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LABORATORY STUDY OF LIMESTONE REGENERATION IN DUAL ALKALI SYSTEMS

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LABORATORY STUDY OF LIMESTONE REGENERATION IN DUAL ALKALI SYSTEMS

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I. SUMMARY

A series of open- and closed-loop laboratory bench scale experiments have been carried out to study a number of parameters which affect the reaction of limestone with dual alkali flue gas desulfurization (FGD) systems process liquors. During the program, which was carried out from July through November, 1976, acceptable operation in terms of limestone utilization and dewatering properties of the product solids was demonstrated for several sets of operating conditions.

By employing a system with four reactors in series, with a total residence time of two hours, and by using Fredonia limestone (a very finely ground material, low in magnesium) good operation was achieved over a reasonable range of liquor compositions. In closed-loop runs at 50°C, utilization of limestone ranged from 78 to 92% with total concentrations of sulfite plus bisulfite (TOS) in the scrubber bleed ranging from 0.56 M to about 1.5 M and the concentrations of sodium sulfate ranging from about 0.7 M to 1.2 M. No special steps were required to control the soluble magnesium level in the liquor or reduce its effects on the regeneration reaction.

Precipitation of calcium sulfate in solid solution with the calcium sulfite took place according to the same relationship as determined in prior work for regeneration using lime.

The fact that soluble magnesium levels did not rise in solutions which were unsaturated with respect to magnesium sulfite, the least soluble magnesium solid phase, suggested either that magnesium may have been coprecipitating from those solutions in a manner similar to the way in which calcium sulfate coprecipitates with calcium sulfite from solutions unsaturated in gypsum; or that not all the magnesium present in the limestone dissolved.

II. INTRODUCTION, PURPOSE AND SCOPE

Limestone is used in many of the flue gas desulfurization (FGD) systems which employ direct slurry scrubbing. In dual alkali FGD systems, the substitution of limestone for lime, which is generally used, would be economically attractive, since limestone is considerably less expensive than lime. However, because lime is more reactive, it is easier to achieve dependable system operation with lime.

The simple neutralization reaction for limestone with a scrubber liquor containing sodium sulfite/bisulfite is:

$$CaCO_3(s) + 2NaHSO_3 \quad CaSO_3(s) + Na_2SO_3 + H_2O + CO_2(g)$$

The sulfite ion is not sufficiently acidic to react with limestone, thus bisulfite is the primary reactive species. Because, in comparison to lime, limestone is very insoluble and only moderately basic toward bisulfite, regeneration of dual alkali liquors proceeds slowly and the solids produced can be difficult to dewater. In earlier work (1) several important parameters which influence the reaction with limestone were identified. The more obvious include: the concentration of total oxidizable sulfur (TOS) in solution; ionic strength of the liquor, related, in part, to sodium sulfate concentration; reaction temperature; and reactor system configuration. It was also observed that the presence of dissolved magnesium in the process liquor (magnesium is a common impurity in limestone) can lower reaction rates and produce product solids with poor dewatering properties. Traces of iron had a similar effect.

Although the earlier laboratory and pilot plant work on limestone regeneration uncovered important factors influencing the regeneration reaction, it was not possible to develop a set of process parameters and reactor conditions which were consistent with both good limestone utilization and the generation of product solids with good dewatering characteristics.

The objective for the current program, then, was to develop one or more sets of acceptable operating conditions by studying the

limestone regeneration reaction in a bench scale laboratory apparatus which could be controlled carefully. Studies were to be focused on operation with "concentrated" sodium sulfite/bisulfite/sulfate liquors. Concentrated dual alkali systems produce liquors saturated with respect to calcium sulfite upon regeneration and generally contain active Na^+ concentrations above 0.15 M. Unsuccessful attempts to regenerate "dilute" (saturated with respect to calcium sulfate upon regeneration) solutions with limestone have been reported previously (2).

The plan for achieving the program goal included the following steps:

- Design and construct a bench scale apparatus for open- and closed-loop studies;
- Carry out open loop experiments to test the apparatus and establish baseline operating conditions;
- Close the loop and conduct experiments to study the effects of temperature, TOS, sodium sulfate, and soluble magnesium.

In order to maximize the chances of finding one or more sets of acceptable operating conditions, the experimental matrix was designed to proceed from conditions where success was most likely -- high temperatures, low magnesium -- to those where acceptable operation was more doubtful -- higher magnesium and sodium sulfate and lower temperatures.

III. EXPERIMENTAL APPARATUS, APPROACH, AND CALCULATIONS

A. DESIGN OF THE APPARATUS

A schematic flow sheet of the apparatus designed for closed-loop operation with limestone is presented in Figure 1. The operation consisted of three basic steps:

- contacting acidic sodium sulfite/bisulfite/sulfate scrubber bleed with limestone in a continuous flow reactor system consisting of four well-mixed tanks in series;
- separating the product solids from effluent in a settler;
- recycling the separated liquor through an absorber in order to add sulfur dioxide; and back again to the absorbent regeneration reactor system.

The four reactors in Figure 1 were constructed from glass beakers with volumes of 0.5, 0.5, 1.0 and 1.5 liters, respectively. Each had a side-arm blown on the wall and was equipped with baffles, a mixer, and an external heater. The reactor series utilized gravity flow with the overflow height of each reactor adjusted as desired. The pH of the fourth reactor was continuously monitored and recorded if necessary. Each reactor was equipped with a polyethylene coated propeller with three pitched blades having a diameter of 4.5 cm. Each reactor had four baffles; each baffle extended inward from the reactor wall a distance 1/10 the diameter of the reactor. The stirring speeds for the impellers were calculated to impart approximately the same power per unit volume for all reactors. Shaft speeds were 350, 350, 500, and 720 RPM from first to fourth reactor, respectively.

Additional components of the system included a settler (with feed well) which was designed to accumulate and retain product solids for about 16 hours of continuous operation. A surge tank received the liquid overflow from the settler. As solids deposited in the settler, liquid was displaced into the surge tank. Continuous underflow filtering was not employed; solids were removed from the settler periodically. The amount of liquid removed with the thickened slurry was estimated and, based on analysis of an aliquot of the liquid, an equal volume

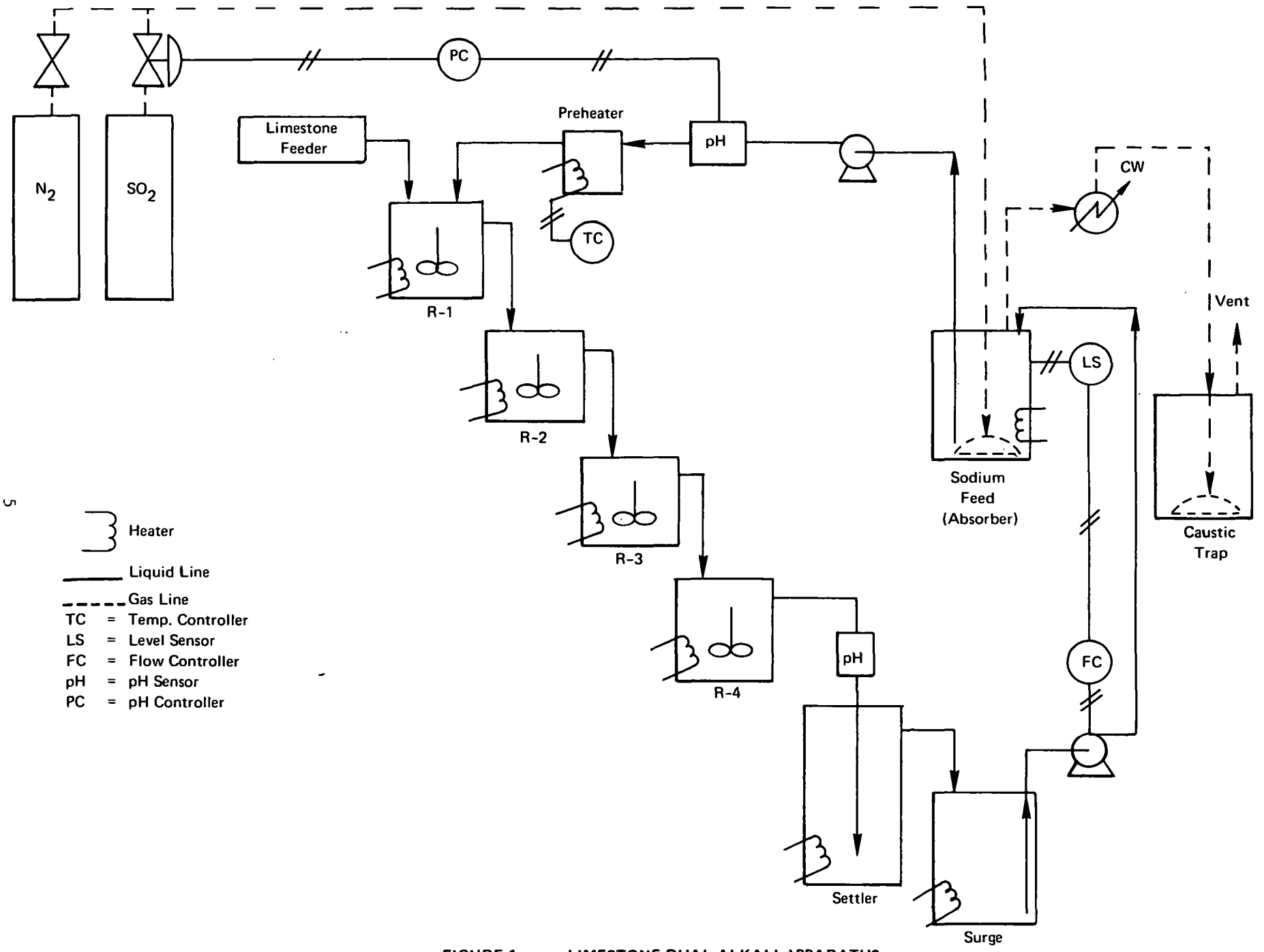

FIGURE 1 LIMESTONE DUAL ALKALI APPARATUS

having the same composition was synthesized and put back into the settler.

Regenerated liquor was pumped from the surge tank to the SO_2 absorber by a Masterflex tubing pump. The flow to the absorber was controlled on the liquid level in the absorber. In the absorber, the liquor was acidified by bubbling a mixture of SO_2 in nitrogen through it. Since the absorber was operated as a relatively inefficient single-stage device (simply to acidify the liquor to a desired pH), a considerable amount of SO_2 was not removed from the gas. The exit gas was therefore scrubbed in a caustic trap prior to venting. The scrubber bleed was pumped to the regeneration reaction system at a constant, predetermined flow rate using a Masterflex tubing pump. The pH of the scrubber bleed stream was monitored, and the on/off output of the pH meter/controller was used to trim the amount of SO_2 which was mixed with nitrogen and fed to the absorber.

All reactors were equipped with heaters, and a preheater was also installed immediately before the first reactor. The heaters were equipped with on/off temperature controllers. The preheater was particularly necessary for operation at high temperatures. Silicone rubber tubing was used wherever possible because of its stability at elevated temperatures.

A major problem was encountered in obtaining a limestone feeder to meet the required flow rates. To completely neutralize 1 ℓ/h of simulated scrubber bleed containing 1.45 M bisulfite, a dry limestone feed of about 1.2 g/m was required. It was not desirable to add the limestone as a slurry because of the tight water balance (little evaporation in the absorber); dry feeding the Fredonia limestone with standard industrial or laboratory equipment proved difficult at the desired flow rate. Packing of the limestone prevented reproducible feeding at rates below about 5 g/m, using either a screw feeder or a rotary plate chemical feeder. Since a suitable off-the-shelf feeder could not be obtained, a feeder was designed and built at Arthur D. Little, Inc. It was a novel design employing the properties of a syringe and plunger to dispense a limestone paste (75% dry solids). The barrel was a plexiglass tube 5 cm in diameter and 50 cm long. The

plunger was actually a piston, pushed down the barrel by a threaded rod driven by a gear and motor arrangement. Limestone was extruded from a constricted opening at the end of the syringe and was fed directly into the reactor system. Constant feed rates of 0.5-3.0 g/m could be obtained with this syringe-type feeder. The total capacity of the syringe was apprxomately 1.2 kg. Thus, depending on the rate of feed, the syringe had the capability to operate unattended for between 7 and 40 hours.

B. EXPERIMENTAL APPROACH

After assembly of the apparatus was completed, four open-loop runs were conducted to test the reactor system and to study the effects of temperature and magnesium concentration on the extent of reaction and the properties of the solids produced. The first three open-loop experiments were carried out in a 3-reactor system with reactor time constants of 15, 15, and 30 minutes for successive reactors. A fourth reactor with a time constant of 1 hour was added to the end of the 3-reactor train for the remainder of the open- and closed-loop experiments.

In conjunction with the open-loop runs, measurements of magnesium sulfite solubility were performed to provide estimates, as a function of temperature, of the levels to which magnesium might build in a closed-loop system before the precipitation of magnesium sulfite would occur limiting further buildup.

Initial attempts at unattended closed-loop operation failed due to both mechanical and process problems. One significant problem was the blockage of the reactor overflow tubing by large, thin pieces of scale that appeared to have been formed on the walls of the first reactor and then chipped off. After two successive problems with plugging, the system was attended constantly and seven successful closed-loop runs, ranging in length from eleven to twenty-nine hours, were carried out. The principal variables studied in the closed-loop runs were liquor temperature (50 and 90°C), TOS concentration (0.55-1.6 M), soluble magnesium concentration (1000 and 2000 ppm), and sulfate concentration (0.65-1.2 M).

In all of the experiments, Fredonia limestone obtained from the EPA/TVA Shawnee test facility was used as the reagent. The Fredonia limestone was chosen because it had been characterized, and use in prior work indicated that it was more reactive than some other forms of limestone tested (1). Analyses indicated that the limestone contained by weight 96.6% Ca (as $CaCO_3$) and 1.1% Mg (as $MgCO_3$). Total available alkalinity (expressed as $CaCO_3$) was 97.2%.

The limestone feeder was initially set so that limestone was fed at 80-90% of the stoichiometric amount required to completely neutralize the bisulfite present in the acidic scrubber bleed where feed stoichiometry is defined as follows:

$$\% \text{ stoichiometry} = \left[\frac{\text{moles } CaCO_3 \text{ fed}}{0.5 \text{ moles } HSO_3^- \text{ fed}}\right] \times 100\%$$

Adjustments were made to the limestone feed rate, if necessary, to hold the pH of the reactor effluent slurry within the range of 6.2-6.5. Those adjustments generally reduced the limestone feed shoichiometry to 70-80%.

In all of the closed-loop experiments, the scrubber bleed feed rate to the first reactor was kept constant at 15 ml/m. At that feed rate, the entire system, including absorber, reactors, settler, and surge tank, had a residence time of about 13 hours.

Since earlier work suggested that poor dewatering of solids was associated with slow regeneration reaction rates, most of the experiments were carried out at relatively high concentrations of TOS in an attempt to increase reaction rates. The acidity of the scrubber bleed fed to the reactor system, H^+ (which is predominantly bisulfite, HSO_3^-) was controlled so that the ratio $HSO_3^-/SO_3^=$ was generally in the range of 4-9. Sulfate concentration was varied from about 0.7 M to 1.16 M, producing $TOS/SO_4^=$ ratios ranging from 0.73 to 2.47.

Because increasing temperature should increase reaction rates, the effects of temperatures greater than 50°C were explored in several runs. However, because of the difficulties and costs associated with the operation of an actual process at elevated temperatures, most of the runs were carried out at 50°C, which is typical of scrubber bleed streams.

C. EXPERIMENTAL CALCULATIONS

In addition to limestone feed stoichiometry, discussed above, the values of two other parameters -- limestone utilization and sulfate precipitation -- were important in characterizing the behavior of the regeneration reaction. Limestone utilization was calculated from the compositions of the product solids as follows:

$$\text{Percent Utilization} = \left[\frac{\text{moles TOS + moles sulfate - 0.5 moles Na}}{\text{(moles Ca + Mg)(Avail. Alkalinity/mole Mg + Ca)}}\right] \times 100\%$$

It should be pointed out that the subtraction of one half of the measured amount of sodium from the numerator to correct for the soluble sodium/sulfur salts entrained in the solids is not rigorously correct for solids produced in reactions with limestone, since some of the TOS in the effluent exists as HSO_3^-. However, this approximation is adequate since in most cases utilizations were high and sodium levels in the cake were low.

Available alkalinity per mole of alkaline earth (Ca + Mg) was determined by dissolving a sample of the limestone in excess acid, boiling, and back-titrating with base to a pH of about 4. The available alkalinity was expressed as $CaCO_3$ and divided by the total moles of Ca and Mg in the same sample.

Magnesium is included in the denominator of the utilization equation because it is assumed that the magnesium in the limestone is a potentially useful regeneration reagent. As will be discussed later, it is not clear whether the magnesium in the Fredonia limestone actually took part in many of the closed-loop runs reported here. The extent to which magnesium participates in the reaction under a given set of experimental conditions is clearly a factor that needs to be determined, particularly for limestones which contain larger amounts of magnesium than the Fredonia limestone.

Further, since the amount of total sulfur in the solids which appears in the numerator is corrected only for sodium/sulfur salts, the precipitation of soluble magnesium present in the scrubber bleed as magnesium sulfite during the course of the neutralization reaction would produce an apparent increase in utilization. This phenomenon would produce erroneous calculated utilizations only in the case of systems which are not at steady-state, e.g., open-loop runs where a

significant portion of the soluble magnesium present in the scrubber bleed is precipitated out during the single pass through the system.

Sulfate precipitation, a measure of the amount of system oxidation that can be accommodated, was calculated as the ratio of $CaSO_4$/ $CaSO_3$ in the solids taken from the reactor effluent according to the relation:

$$CaSO_4 = \left[\frac{\text{Total moles sulfate in solids - moles soluble sulfate}}{\text{Total moles sulfite in solids - moles soluble TOS}}\right] \times 100\%$$

where:

$$\text{moles soluble sulfate} = \left[\frac{\text{moles Na in solids}}{\text{conc. } Na^+ \text{ in liquor}}\right] \times \text{conc. of } SO_4^{=} \text{ in liquor}$$

and

$$\text{moles soluble TOS} = \left[\frac{\text{moles Na in solids}}{\text{conc. of } Na^+ \text{ in liquor}}\right] \times \text{conc. of TOS in liquor}$$

The total moles of sulfate in the washed and dried solids was corrected for occluded soluble sodium sulfate. The latter was determined by multiplying the concentration of sulfate in the process liquor by the ratio of the amount of sodium in the solids to the concentration of sodium in the liquor. Similarly, the solid sulfite was corrected for occluded sodium salts. It should be recognized, however, that no correction was made for magnesium salts present in the solids. Under steady state operating conditions, that treatment is completely appropriate, since sulfur (IV) and sulfur (VI) can be removed both as magnesium salts and as calcium salts.

IV. RESULTS AND DISCUSSION

An overview of the conditions under which each of the four open-loop and seven closed-loop runs were carried out along with a summary of the salient results obtained from each are presented in Table I. Included in the table are the operating temperatures, limestone feed stoichiometries, and the compositions of the scrubber bleed stream fed to the regeneration reactor system for each run. For the closed-loop runs, the scrubber bleed compositions are those measured after steady-state had been achieved; in the open-loop runs the simulated scrubber bleed compositions were invariant throughout each run.

The performance of the reactor system in each experiment was characterized by measurements of pH in the reactor effluent and limestone utilization based on the composition of the solids discharged from the final reactor. The dewatering properties of the solids produced were characterized by performing settling tests in a 100-ml graduated cylinder, determining the meniscus position after 30 minutes of settling, and calculating the density of the settled solids. In a number of cases, the percent solids in the wet cake produced by vacuum filtration on a laboratory Buchner funnel was determined.

The results of analyses of the product solids which were used to calculate utilization and sulfate precipitation are shown in Table II. Some of the factors responsible for the observed variations in limestone utilization are discussed in more detail in the sections which follow.

A. FACTORS AFFECTING LIMESTONE UTILIZATION

Earlier studies of the dual alkali regeneration reaction have shown that the utilization of limestone is dependent upon a number of variables including soluble magnesium concentration, reaction temperature, reactor holdup time, limestone feed stoichiometry, sodium sulfate concentration, and bisulfite acidity. It is not possible to clearly discern the independent effect of each of these variables on the utilizations obtained in this program because in many cases more than one independent variable was changed from one experiment to the next. Furthermore, since the primary aim of this work was to determine

TABLE I

SUMMARY OF LIMESTONE BASED DUAL ALKALI REGENERATION EXPERIMENTAL RESULTS

			Scrubber Bleed Steady State Composition								Settling Properties					
Run	Type[1]	Temp (°C)	TOS (M)	H^+(M)	Mg^{++}(ppm)	$SO_4^=$(M)	$H^+/SO_4^=$	Stoich.(%)[2]	Reactor Effluent pH	Limestone Utilization (%)[3]	Meniscus (ml)[4]	Density[5]	Filter Cake % Solids	Sulfate[6] Precipitation	Duration of Run(hrs)
100	3R-OL	45	1.58	1.42	300	0.64	2.2	90	6.6	88	15	ND	ND	2.7	4.1
101	3R-OL	50	1.61	1.45	4450	0.69	2.1	86	6.0	41	23	38	ND	8.1	4.0
102	3R-OL	90	1.60	1.42	4450	0.71	2.0	84	6.1	81	20	40	ND	6.6	4.3
Magnesium effect → 103	4R-OL	70	1.62	1.47	7830	0.73	2.0	78	6.0	79	66	12	ND	--	8.8
108	4R-CL	90	1.43	1.26	1270	0.80	1.6	65-75	6.2	102	26	36	42	5.7	28.6
109	4R-CL	50	1.44	1.37	1030	0.70	2.0	70-75	6.5	92	15	ND(>30)	ND	3.6	28.2
110	4R-CL	50	1.49	1.21	1940	0.67	1.8	72	6.5	90	18	34	75	4.7	28.8
111	4R-CL	50	0.56	0.49	2020	0.77	0.64	68-75	6.4	84	32	8	35	12.5	14.0
112	4R-CL	50	1.02	0.83	2010	0.77	1.1	81	6.5	82	21	23	56	6.6	11.0
113	4R-CL	50	1.03	0.84	2020	0.99	0.85	78	6.5	81	24	18	59	7.6	11.0
114	4R-CL	50	1.33	1.20	1900	1.16	1.0	78	6.5	78	30	26	57	6.2	14.4

[1]Number of reactors -- open/closed loop.

[2]Percent of amount required to neutralize acidity (see text).

[3]Calculated from solids composition (see text).

[4]Meniscus position in 100-ml graduated cylinder after settling for 30 minutes.

[5]Weight of dry solids (g) per 100 ml of settled slurry.

[6][Solid Sulfate]/[Solid Sulfite] x 100% (see text).

TABLE II

COMPOSITION OF SOLIDS PRODUCED IN LIMESTONE DUAL ALKALI REGENERATION STUDIES

Run	Ca^{++} (mmoles/g)	TOS (mmoles/g)	$SO_4^{=}$ (mmoles/g)	Mg^{++} (mmoles/g)	Na^{+} (mmoles/g)
100	7.37	6.48	0.264	0.053	0.398
101	8.13	3.39	0.338	0.60	0.271
102	6.87	5.99	0.574	0.83	0.680
103	6.09	4.81	0.786	0.772	ND[2]
108[1]	7.34	7.38	0.462	0.230	0.180
109	7.37	6.75	0.326	0.104	0.35
110	7.50	6.65	0.380	0.143	0.31
111	7.52	5.74	0.830	0.095	0.29
112	7.55	5.99	0.472	0.124	0.26
113	7.44	5.70	0.514	0.103	0.26
114	7.44	5.66	0.508	0.117	0.51

[1] Sample taken from settler after last reactor.

[2] Not determined.

a range of conditions under which acceptable operation could be realized, operating conditions were changed in relatively small increments from one experiment to the next.

1. Effect of Soluble Magnesium

The dramatic impact that dissolved magnesium can have on limestone utilization can be seen by comparing Runs 100 and 101, both open-loop runs. With all other conditions kept relatively constant, raising the magnesium level from 300 to 4,450 ppm caused the utilization to decrease from 88 percent to 41 percent.

2. Effects of Temperature and Reactor Holdup Time

The improved utilization which can be obtained by operating at elevated temperatures can be seen by comparing the 79 percent and 81 percent utilizations obtained in open-loop Runs 102 (70°C) and 103 (90°C) with the poor utilization of 41 percent in Run 101 (50°C).

The fact that the utilization in Run 103 was about the same as that in 102, even though the temperature was somewhat lower and the magnesium concentration somewhat higher, was due to the fact that a fourth reactor with a residence time of 1 hour was added to the series of three reactors which had been used in Runs 100-102. Although the solids in the effluent from the third reactor in Run 103 were not analyzed, and consequently a 3-reactor utilization based on solids composition could not be calculated, the TOS and acidity in the effluent from the third reactor during Run 103 indicated that a utilization of about 65% would have been obtained if only three reactors had been used.

In the closed-loop experiments, the effect of operation at 90°C on utilization can be seen clearly by comparing Runs 108 and 109 made at approximately 1000 ppm magnesium. In Run 108 at 90°C, the utilization was 102%, while in Run 109 at 50°C utilization was 92%.

3. Effect of Limestone Feed Stoichiometry

Limestone feed stoichiometry is another factor affecting utilization. As the limestone feed stoichiometry is reduced, utilization tends to increase. The increased utilization, however, is realized at the expense of a decrease in the extent to which the liquor is regenerated.

In the open-loop runs, reducing the limestone feed stoichiometry

from 90% in Run 100 to 84% and 78%, respectively, in Runs 102 and 103, was a factor which caused the utilization to drop only from 88 percent to about 80 percent when magnesium concentration was increased dramatically.

The effect of feed stoichiometry on utilization in the closed-loop experiments is not clearcut, because both feed stoichiometry and scrubber bleed composition were being changed at the same time in many cases. However, comparison of the results of Runs 109-111 with Runs 112-114 show that generally higher utilizations were obtained in the former group (84-92% vs. 78-82%) in which the feed stoichiometry was somewhat lower (68-75% vs. 78-81%).

4. Effects of Sodium Sulfate Concentration and Bisulfite Acidity

The concentrations of sulfate and bisulfite also importantly affect the limestone regeneration reaction rate and therefore utilization. Increasing the sulfate concentration raises the ionic strength which retards the reaction rate; on the other hand, the increased acidities which accompany elevated bisulfite concentrations tend to drive the reaction faster. Increasing TOS from 0.56 M to 1.49 M (Runs 111 and 110, respectively) resulted in an increase in utilization from 84% to 98% at about the same feed stoichiometry. The antagonistic, or counterbalancing, effects of TOS acidity and sulfate concentration are clearly indicated in Runs 113 and 114 in which there was little change in utilization (81% vs. 78%) when both TOS (and acidity) and sulfate were comparably increased. This suggests that the acidity-to-sulfate ratio in the reactor feed may be an important parameter in predicting utilization.

B. DEWATERING PROPERTIES OF PRODUCT SOLIDS

With the exception of Run 103 (7830 ppm magnesium) in which very poor settling behavior was observed, the solids in the product slurries from all of the other runs settled reasonably well. After 30 minutes of settling in a 100-ml graduated cylinder, the slurry had generally settled to 15-30% of its original height.

Settling curves for samples of the product slurry taken at the end of each of the four open-loop runs are shown in Figure 2. The solids from Run 100, the run with the lowest magnesium, and Run 102,

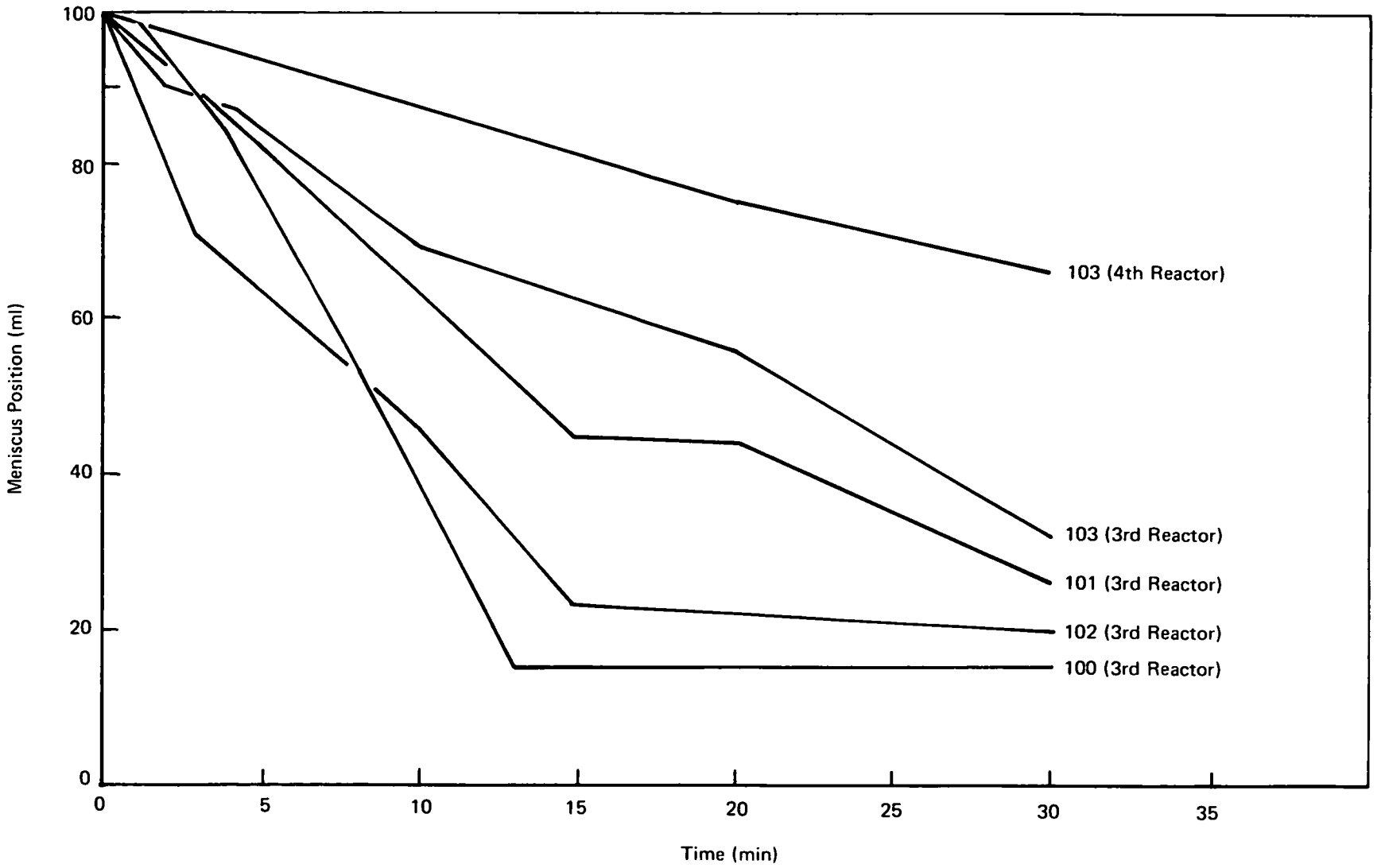

FIGURE 2 SETTLING CURVES FOR OPEN-LOOP RUNS

the run at 90°C, exhibited the best settling behavior. Not only were the final settled volumes the lowest, but the initial settling rates were also the most rapid -- the solids had settled to essentially their final settled volumes in fifteen minutes or less. The solids from Runs 101 and 103, the high magnesium runs at 50°C and 70°C, settled more poorly both in terms of initial settling rate and settled volume after 30 minutes. The settling behavior of the solids from the three-reactor system used in Run 101 was reasonably similar to that of the effluent from the third reactor of the four-reactor system used in Run 103. However, in Run 103, passage of the reaction slurry through the fourth reactor which had been added to the system resulted in a significant deterioration in the settling properties of the solids.

The settling curves for the third reactor effluent from Runs 101 and 103, shown in Figure 2, exhibit breaks due to disruption of the settling process by rising bubbles of CO_2 which were produced as a result of a continuing reaction in the settled mass. Such bubbling was observed in settling tests in previous work (1) where low utilizations were achieved. In Run 101 utilization was only 41%, and in the third reactor in Run 103 utilization is estimated to have been approximately 65%. Off-gassing was not observed in the final effluent from Run 103 which had reacted for an additional hour in the fourth reactor.

Settling curves for the three extended closed-loop runs (108-110) and the four shorter closed-loop runs (111-114) are shown in Figures 3 and 4, respectively. All indicate good settling behavior. No significant effervescence due to continued reaction was observed in samples taken from any of the closed-loop experiments (four reactors were used for all). In a few instances, a number of small bubbles were detected within the mass of settled solids; however, they did not grow large enough to rise and disrupt the settling process.

In earlier work (1) the settling properties of the solids were sometimes observed to deteriorate as a run progressed. Initial settling rates frequently decreased with time and the form of the settling curves changed from being concave to becoming almost straight lines. Care was taken in this program to monitor the settling properties periodically so that unstable settling behavior would be detected. For

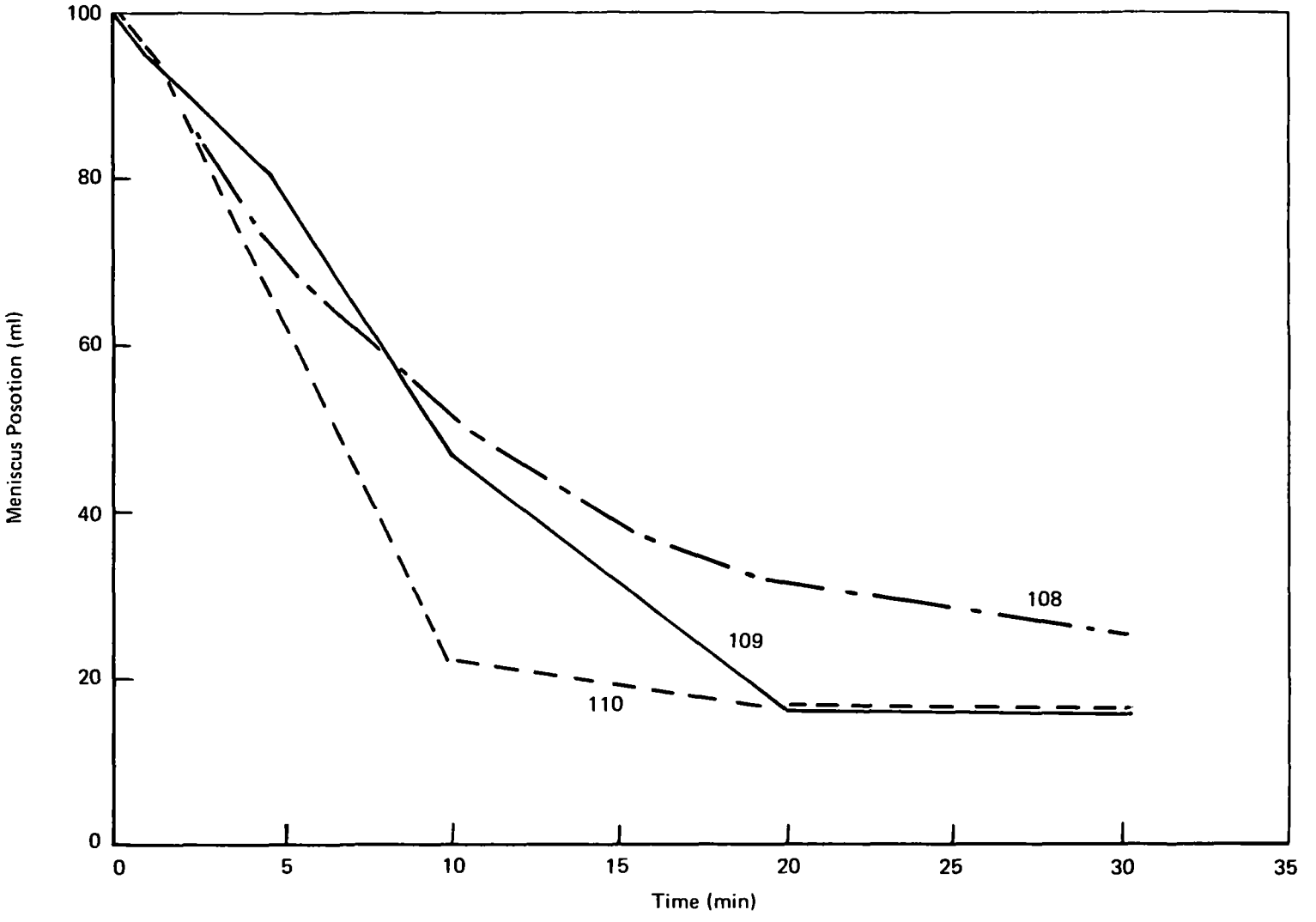

FIGURE 3 SETTLING CURVES FOR EXTENDED RUNS 108-110

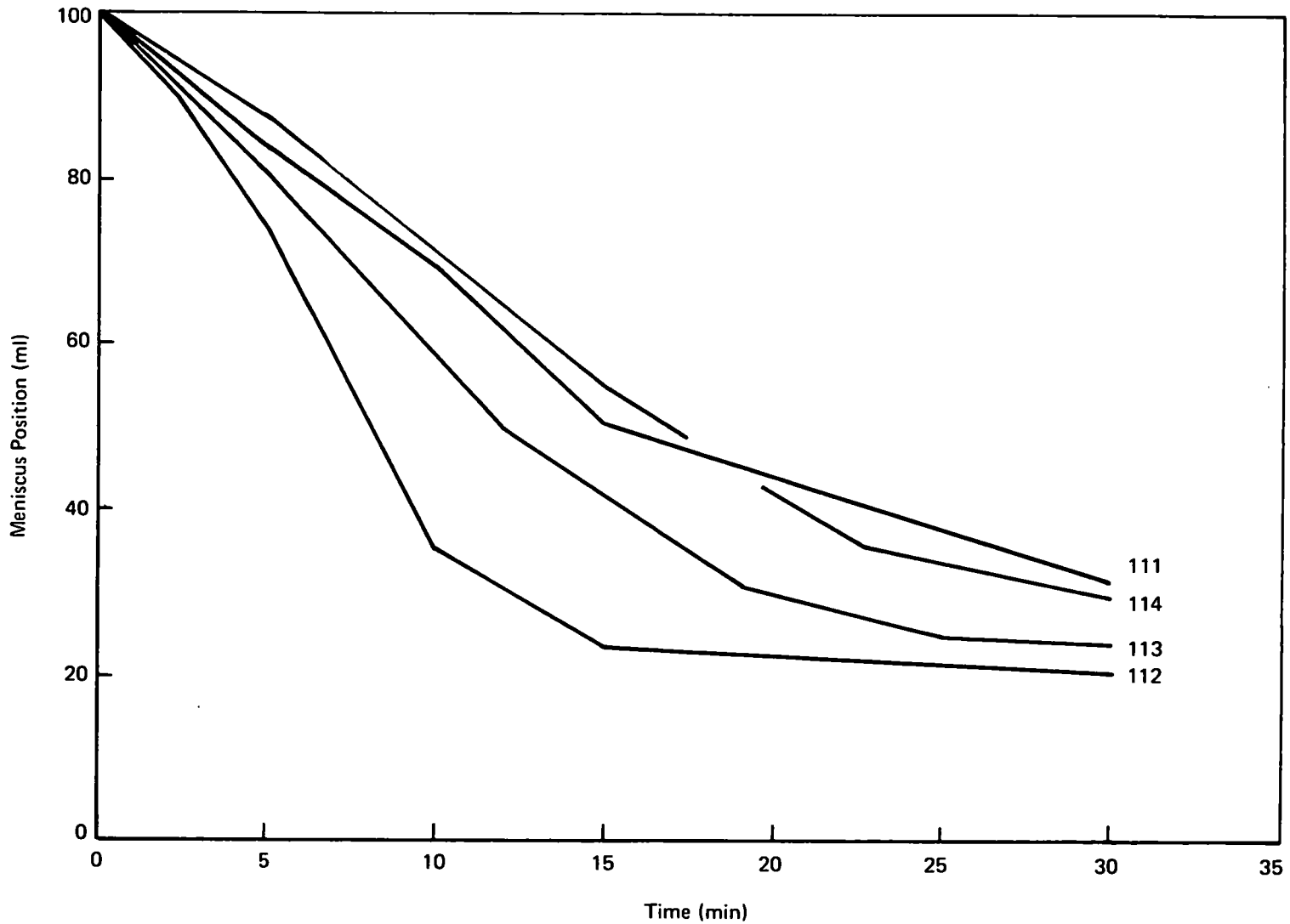

FIGURE 4 SETTLING CURVES FOR RUNS 111-114

most of the closed-loop runs, the settling behavior was quite stable throughout the run. The greatest change in settling was observed throughout the course of Run 111. Settling curves for four samples taken during and at the end of the run are shown in Figure 5. Although settling seemed to deteriorate during the first ten hours of the experiment, the last two samples indicate that settling behavior had stabilized before the experiment was terminated.

In the complete set of experiments which were carried out in this program, a range of TOS concentrations was studied at more or less constant limestone feed stoichiometry. Thus, the concentrations of solids in the final product slurries varied. Consequently, the final settled volumes alone are not the best indicator of the dewaterability of the product slurries. The settled densities included in Table I take into account the variation in slurry percent solids. They ranged from eight grams of dry solids per 100 ml of settled slurry to as high as 40 g/100 ml. The settled densities observed in all of the open- and closed-loop experiments are plotted as a function of the ratio $HSO_3^-/SO_4^=$ in the feed liquor in Figure 6. The general increase in settled density with the ratio $HSO_3^-/SO_4^=$ supports the thesis that better settling behavior is exhibited by solids produced in faster reactions.

It is not clear why the settled density of the solids produced in Run 103 was so low, even though the $HSO_3^-/SO_4^=$ ratio was high and good limestone utilization was achieved. However, solution analyses indicated that in Run 103 only about 54% of the TOS was precipitated in the first two reactors. In all of the other runs, 70-75% of the TOS precipitation took place in the first two reactors. The slower reaction rates in the first reactors could have caused the solids to settle poorly. An explanation of this sort is consistent with the observation made during the discussion of settling curves in Figure 2 that in Run 103 the effluent slurry from the fourth reactor settled more poorly than that from the third reactor.

C. SULFATE PRECIPITATION

The amount of sultate that is precipiated as a calcium salt (as opposed to being occluded as a soluble salt) is of interest since it provides a measure of the amount of oxidation that can be accommodated

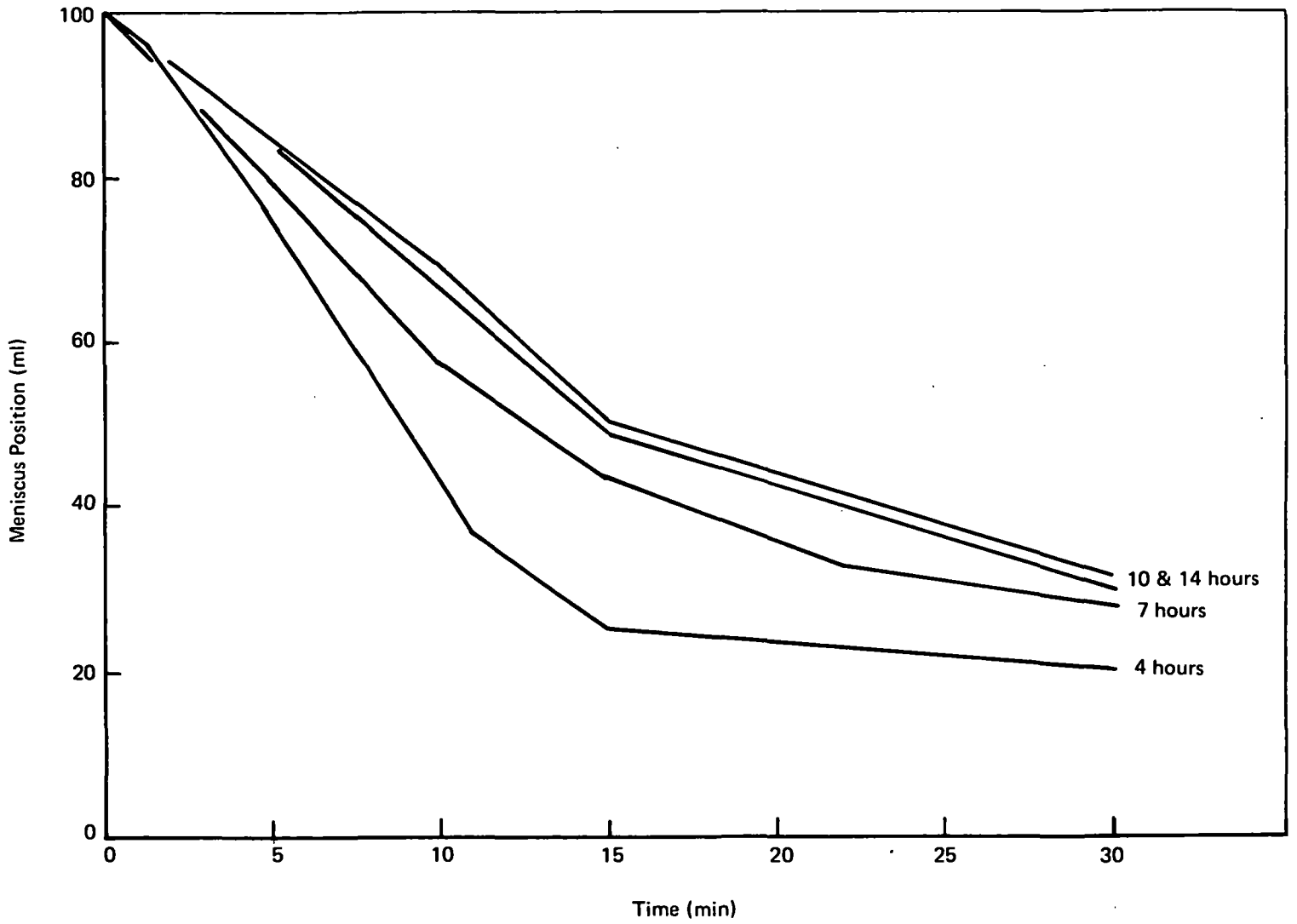

FIGURE 5 RUN 111 SETTLING CURVES – SAMPLED AT DIFFERENT TIMES

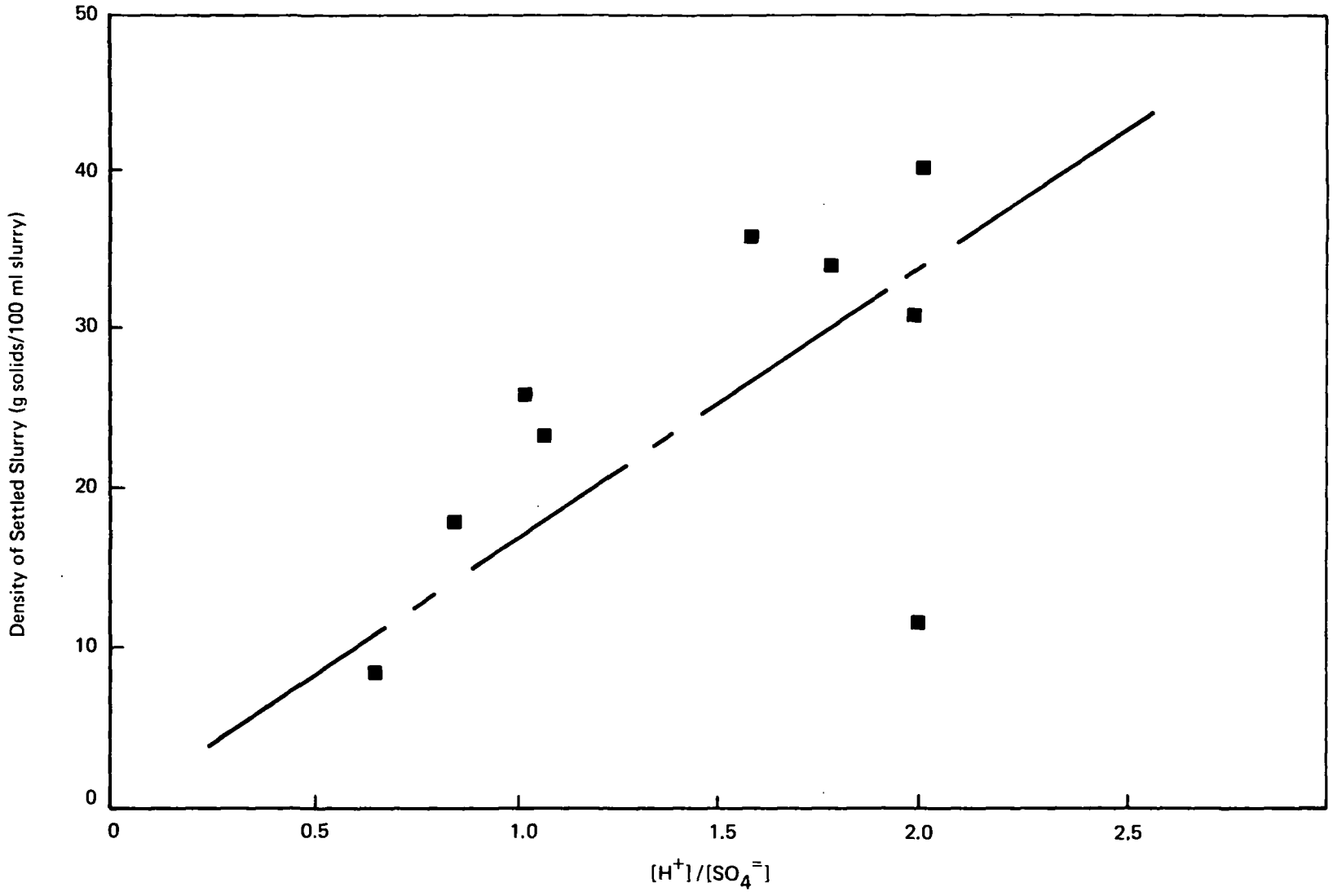

FIGURE 6 VARIATION IN SETTLED DENSITY WITH ACIDITY/SULFATE RATIO IN SCRUBBER BLEED

without purging soluble salts. In earlier laboratory and pilot plant studies of the use of lime and limestone to regenerate dual alkali liquors (1) it was found that a good correlation existed between the ratio $CaSO_4/CaSO_3$ in the product solids and the ratio $SO_4^=/SO_3^=$ in the regenerated process liquor. The values for the $CaSO_4/CaSO_3$ ratio obtained in these bench scale limestone experiments were calculated and are included in Table I. The values are also plotted as a function of $SO_4^=/SO_3^=$ in Figure 7. Included on that plot are the values determined previously in laboratory and pilot plant studies using lime and limestone. The agreement between the limestone values determined in this work and the earlier values is surprisingly good.

D. FATE OF MAGNESIUM IN LIMESTONE REGENERATION EXPERIMENTS

Because of the problem which elevated levels of soluble magnesium can cause when limestone is used for regeneration, an important concern is the final steady state magnesium concentration in the process liquor. At steady state the input of magnesium from dissolution of limestone (and possibly from flyash, if it is collected in the scrubbing system) is in equlibrium with its removal with the product solids. In the pH range of 5-7 where most limestone dual alkali systems would operate, magnesium sulfite would be the least soluble magnesium salt; so its precipitation would be expected to limit the soluble magnesium level. Magnesium hydroxide is less soluble than magnesium sulfite, but it would become the limiting solid phase only at higher pH values.

The changes in soluble magnesium concentration observed across the regeneration reactor system in each of the experimental runs are shown in Table III. The initial and final magnesium concentrations in the feed are the results of analyses of samples of scrubber bleed entering the reactor system at the beginning and end of each run. Since the open-loop experiments were fed from a single tank of simulated scrubber bleed with no recycle, the initial and final values are the same. The final effluent concentration is that measured in a sample of reactor effluent taken at the end of a run.

In Run 100, the relatively low, 300 ppm concentration in the feed rose to 390 ppm upon passage thorugh the reactor system. However, based on the amount of limestone which was fed and its magnesium content

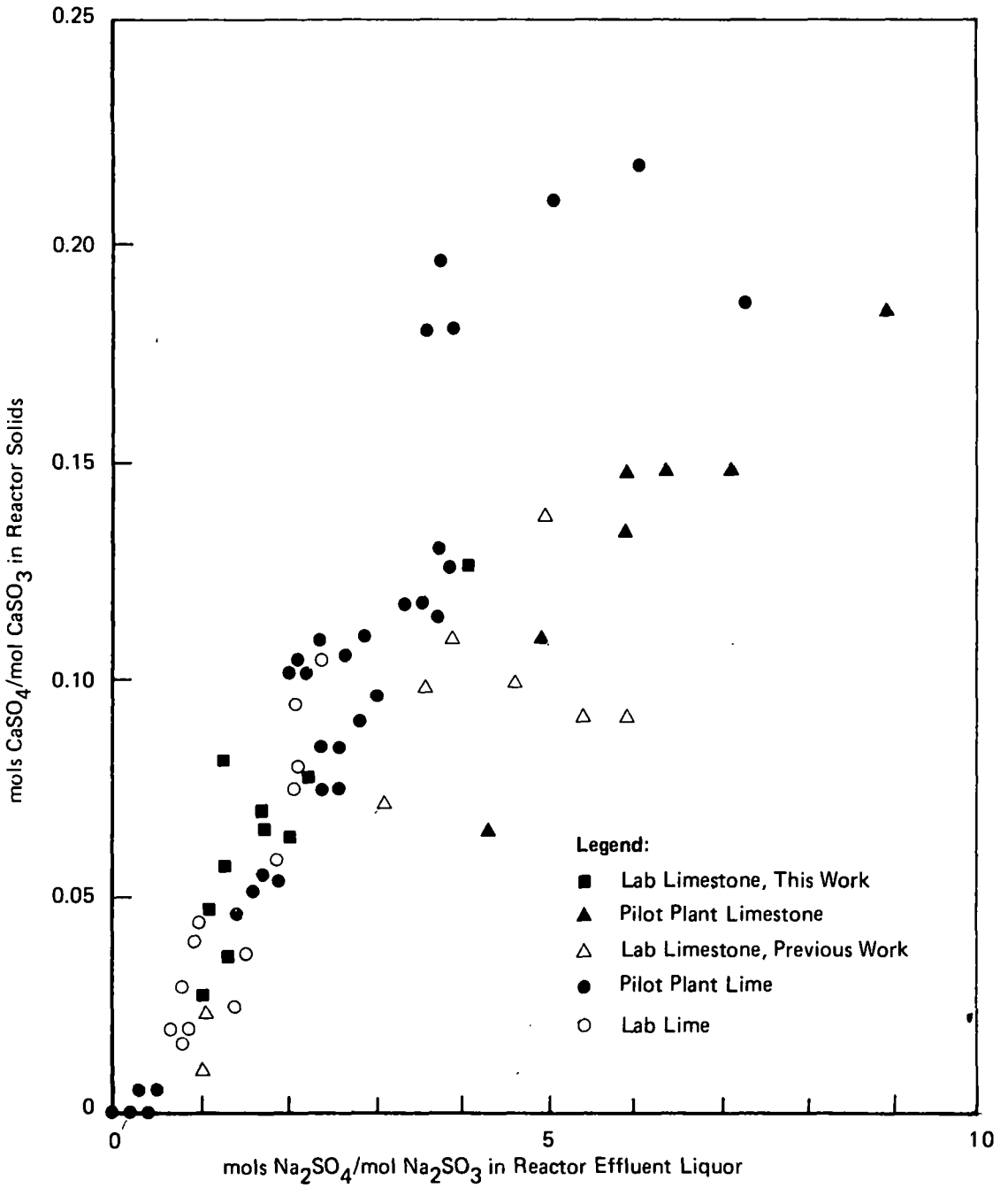

FIGURE 7 SULFATE PRECIPITATION OBSERVED IN THIS LABORATORY WORK COMPARED WITH THAT OBSERVED IN EARLIER STUDIES (Ref. 1)

TABLE III

BEHAVIOR OF SOLUBLE MAGNESIUM IN LIMESTONE
DUAL ALKALI REGENERATION STUDIES

			Scrubber Bleed Steady State Composition			Magnesium Concentration (ppm)			In Final Reactor Effluent		
Run	Type[1]	Temp(°C)	TOS (M)	H^+(M)	$SO_4^=$(M)	Initial Reactor Feed	Final Reactor Feed	Final Reactor Effluent	Mg^{++}(M)	$SO_3^=$(M)	$Mg^{++} \times SO_3^=$
100	3R-OL	45	1.58	1.42	0.64	300	300	390	0.016	0.64	0.010
101	3R-OL	50	1.61	1.45	0.69	4450	4450	4180	0.172	0.56	0.10
102	3R-OL	90	1.60	1.42	0.71	4450	4450	1900	0.078	0.42	0.033
103	4R-OL	70	1.62	1.47	0.73	7830	7830	6040	0.248	0.42	0.10
108	4R-CL	90	1.43	1.26	0.80	2150	1270	960	0.039	0.63	0.025
109	4R-CL	50	1.44	1.37	0.70	1035	1030	1030	0.042	0.55	0.023
110	4R-CL	50	1.49	1.21	0.67	2200	1940	1890	0.078	0.64	(0.050)
111	4R-CL	50	0.56	0.49	0.77	2050	2020	2040	0.084	0.19	0.016
112	4R-CL	50	1.02	0.83	0.77	2040	2010	1990	0.082	0.45	0.037
113	4R-CL	50	1.03	0.84	0.99	2050	2020	2010	0.083	0.45	0.037
114	4R-CL	50	1.33	1.20	1.16	1975	1900	1900	0.078	0.59	0.046

[1] Number of reactors -- open/closed loop

(0.13 mmoles/g), the observed increase of 90 ppm could be accounted for by dissolution of only about 30% of the magnesium which entered the reactor with the limestone. Analyses of the solids indicated that about 50% of the magnesium dissolved. The fact that a substantial amount of magnesium remained in the Run 100 product solids (Table II) indicated that either all of the magnesium entering the system did not dissolve, or if it did, a substantial amount reprecipitated.

Run 101 was carried out with 4,450 ppm of magnesium in the feed liquor. That magnesium level was chosen on the basis of a test in which product solution from Run 100 was saturated with respect to magnesium sulfite at room temperature. Although the limestone utilizaton achieved in Run 101 was quite poor, a slight decrease in soluble magnesium across the reactor system was observed.

When the preceding experiment was repeated at 90°C as Run 102, not only was good utilization achieved, but a decrease in soluble magnesium concentration of greater than 50% was also observed. The relatively large amounts of magnesium found in the Run 102 product solids (0.83 mmoles/g) is consistent with the decrease. (A magnesium content of about 1.0 mmole/g in the solids would correspond to the observed change in soluble magnesium concentration). Experiment 102 was encouraging not only because good utilization and settling were achieved, but also because it demonstrated that under those conditions the soluble magnesium level would not rise above a tolerable level.

A comparison of the magnesium solubilities observed in Runs 101 and 102 (values of the product $[Mg^{++}] \times [SO_3^{=}]$, the apparent solubility product, K_{sp}', are included in Table III) suggest an inverse relationship between the solubility of magnesium sulfite and temperature. That observation is consistent with data reported in Gmelin (3) which indicate that the solubility of magnesium sulfite goes through a maximum value at about 40°C and then decreases to about 50% of the maximum value at 90°C. A change in the hydration state of the stable solid phase from the hexahydrate to the trihydrate in the vicinity of 40°C is the reason for the maximum in the solubility/temperature relationship.

The equilibrium solubilities as a function of temperature for magnesium sulfite in solutions with ionic strengths representative of those which would be encoutnered in limestone dual alkali systems were determined by adding an excess of $MgSO_3 \cdot 6H_2O$ (which had been synthesized in the laboratory) to synthetic solutions and analyzing the final concentrations of soluble magnesium and sulfite. With sulfite concentrations in the range of 0.6-0.9 M and sulfate at 0.6 M, the following values for the apparent solubility product, K_{sp}', were determined at the indicated temperatures:

Temperature (°C)	$[Mg^{++}] \times [SO_3^{=}]$
25	0.098
50	0.32
70	0.24
90	0.034

The result of the equilibrium solubility measurement at 90°C is in excellent agreement with the solubility observed in Run 102. However, the equilibrium K_{sp}' measured at 50°C was about three times the value observed in Run 101; and the calculated K_{sp}' for Run 103 at 70°C was the same as that for Run 101 (0.10) and considerably lower than the 0.24 measured in the equilibrium solubility experiment at 70°C. The seemingly low values found in Runs 101 and 103 could have been produced if the samples had cooled while the solids were being separated by vacuum filtration. The values which were observed were very close to the 0.098 value measured at 25°C.

The first closed-loop run, Run 108, was carried out at 90°C with a magnesium level of 2,150 ppm. That magnesium concentration, slightly above the solubility limit for the reactor effluent based on the results of Run 102, was chosen so that the system would have a reasonable chance of reaching equilibrium by the end of the run. Interestingly, after nearly 29 hours of operation at 90°C, the magnesium level in the system had fallen to 1,270 ppm; and with that concentration being fed to the reactor, the corresponding concentration in the effluent was 960 ppm.

In Run 109 an attempt was made to determine whether or not operation at 50°C in the presence of about 1000 ppm of soluble magnesium would be feasible, producing solids with acceptable properties. The

regeneration reaction proceeded well, and surprisingly, the soluble magnesium level remained virtually constant in the system during 28 hours of operation -- even though the magnesium level was well below that corresponding to saturation with respect to magnesium sulfite at 50°C.

Experiment 110 was a repeat of 109 with the soluble magnesium concentration approximately doubled. Even though the product of $[Mg^{++}]$ x $[SO_3^{=}]$ in the reactor effluent at the end of the experiment was about 0.05, well below the equilibrium value of 0.32 at 50°C, a significant decrease in soluble magnesium appeared to have occurred during the 29 hours of operation. A 50-ppm reduction was observed across the reactors at the end of the experiment.

The remaining closed-loop experiments were all carried out with about 2000 ppm of magnesium in the feed initially, but in all cases, the TOS level was lower than that in Run 110. Even though in each of those experiments the solutions should have been unsaturated with respect to magnesium sulfite, no measurable rise in soluble magnesium could be detected.

Soluble magnesium concentrations measured in the feed to, and effluent from, the regeneration reactor system during the three extended, closed-loop runs are plotted in Figure 8. Magnesium concentrations in the Run 108 reactor effluent were essentially constant at about 1000 ppm. A gradual decrease in soluble magnesium was observed in the scrubber bleed as the regenerated liquor lower in magnesium replaced the prime liquor (which initially contained about 2150 ppm) in the settler, surge tank and absorber. A discontinuity in the Run 108 scrubber bleed magnesium level was observed at about 20 hours. The elevated magnesium level was due to the addition of makeup liquor to the settler which had an erroneously high magnesium concentration.

Levels in both the reactor feed and effluent throughout Run 109 were quite constant at about 1000 ppm. Run 110 was intermediate in behavior between Runs 108 and 109. In Run 110, with only one exception, the magnesium concentration in the reactor effluent was always about 70-100 ppm less than that in the corresponding feed sample. That small decrease in magnesium concentration across the reactor system produced

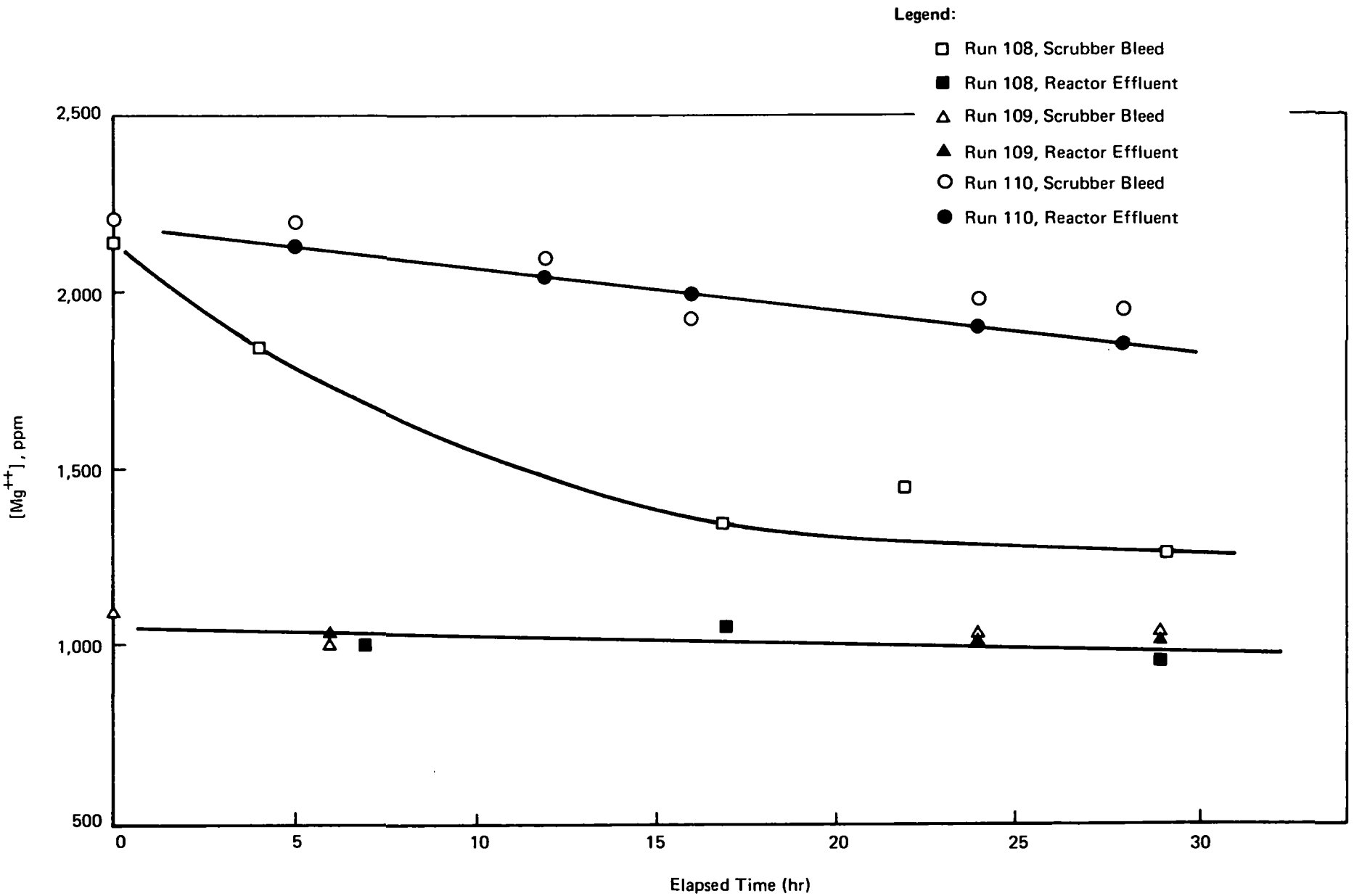

FIGURE 8 CHANGES IN SOLUBLE MAGNESIUM OBSERVED DURING EXTENDED RUNS

the constant slow decrease in the magnesium level in the reactor effluent (and for the most part, in the scrubber bleed as well) throughout the duration of the experiments.

There did not seem to be a clear reason for the slow drop in magnesium which was observed in Run 110. The apparent solubility product for magnesium sulfite in the effluent from the reactor was well below the previously measured equilibrium value. The slow downward drift was also not due to a corresponding rise in sulfite concentration. The sulfite concentration varied more or less randomly in the samples taken (by about $\pm$ 7%). The water which entered the system as part of the limestone paste could have been partly responsible for the downward drift but its maximum effect would have been to reduce the magnesium concentration by only 2% instead of the 4-5% drop observed across the reactors at most times. The apparent unsaturation of the reactor effluent with respect to magnesium sulfite in Run 110, and other runs as well, could, however, have been due to coprecipitation of magnesium salts with the calcium salts. That same type of coprecipitation phenomenon involving calcium sulfate produces reactor effluent solutions unsaturated with respect to gypsum.

V. CONCLUSIONS

The results of the experiments carried out during the course of this program demonstrate quite clearly that within certain constraints, it should be possible to use limestone for the regeneration of dual alkali liquors without inordinate increases in the complexity of the system as compared to systems using lime. Using a four-reactor system with a total residence time of two hours, and finely ground, low-magnesium (1.1% Mg as $MgCO_3$) Fredonia limestone, utilizations of 78-92% were achieved over a reasonable range of solution concentrations without heating the solution above 50°C (typical of actual scrubber bleed temperatures) and without actively controlling soluble magnesium. Under those conditions, the solids which were produced settled well and could be vacuum filtered easily. In most cases they settled to 20-40% w/w in static batch settling tests; they could be filtered on a laboratory Buchner funnel to produce cakes having 40-75% solids.

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16. ABSTRACT

The report describes a series of open- and closed-loop laboratory bench scale experiments which were carried out to study parameters which affect the reaction of limestone with dual alkali flue gas desulfurization system process liquors. It gives details of several sets of operating conditions which permitted good limestone utilization to be achieved and product solids with good dewatering properties to be produced. It discusses the effects of temperature and soluble magnesium on the behavior of the regeneration reaction as well as the effects of total sulfur (IV) concentration, ionic strength, acidity of the solutions, and reactor system configuration. It presents data which suggest that regenerated liquors may have been unsaturated with respect to magnesium sulfite as a result of its coprecipitation with the calcium sulfite product solids.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS		b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
Pollution	Alkalies	Pollution Control	13B
Limestone	Magnesium	Stationary Sources	08G
Regeneration (Engineering)		Dual Alkali Process	
		Magnesium Sulfite	14B
Flue Gases		Calcium Sulfite	21B
Desulfurization			07A,07D

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