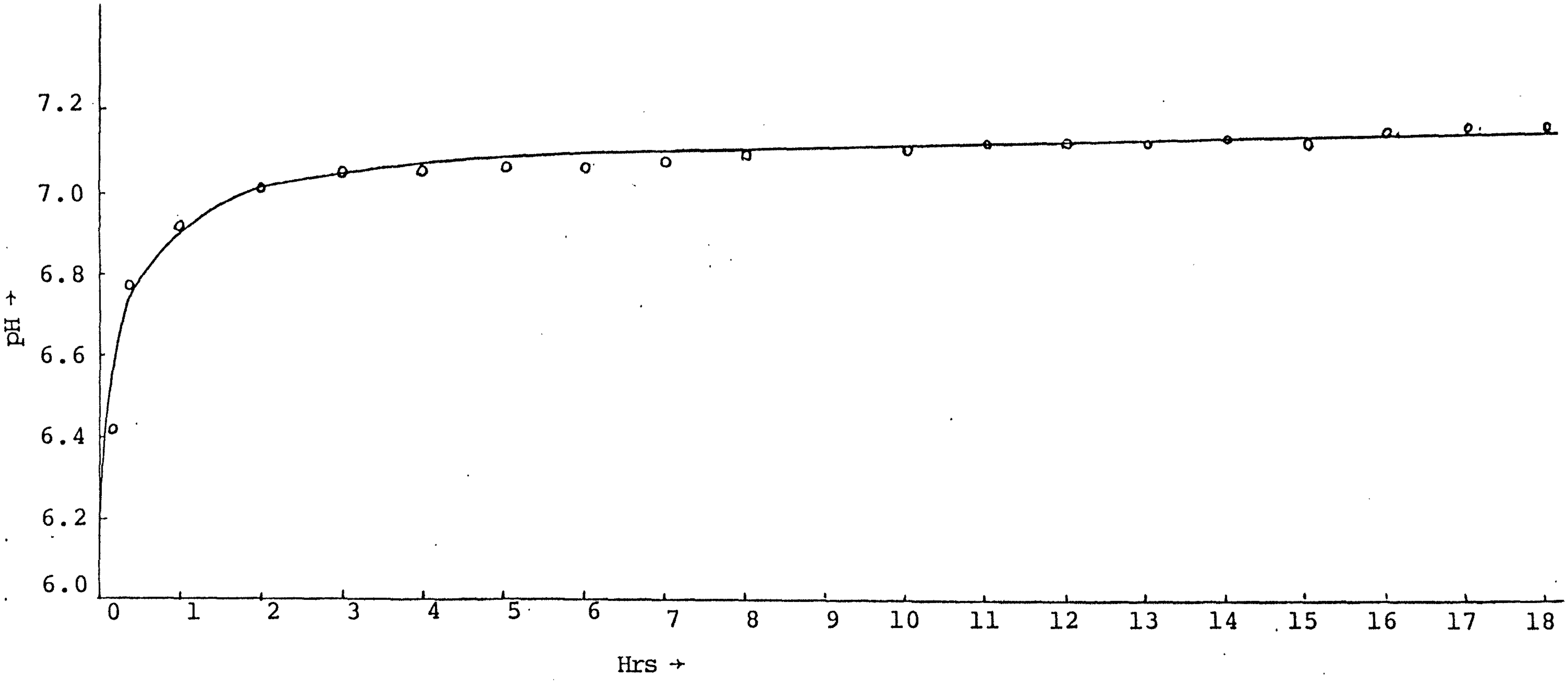


FIGURE 21. Batch Reactor Data: pH vs. Mixing Time

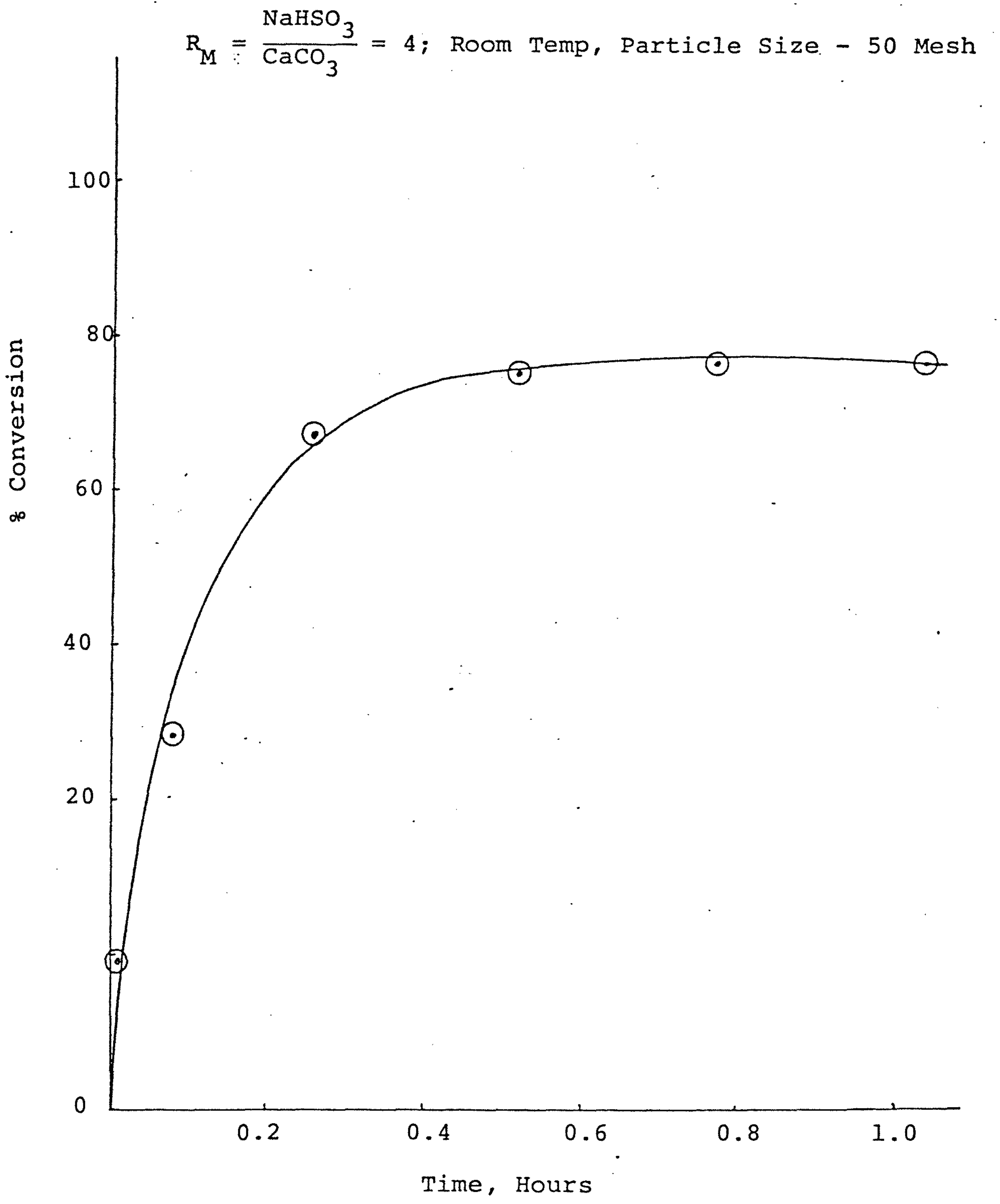


FIGURE 22. Batch Reactor Data: Conversion Vs. Agitation Time

depleted system (Run 47-4) and 100% conversion for excess limestone system, when batch residence time is held to two hours (Run 33).

The object of this part of the study was to evaluate the effect of flow rates and Reactant molar ratio on conversion in a tubular reactor. Such data recorded in Table 20 show 17 experiments were conducted to evaluate this effect. Two flow parameter values were considered. There were 230 cc/minute and 685 cc/minute of total flow. Reactant molar ratio varied between 0.39 to 1.55.

The first six experiments comprising of three pairs of sets (37-1 and 2, 38-1 and 2, 39-1 and 2) show the following

(a) For Run 37-1 and 37-2, Reactant molar ratio was 1.55, filtration time was 1040 seconds. Only the flow rate was varied and conversion values of 1.4% and 29.6% were obtained at a total flow rate of 230 cc/minute and 665 cc/minute, respectively.

(b) For Runs 38-1 and 38-2 the conditions were the same as in Run 37 series except the filtration time varied and was only 90 seconds. A conversion of 0.9 and 8.8% was obtained at flow rates of 230 cc/minute and 685 cc/minute, respectively.

(c) For Runs 39-1 and 39-2, the system operated at excess lime R_M and filtration times were 0.39 and 260 seconds, respectively. Conversion values were 1.2 and 54.7% at low and high flow rates respectively.

The results of 37, 38 and 39 series runs are plotted in Figure 23.

(d) The next eight experiments (51-1, 51-2, 37-3, 44-1, 38-2R, 43-1, 52-1 and 37-2R) show conversion values for a given R_M (1.55) and a fixed flow rate (685 cc/minute). Filtration time varied between 15 seconds (51-1) to 1040 seconds (37-2R). A plot of conversion values obtained is shown in Figure 24 and shows conversion variations between 0.76% (37-3) to 28.6 (38-2R).

(e) For Runs 45-1, 50-1, 46-1, 39-2, the R_M and total flow rates values were 0.39 and 685 cc/minute respectively. Filtration time varied between 70 seconds (45-1) to 260 seconds (39-2). Conversion values varied between 1.4% (45-1) to 54.7% (39-2).

Analysis

A review of the data show the following:

(1) Regeneration of sodium bisulfite using limestone is feasible. The following variable, namely flow rates, reactant molar ratio and filtration (hold) time ultimately govern the degree of regeneration.

(2) From run series of 37, 38 and 39 it was observed that increasing flow rates at a given reactant molar ratio and filtration time brings about a significant increase in conversion values.

This effect is vividly seen in Figure 23. At low flow rates, neither filtration nor reactant molar ratio has any remarkable effect on conversion (all values less than 3%). At high flow rates, increasing calcium carbonate level increases conversion; and increasing filtration (hold) time for a given reactant molar ratio also brings about an increase in conversion levels.

(3) Filtration (hold) time has an effect if the batch is well mixed initially. Note, when total flow rate value was 685 cc/minute (tubular reactor of 3/16" ID, Y post connection), increasing

filtration time from 15 to 1040 seconds, conversion values ranged between 0.8 to 28.6% (at R_M = 1.55) and for R_M = 0.39, conversion values varied between 1.4 to 54.7 at 70 to 260 seconds filtration times.

Final Comments

This work has demonstrated the following:

(1) 100% conversion is obtainable for limestone systems in a backmix reactor under good agitation by controlling the particle size and the reactant molar ratio. Regeneration time is about 30 minutes.

(2) Regenerator in a tubular reactor is not feasible. Unlike the lime system which showed 95 to 100% regeneration at high turbulence flow conditions with a few seconds residence, this system differs completely.

In addition to the need of high turbulence initial mix, the limestone system mandates the need of a back up system, which essentially is nonstirred tank equipped with a filtering device. Residence time of these two units is in the order of minutes and comparable to a stirred back mix reactor. However, the unusual advantage this system offers is that high conversion levels are obtainable in an "non-agitated" system instead of in a conventional stirred tank reactor.

Stirring may not be only unnecessary but also detrimental. The formation of the product produces a local acidic environment in the vicinity of the solid limestone. This acidity will accelerate the dissolution of limestone, which is apparently under these conditions the rate limiting step-in contrast, however, rapid stirring will diminish the local relatively low pH conditions, and therefore decrease the rate at which limestone dissolves.

TABLE 20

TUBULAR REACTOR DATA: SODIUM BISULFITE-LIMESTONE SYSTEM

CONVERSION DATA AS A FUNCTION OF FLOW RATES AND FILTRATION TIME

Run No	Sod Bisulfite M	Sod Bisulfite cc/min	Calcium Carbonate M	Calcium Carbonate cc/min	$\frac{NaHSO_3}{CaCO_3}$	Total Flow cc/min	Filtration Time Seconds	$SO_3^=$ Analysis of Dried Cake	$SO_3^=$ at 100% Conver.	Conversion
37-1	.4	100	.2	130	1.55	230	1040	0.85	62.0	1.4
37-2	↓	300	↓	385	↓	685	↓	18.33	↓	29.6
38-1	↓	100	↓	130	↓	230	90	0.57	↓	0.9
38-2	↓	300	↓	385	↓	685	↓	5.5	↓	8.8
39-1	.2	100	.4	130	0.39	230	260	0.34	28.0	1.2
39-2	↓	300	↓	385	↓	685	↓	15.30	↓	54.7
51-1	.4	300	.2	385	1.55	685	15	0.86	62.0	1.4
51-2	↓	↓	↓	↓	↓	↓	17	0.56	↓	0.90
37-3	↓	↓	↓	↓	↓	↓	25	0.47	↓	0.76
44-1	↓	↓	↓	↓	↓	↓	75	1.4	↓	2.3
38-2R	↓	↓	↓	↓	↓	↓	90	5.5	↓	8.8
43-1	↓	↓	↓	↓	↓	↓	95	1.3	↓	2.1
52-1	↓	↓	↓	↓	↓	↓	330	6.2	↓	10.0
37-2R	↓	↓	↓	↓	↓	↓	1040	17.7	↓	28.6

TABLE 20 (Cont'd.)

Run No	Sod Bisulfite M	Sod Bisulfite cc/min	Calcium Carbonate M	Calcium Carbonate cc/min	$\frac{NaHSO_3}{CaCO_3}$	Total Flow cc/min	Filtration Time Seconds	$SO_3^=$ Analysis of Dried Cake	$SO_3^=$ at 100% Conver.	Conversion
45-1	.2	300	.4	385	0.39	685	70	0.40	28	1.4
50-1	↓	↓	↓	↓	↓	↓	75	0.47	↓	1.7
46-1	↓	↓	↓	↓	↓	↓	85	0.60	↓	2.2
39-2	↓	↓	↓	↓	↓	↓	260	15.3	↓	54.7

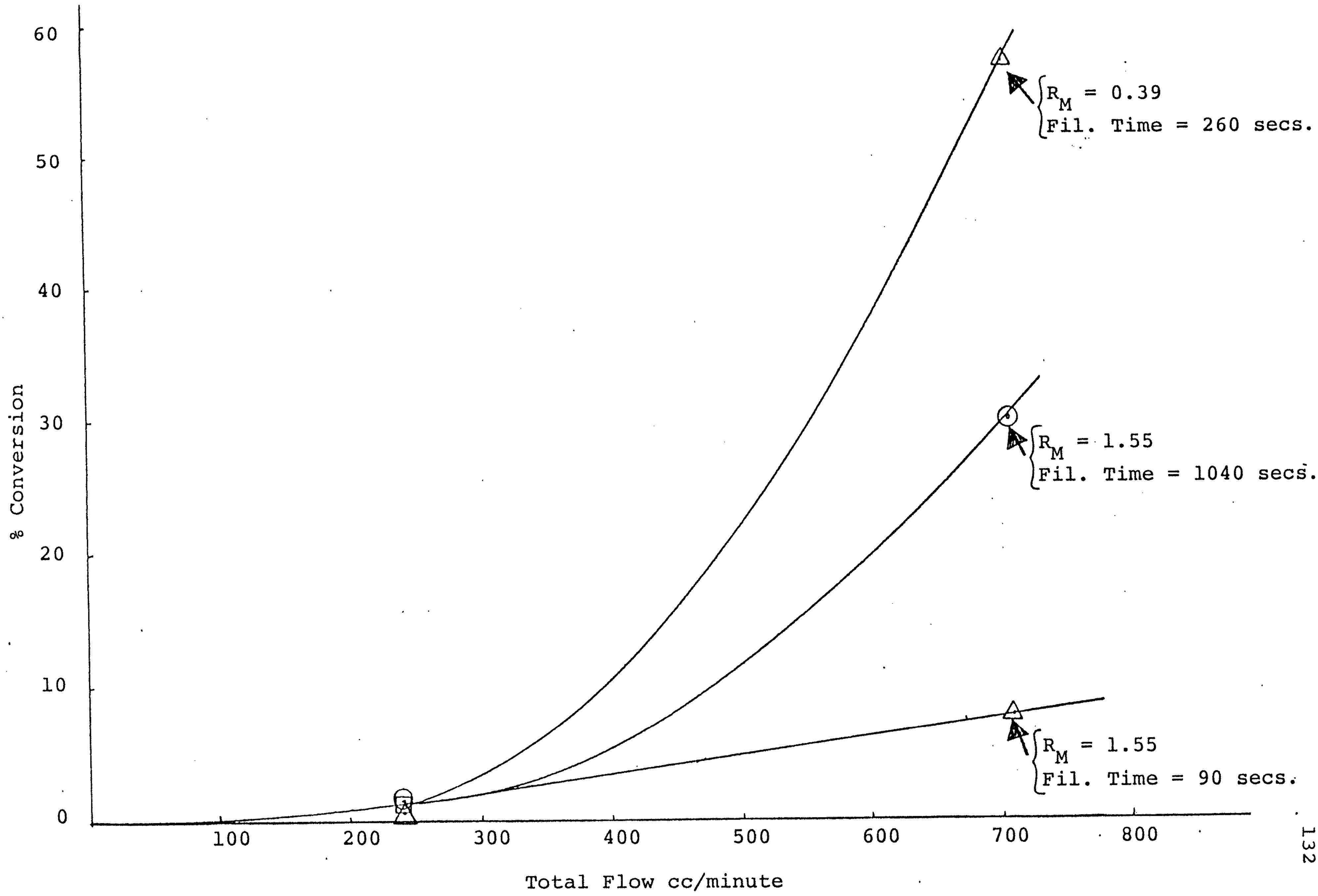


FIGURE 23. Conversion Versus Total Flow Rate (cc/minute) as a Function of R_M and Filtration Time

System: Sodium Bisulfite-Limestone; Particle Size: 50 Mesh

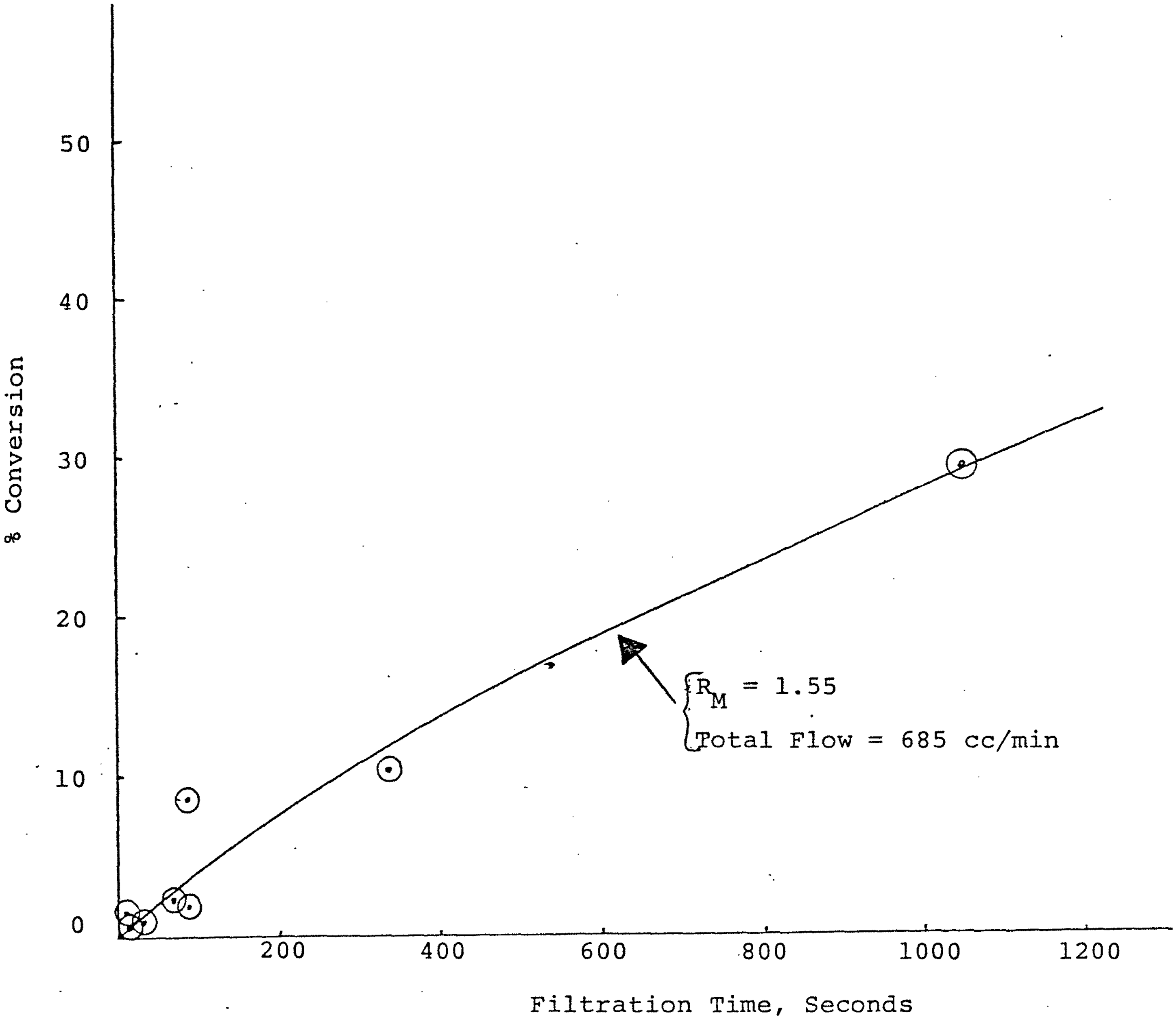


FIGURE 24. Conversion Data Vs. Filtration Time for a Given R_M and Flow Conditions

CHAPTER X

Energy Consumption Estimates

Experimental data for both Sodium Bisulfite-Lime slurry and Sodium Bisulfite-Limestone slurry systems has revealed that effective regeneration can be achieved by controlling initial mixing parameters. Models and postulates as to why this is critical have been dealt with in prior sections. This work has also cited the reactor configuration that is desirable on a plant scale to achieve efficient regeneration.

Additional pilot plant experimentation is needed to evaluate its benefits on capital savings, etc.

Also, this work has shown that substantial energy savings can result with this envisioned scheme. For the reaction configuration that has evolved from this study energy is needed to pump the reactant solution and slurry into the "Y" port tubular reactor. However, for the existing mode of regeneration, energy is needed not only for feeding the reactant solution and slurry into the backmix reactor; but additional energy is needed to mix the heteregenous slurry in the backmix reactor. The magnitude of this excess energy is dictated by the regeneration time which is ultimately governed by the agglomeration phenemenon.

Though the objective of this work was not to evaluate this effect, the following estimate compares the energy utilization for the sodium bisulfite-limestone system for these two reactor configurations. It should be pointed out that this estimate should be used as a guide, as no optimization was performed.

Energy Calculations

A. Back Mix Reactor Data

1. Experimental Conditions:

   Reaction time: One hour

   Molarity of sodium bisulfite = 0.20

   Molarity of calcium carbonate = 0.10

   % Conversion = 30

   Ratio (molar), $NaHSO_3/CaCO_3$ = 2.0

   Particle size of calcium carbonate = 50 mesh

   'H.P.' of agitator = 1/18 HP

2. Productivity (lbs $CaSO_3 \cdot 1/2H_2O$ regenerated)

   $WCaSO_3 \cdot 1/2H_2O$ = 0.10 (moles $CaCO_3$) x 0.3 (moles $CaSO_3 \cdot$-$1/2H_2O$) x 1/453.9 = .01 lbs/hr

3. Power Consumption

   Pump - 1/18 HP motor used for mixing slurry neglecting energy input to feed reactants,

   P_c, Power consumption = 1/18 x 745.7 = 41.4 watts

4. Power/Material Ratio

   $P_c/WCaSO_3 \cdot 1/2H_2O$ = 41.4/.01 = 4140 watts/lb

5. Energy Cost (for 100 lbs of $CaSO_3 \cdot 1/2H_2O$)

   E_c, energy cost = 4140 (watts/lb) x 100 (watts/100 lbs)-x 1/1000 (KW/100 lbs) x .04 = \$16.56

B. Tubular Reactor/Holding Tank

1. Experimental Conditions

Reactant	Molarity	Flow
Sodium Bisulfite	0.4 M	300 cc/minute
Calcium Carbonate	0.2 M	385 cc/minute

% Conversion = 30

Residence time in tubular reactor = 1.3 seconds, approximately 2 seconds

Residence time in hold tank (no agitation) = 1100 seconds (18.4 minutes)

Total Residence time = 18.4 minutes

2. Productivity (lbs $CaSO_3 \cdot 1/2H_2O$ regenerated)

$WCaSO_3 \cdot 1/2H_2O$ = 0.2/2000 (moles $CaCO_3$/liter solution) x - 0.685 liters/min (moles $CaCO_3$/minute) x 0.30 conv (moles - $CaSO_3 \cdot 1/2H_2O$/minute) x 129 M.Wt. (gm $CaSO_3 \cdot 1/2H_2O$/minute) - x 60/18.41 (gms/hr) x 1/453.5 (lbs/hr) = .02 lbs/hr

3. Power Consumption

Pumps - 2 1/10 HP motor used for feeding reactants, two second residence time

P_c, power consumption = [1/10 + 1/10] x 745.7 x 2/3600 = .08 watts

4. Power/Material Ratio

$P_c/WCaSO_3 \cdot 1/2H_2O$ = .08/.02 = 4 watts/lb

5. Energy Cost (for 100 lbs of $CaSO_3 \cdot 1/2H_2O$)

E_c, energy cost = 4 (watts/lb) x 100 (watts) x 1/1000 (KW) - x .04 ($/KW) = .016 $

C. Energy Consumption Comparison

Reactor Configuration	E_c/lb $CaSO_3 \cdot 1/2H_2O$, ¢/lb
Backmix Reactor	16.56
Tubular Reactor/Holdup Tank	~0.02

CHAPTER XI

Recommendations

This work has demonstrated the importance of initial mixing in the regeneration area. Initial good mixing is needed for both lime/limestone systems; however, the limestone systems differs in that additional "hold up" time is necessary to effect regeneration.

Advantages of this system over the conventional system are many: Low capital investment, simplicity of design and less energy consumption.

Based on our laboratory scale experiments, this energy difference amounted to savings of 16.36¢/lb of $CaSO_3 \cdot 1/2H_2O$ regenerated, for the sodium Bisulfite-Limestone system.

This thesis has pinpointed the following areas worth further exploration:

(1) For the lime-sodium bisulfite system, evaluate 'scale up' effects.

(2) For the limestone-sodium bisulfite system, evaluate the effect of high initial mixing at residence time in minutes instead of seconds; i.e. evaluate regeneration aspects in a perforated plate tubular reactor or such similar devices.

After conditions have been obtained for optimum initial mixing, determine whether or not as has been proposed whether subsequent mixing will have detrimental effect because of the elimination of local pH fluctuations.

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