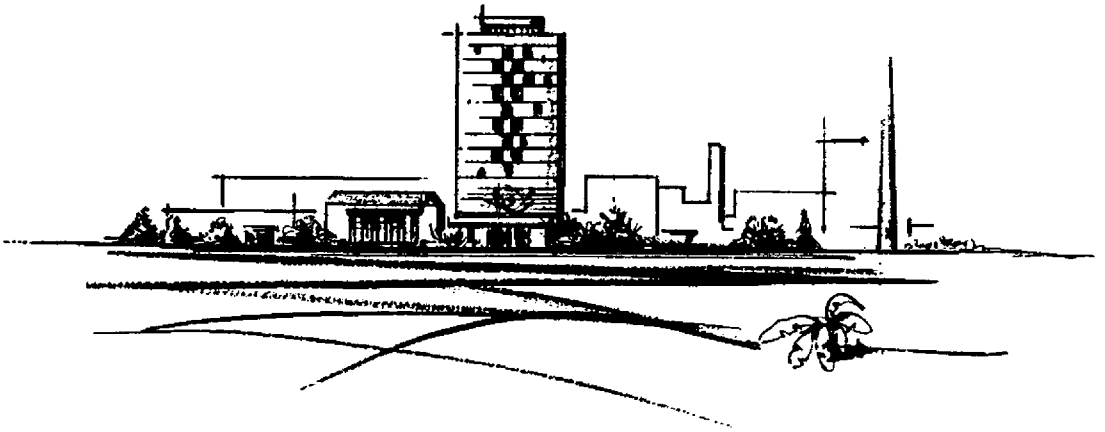
RESEARCH REPORT

to

NATIONAL AIR POLLUTION CONTROL ADMINISTRATION

CONTRACT NO. PH 86-68-84
Task Order No. 17

November 30, 1969



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FINAL REPORT

on

INVESTIGATION OF THE LIMESTONE-SO_2 WET SCRUBBING PROCESS

to

NATIONAL AIR POLLUTION CONTROL ADMINISTRATION

CONTRACT NO. PH 86-68-84
Task Order No. 17

November 30, 1969

by

R. W. Coutant, R. H. Cherry, H. Rosenberg,
J. Genco, and A. Levy

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MANAGEMENT SUMMARY

The wet lime-SO_2 scrubbing process was investigated on a laboratory scale in support of full-scale prototype studies being undertaken by the National Air Pollution Control Administration (NAPCA).

This investigation consisted of laboratory scale experiments in the following areas:

1. Measurement of the overall rate of uptake of SO_2 in a stirred-pot reactor,
2. Measurement of the relative rates of hydration of selected limestones and dolomites,
3. Measurement of the relative rates of dissolution of selected limestone and dolomite materials,
4. Chemical analysis of selected dolomite- and limestone-based liquors prepared at three temperatures.

These experiments were designed to yield qualitative indications of the importance of individual physical and chemical processes to the overall limestone-SO_2 wet scrubbing process.

The results of the current experiments indicate that lime in particulate form reacts readily with various sulfur species or carbonate in solution to yield a coating which inhibits utilization of the bulk of the lime. Fine grinding of the lime might alleviate this problem to some extent. However, because of the observed tendency for particles to become cemented together forming large clusters, a high degree of utilization of the lime may not be possible as long as the lime is admitted to the scrubber in particulate form. It is therefore recommended that

further consideration be given to the importance of particle size in the overall scrubbing process. It is further recommended that consideration be given to the possibility of predissolving the lime, or limestone, in the feed water to the scrubber through the use of excess CO_2 or other solubilizing agents.

Further development is also needed in the area of modeling of the overall reaction system. The model given in this report is only a first attempt at description of the scrubbing process, and as such does not give adequate representation of the mechanical and chemical factors involved. For instance, the dependence of the equilibrium partial pressure of SO_2 on solution composition is not explicit in the model given. Also, a detailed analysis of these data will yield only rudimentary information on the various mass transfer resistances in this system, which may not be directly applicable to large-scale systems.

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INTRODUCTION

One of the major air pollutants in the United States is sulfur dioxide produced by burning fuels containing sulfur. As part of a national program to develop air pollution control processes, the National Air Pollution Control Administration is undertaking prototype studies of the lime/limestone scrubbing process. These studies will be carried out in three scrubbing systems, each capable of handling 30,000 acfm of flue gas.

Aqueous lime scrubbing to control SO_2 from combustion flue gas dates back to the early 1930's when several pilot and large scale projects were conducted in England to develop a cyclic process in which all of the scrubbing liquor would be recycled and only a solid waste product would be formed. This work was never completed partly because of the interruption of World War II and partly because of the development of the non-cyclic process still in use at Battersea and Bankside near London. These units require large quantities of Thames River water for scrubbing on a once-through basis. Little information on the cyclic lime process is available as a basis for current studies.

A major departure from the earlier English practice involves the use of the power-plant boiler as a calciner to produce the lime. In this procedure limestone or dolomite is pulverized and injected into the furnace. The calcined lime is subsequently collected in the scrubber as the reactant for removing SO_2. In this system several factors could be key to a successful process design. For

example, the availability of the lime for reaction in the scrubber could be dependent on its rate of hydration or rate of dissolution. Any tendency for insoluble carbonates or other reaction products to form dense layers on the otherwise active reactants as well as on scrubber equipment could be important. Little is known about these or other potentially important reactions and reaction rates.

This study was conducted under Contract No. PH 86-68-84 (Task Order No. 17) to provide preliminary information on the chemistry and relative reaction rates of some of the more important reactions as a basis for estimating their probable importance in the more complex large scale lime/limestone scrubbing process. Its purpose was to investigate several of the individual chemical processes which occur during the overall limestone-SO_2 wet scrubbing process: takeup of SO_2 by lime solutions and slurries, hydration of burnt lime, and dissolution of hydrated lime. This Final Report covers work done during the period of April 15 through July 15, 1969.

SUMMARY

The wet-lime-SO_2 scrubbing process was investigated on a laboratory scale in support of full-scale prototype studies being undertaken by the National Air Pollution Control Administration (NAPCA).

This investigation consisted of laboratory scale experiments in the following area:

1. Measurement of the overall rate of uptake of SO_2 in a stirred-pot reactor,
2. Measurement of the relative rates of hydration of selected limestones and dolomites,

3. Measurement of the relative rates of dissolution of selected limestone and dolomite materials,
4. Chemical analysis of selected dolomite- and limestone-based liquors prepared at three temperatures.

The SO_2 uptake experiments were performed with simulated flue gas in a stirred-pot reactor at 125°F operated batchwise with respect to the liquid charge. Preliminary runs were made to determine the effects of gas-bubble size, and gas-flow rate on the observed rate of uptake of SO_2 by the liquid. The experiments were limited to a brief exploration to assess the magnitude of the effects and did not involve a detailed study of these variables. Within the range of operations undertaken the effects of variation of these experimental parameters were judged to be not significant.

The two primary variables studied were the flue gas and the scrubber-liquor compositions. The change of pH of the scrubber liquor during a run generally follows a trend which includes a sharp initial drop as CO_2 is sorbed. The pH remains reasonably constant at values in the range 6-7 until the reactants of the liquid phase become exhausted or are rendered unavailable. At this point a sharp drop in liquor pH is accompanied by SO_2 breakthrough. SO_2 breakthrough occurred at liquor pH values in the range of 3-4 when no NO_x was present in the simulated flue gas; with NO_x, breakthrough occurred in the pH range of 4-5.

Little or no SO_2 appears in the scrubber outlet gas until the reactant is either exhausted or rendered unavailable. The stoichiometry at the point of SO_2 breakthrough generally corresponds to the formation of the sulfite from the available reactants. After breakthrough, the SO_2 concentration in the outlet gas increases rapidly and asymptotically approaches the value of the inlet concentration of SO_2.

The rates of hydration of several samples of burnt limes supplied by NAPCA were determined by a temperature-rise procedure similar to ASTM Test C-110. The results indicate a strong dependence of hydration rate on the conditions of calcination of the stone and particle size. As particle size is increased, or as temperature of calcination is increased, the rate of hydration of the resultant lime decreases. The results indicate that the rate of the hydration process is limited by diffusion of water through the lime particle, and that overburning of the lime markedly decreases hydration rate. Other experiments, using partially sulfated limes or solutions containing $SO_4^{=}$, showed that hydration rates are severely limited by the presence or formation of a layer of sulfate on the lime particles.

Rates of dissolution of hydrated lime were determined in a well-stirred system using a calcium ion-specific electrode and a pH electrode for monitoring the concentrations of Ca^{++} and OH^- in solution. The results indicate that dissolution in water is rapid, only a few seconds being required for saturation with $Ca(OH)_2$. However, when the solvent contains sulfite, sulfate, or carbonate, the rate of dissolution of $Ca(OH)_2$ is greatly decreased.

Analyses of solutions saturated with respect to $CaSO_3$, $CaSO_4$, $MgSO_3$, and $MgSO_4$ showed that these solutions contained primarily $MgSO_4$. These analyses also indicated a buffering effect of these salts on the pH of the solutions.

EXPERIMENTAL WORK AND DISCUSSION

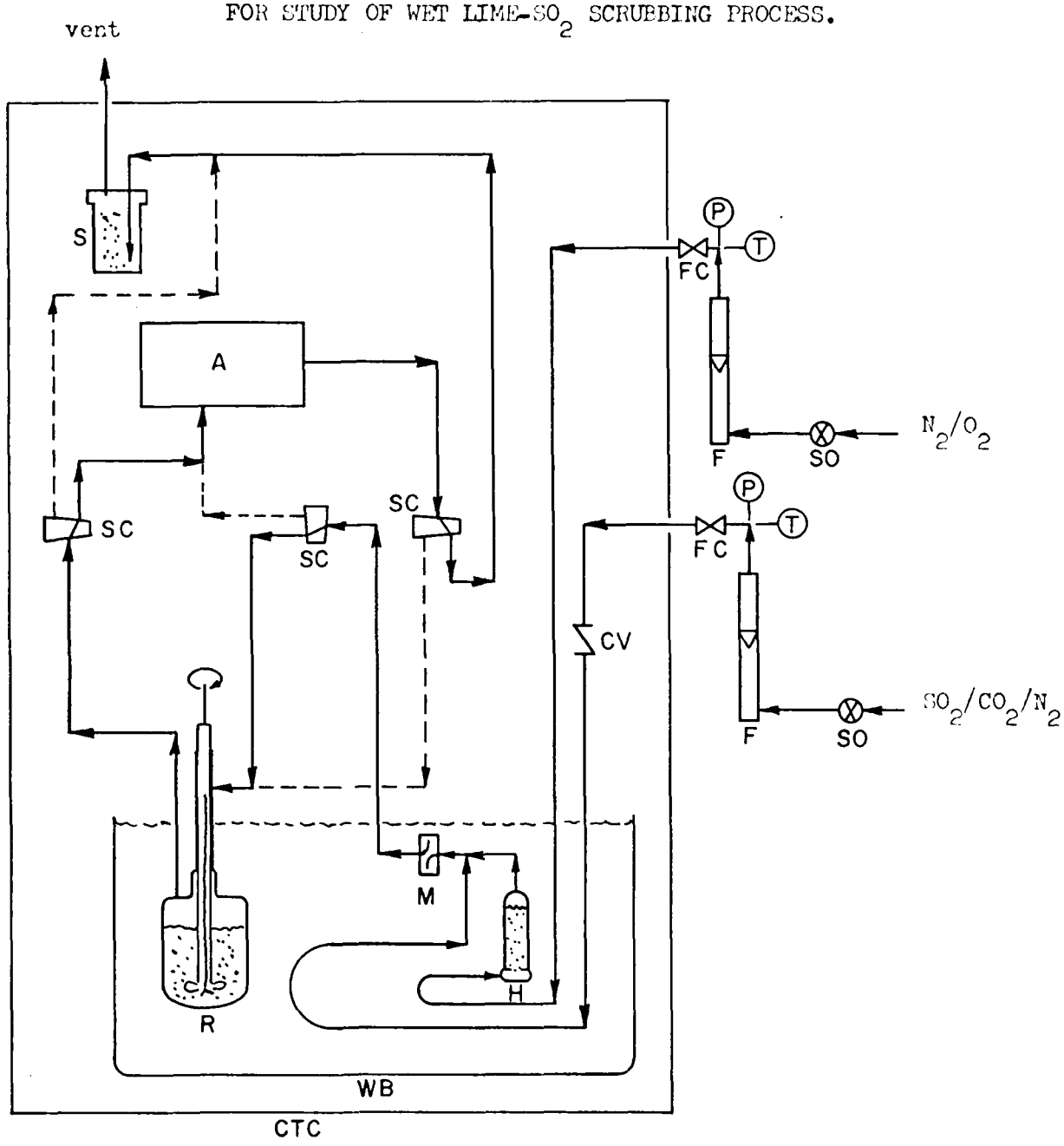
The limestone-SO_2 wet-scrubbing process may be considered in terms of a series of physical and chemical interactions involving: (1) transfer of the SO_2 to the surface of the liquid sorbent, (2) dissolution of SO_2 and reaction with dissolved components of the liquor, and (3) regeneration of active liquor through hydration and dissolution of solid lime. It is generally expected that the homogeneous solution reactions will be relatively fast and not important in determining the overall rate of the scrubbing process. Hence, this program has been concerned with an exploratory examination of the heterogeneous processes; SO_2 uptake, hydration of the lime, and dissolution of the lime. As will be seen from the results, the rates of these processes will not be independent of each other in any real scrubbing system. These results are therefore, at best, qualitative indications of the importance of individual segments of the overall scrubbing process.

SO_2-Uptake

The apparatus shown schematically in Figure 1 was developed to perform laboratory-scale experiments to study the wet lime-SO_2 scrubbing process. Simulated flue gas was obtained by mixing gases from two cylinders, one containing 90 mole percent nitrogen and 10 mole percent oxygen and the other containing 75.5 mole percent nitrogen, 24 mole percent CO_2, and 0.5 mole percent SO_2. Other cylinders were available, so that SO_2 or CO_2 could be deleted from the mix, or NO_x could be added to the mix. The gases from the cylinders were passed through calibrated rotameters equipped with dial thermometers and pressure gauges. The rotameters were operated at 15 psig, and flow controllers were used to reduce the pressure to atmospheric conditions. The line from the cylinder containing SO_2 had a check valve after the flow controller to prevent backflow from the N_2/O_2 cylinder. A nitrogen line (not shown) was connected to each of the gas-cylinder lines immediately downstream from the shut-off valves and was separated from the latter lines by check valves. The N_2 was used for purging and standardizing purposes. The line from the N_2/O_2 cylinder was constructed of copper and the line from the $SO_2/CO_2/N_2$ cylinder was constructed of stainless steel. However, downstream from the flow controllers, the entire flow system, with the exception of the SO_2 analyzer, was constructed of Pyrex glass.

After leaving the flow controller, the N_2/O_2 stream passed through a preheat loop in a water bath and then through a water-bubbler humidifier, where the stream was saturated with H_2O. The $SO_2/CO_2/N_2$ stream also passed through

FIGURE 1. SCHEMATIC DIAGRAM OF LABORATORY APPARATUS FOR STUDY OF WET LIME-SO_2 SCRUBBING PROCESS.



LEGEND

A	- Analyzer, SO_2	P	- Pressure gauges
CTC	- Constant temp. chamber, 130°F	R	- Reactor
CV	- Check valve	S	- H_2O_2 scrubber
F	- Flowmeters	SC	- Stopcocks, 3-way
FC	- Flow controller	SO	- Shut-off valves
H	- Humidifier	T	- Thermometer
M	- Mixing chamber	WB	- Water bath, 125°F

a mixing chamber which was immersed in the water bath. From the mixing chamber, the gas stream flowed to a manifold containing 3 three-way stopcocks so that the flow could be directed either to the reactor and then to the SO_2 analyzer or vice versa. The stopcock manifold permitted checking of the SO_2 content of the inlet gas to the reactor periodically during the course of a run. The SO_2 content of the outlet gas from the reactor was monitored continuously except for short periods when the inlet concentration was being checked. After returning to the stopcock manifold, the gas stream was routed to an H_2O_2 scrubber to remove residual SO_2 before being vented to the hood. The reactor was also immersed in the water bath, which was maintained at 125°F, and the entire flow system, between the flow controller and the H_2O_2 scrubber, was enclosed in a plastic cabinet maintained at 130°F.

A detailed sketch of the reactor is shown in Figure 2. The gas entered the reactor through a hollow glass stirring rod and was dispersed through a coarse glass frit at the bottom of the rod. Two sets of three glass propeller blades were located just above the frit, to insure good mixing. In several runs, a six-bladed Teflon impeller, having small holes drilled through the bottom, was substituted for the glass frit-propeller blade combination. The gas left the reactor through a small packed bed of glass beads in order to remove any entrained liquid. The reactor was equipped with a thermocouple well and fittings for sealing in pH and calcium-ion electrode systems.

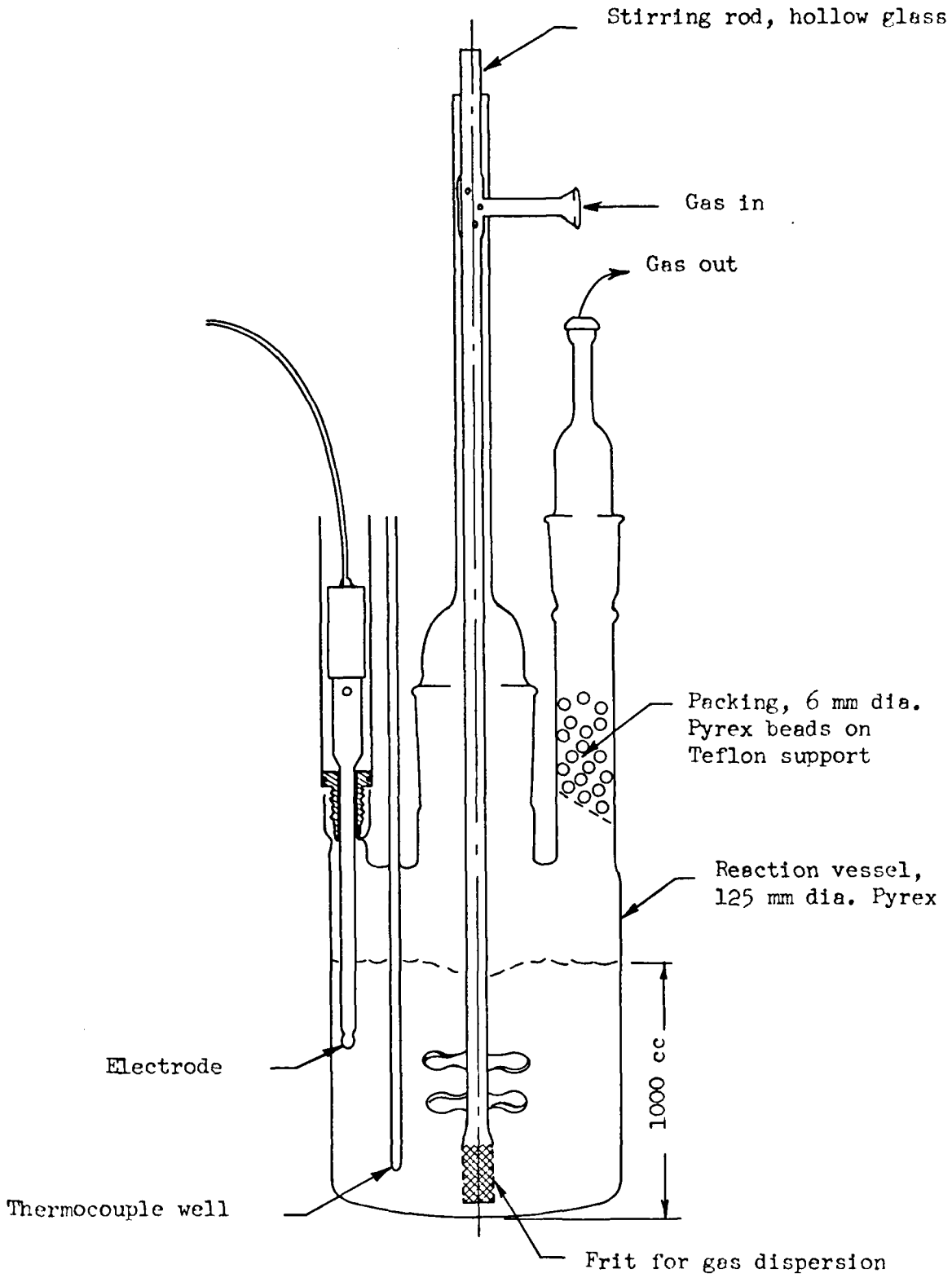
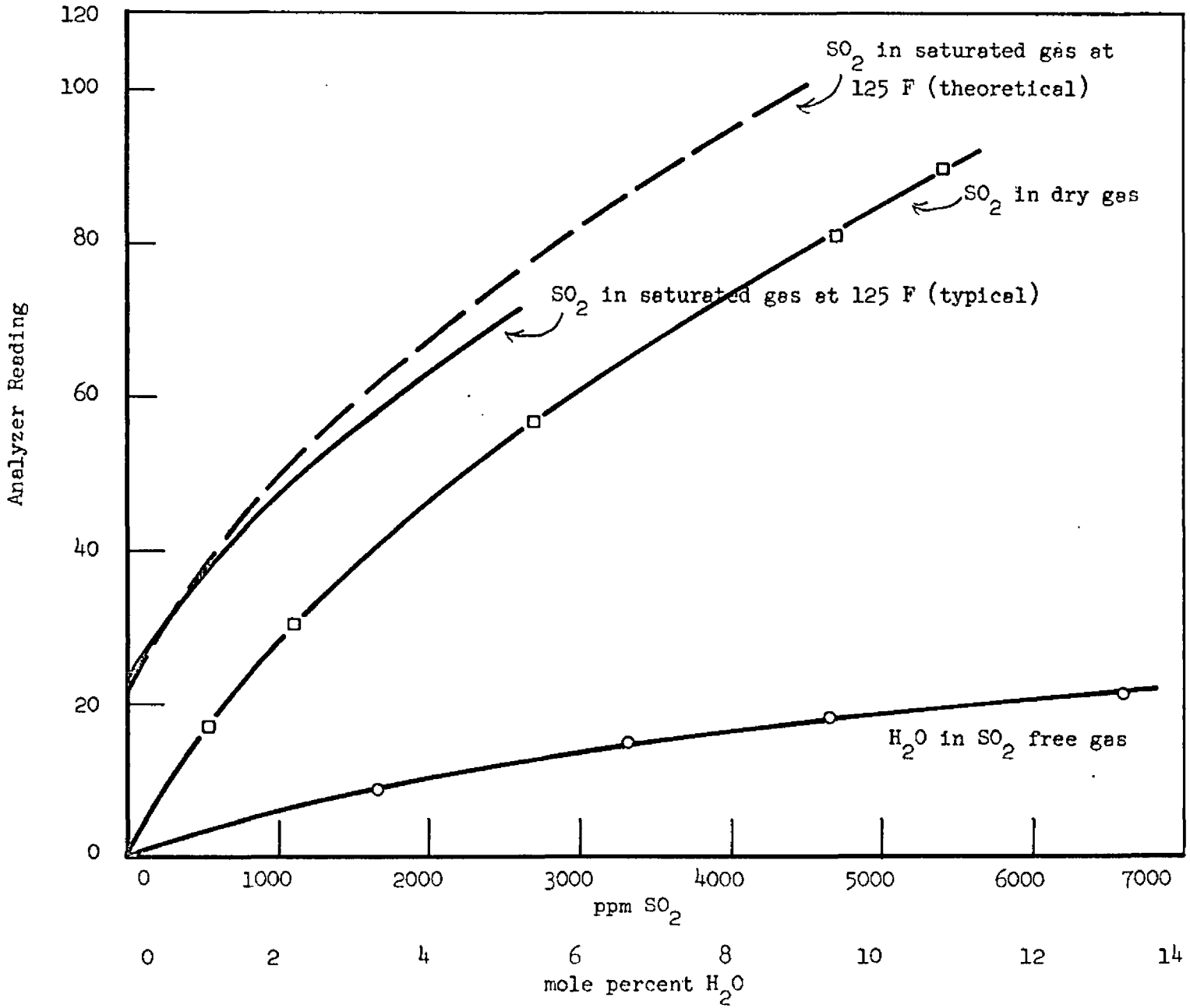


FIGURE 2. REACTION VESSEL FOR STATIC CHARGE OF SCRUBBER LIQUOR.

The SO_2 analyzer was a Model 315 A Beckman Infrared Analyzer which was calibrated with known mixtures of SO_2-containing dry gases. This calibration, shown in Figure 3, was double-checked by using gases directly from several cylinders containing known amounts of SO_2. It was found that CO_2 had a negligible effect on the analyzer readings (10 mole percent CO_2 was equivalent to about 10 ppm of SO_2), but that H_2O had a considerable effect on the readings. Figure 3 also shows a curve for analyzer reading versus H_2O composition in mole percent. The theoretical calibration curve for SO_2 in gas saturated with H_2O at 125°F was obtained by adding the analyzer reading for 13.2 mole percent H_2O (gas saturated at 125°F) to the analyzer readings for SO_2 in dry gas. However, it was determined that the effects of SO_2 and H_2O on the analyzer were not additive. Therefore, calibration curves had to be faired in for each run, as shown in Figure 3, based on analyzer readings for the inlet gas to the reactor, with and without the $SO_2/CO_2/N_2$ stream. That is, a zero reading was obtained from the saturated N_2/O_2 stream, and another point on the curve was obtained from the reading for the N_2/O_2 stream and the $SO_2/CO_2/N_2$ stream mixed together after correcting this stream to saturated conditions. The above two points were then used to fair in the curve.

The SO_2 analyzer readings, reactor pH, and H_2O_2 pH were recorded continuously on strip-chart recorders. An attempt was also made to monitor the calcium-ion concentration; however, difficulty was encountered with the calcium-ion electrodes because of the changing pH of the scrubbing liquor. Use of these electrodes was abandoned during the experiments. However, the calcium ion electrodes were used to determine the initial concentration of the scrubbing liquors, and two batches of these liquors were analyzed by atomic absorption as a check. Good agreement was obtained between the atomic absorption and calcium-ion electrode analyses.

FIGURE 3. CALIBRATION OF INFRARED ANALYZER FOR SO_2.



Results

Sixteen experiments were performed to study the SO_2 uptake by various scrubbing liquors. The simulated flue-gas compositions for the experiments are listed in Table 1, and the experimental parameters are summarized in Table 2. Runs A, B, and 2A were performed in addition to the runs listed in the original work statement and Runs 10 and 11 from this statement were not performed, in accordance with verbal agreements made with Mr. J. Phillips of NAPCA. Curves of SO_2 concentration versus time for the inlet gas to the reactor and the outlet gas from the reactor, and curves of pH versus time are shown for each run in Figures 4 through 19. All of the runs yielded essentially the same type of curve for the SO_2 concentration in the gas leaving the reactor, i.e., little or no SO_2 in the outlet gas until breakthrough time, at which time the SO_2 concentration began increasing and asymptotically approached a value close to the inlet value. Even when the scrubber liquor becomes saturated with SO_2, the SO_2 concentration in the outlet gas should be slightly lower than that in the inlet gas because of the added moisture picked up by the gas in passing through the reactor. It is fairly safe to assume that the gas leaving the reactor is saturated with H_2O and, thus, contains 13.2 mole percent H_2O. In most of the runs, the gas entering the reactor contained 7.06 mole percent H_2O. Calculated values for the SO_2 concentration in the outlet gas at liquor saturation are listed for each run in Table 2 on line 3. In the runs in which the outlet SO_2 concentration had leveled off, indicating that liquor saturation had occurred, there is good agreement between the experimental value and calculated value of SO_2 concentration in the outlet gas at liquor saturation. It is estimated that the SO_2 concentrations are accurate to within ±10% for all runs except A, B, 6, 7, 8, and 9 in which cases

TABLE 1. COMPOSITION OF SIMULATED FLUE GAS FOR SO_2 UPTAKE EXPERIMENTS (INLET GAS TO REACTOR)

Run No.	Concentration, mole percent					
	SO_2	N_2	O_2	CO_2	H_2O	NO_x
A	0.22	75.76	4.65	12.31	7.06	0.00
B	0.22	75.76	4.65	12.31	7.06	0.00
1	0.22	75.76	4.65	12.31	7.06	0.00
2	0.22	75.76	4.65	12.31	7.06	0.00
2A	0.22	75.76	4.65	12.31	7.06	0.00
3	0.22	75.76	4.65	12.31	7.06	0.00
4	0.22	75.76	4.65	12.31	7.06	0.00
5	0.22	75.76	4.65	12.31	7.06	0.00
6	0.22	75.76	4.65	12.31	7.06	0.00
7	0.22	75.76	4.65	12.31	7.06	0.00
8	0.26	73.31	4.65	14.68	7.06	0.046
9	0.25	73.31	4.65	14.68	7.06	0.046
12	0.089	77.09	7.03	5.08	10.71	0.00
13	0.044	77.62	7.87	2.49	11.98	0.00
14	0.00	77.00	4.65	11.29	7.06	0.00
15	0.25	88.04	4.65	0.00	7.06	0.00

TABLE 2. SUMMARY OF SO_2 UPTAKE EXPERIMENTS AT 125°F AND 1 ATMOSPHERE

	Run Number															
	A	B	1	2	2A	3	4	5	6	7	8	9	12	13	14	15
Inlet gas flow rate, cc/min at STP	10,760	10,760	1,076	1,076	1,076	1,076	1,076	1,076	1,076	1,076	1,076	1,120	1,136	1,136	1,076	1,076
SO_2 in inlet gas, ppm	2,200	2,200	2,200	2,200	2,200	2,200	2,200	2,200	2,200	2,200	2,500	2,500	890	440	0	2,500
SO_2 in outlet gas at liquor saturation[a], ppm	2,060	2,060	2,060	2,060	2,060	2,060	2,060	2,060	2,060	2,060	2,340	2,340	865	434	0	2,340
Impeller type[b]	TI	TI	TI	TI	GDT	TI	GDT	GDT	GDT	TI	GDT	GDT	GDT	GDT	GDT	GDT
Impeller speed, rpm	1,500	1,500	1,500	1,500	1,500	0	1,500	1,500	1,500	1,500	1,500	1,500	1,500	1,500	1,500	1,500
Scrubber liquor volume, cc	1,000	1,000	1,000	1,000	1,000	1,000	1,000	1,000	1,000	1,000	1,000	1,000	1,000	1,000	1,000	1,000
Scrubber liquor composition	1.43×10^{-3}M NaOH	Distilled H_2O	1.00×10^{-1}M NaOH	0.975×10^{-3}M NaOH	1.05×10^{-3}M NaOH	0.925×10^{-3}M NaOH	1.20×10^{-2}M calcium hydrate	6.06×10^{-3}M dolomitic hydrate	9.80×10^{-3}M calcium hydrate + 4.00 gm solid calcium hydrate	4.42×10^{-3}M dolomitic hydrate + 4.00 gm solid dolomitic hydrate	4.42×10^{-3}M calcium hydrate	6.85×10^{-3}M dolomitic hydrate	1.09×10^{-2}M calcium hydrate	1.02×10^{-2}M calcium hydrate	1.04×10^{-2}M calcium hydrate	1.03×10^{-2}M calcium hydrate
Experimental breakthrough time, min	<1	0	>180[c]	5	5	8	119	70	480	650	76	105	155	362	—	112
Calculated breakthrough time[d], min	0.81	0	566	5.51	5.94	5.24	136	68.6	722	841	43.8	67.8	290	542	—	102
Ratio: experimental/calculated	—	—	—	0.9	0.85	1.5	0.88	1.02	0.66	0.77	1.7	1.5	0.53	0.67	—	1.1
r, moles of reactant consumed per mole of SO_2 consumed	2	—	2	2	2	2	1	1	1	(e)	1	1	1	1	—	1

Footnotes appear on following page.

FOOTNOTES FOR TABLE 2

(a) Assuming reactor outlet gas is saturated with H_2O.

(b) TI = Teflon impeller; GDT = gas dispersion tube.

(c) Run was terminated at 180 min and no breakthrough had occurred.

(d) Based on simplified process model.

(e) r = 1 for dolomitic hydrate solution and r = 0.5 for solid dolomitic hydrate.

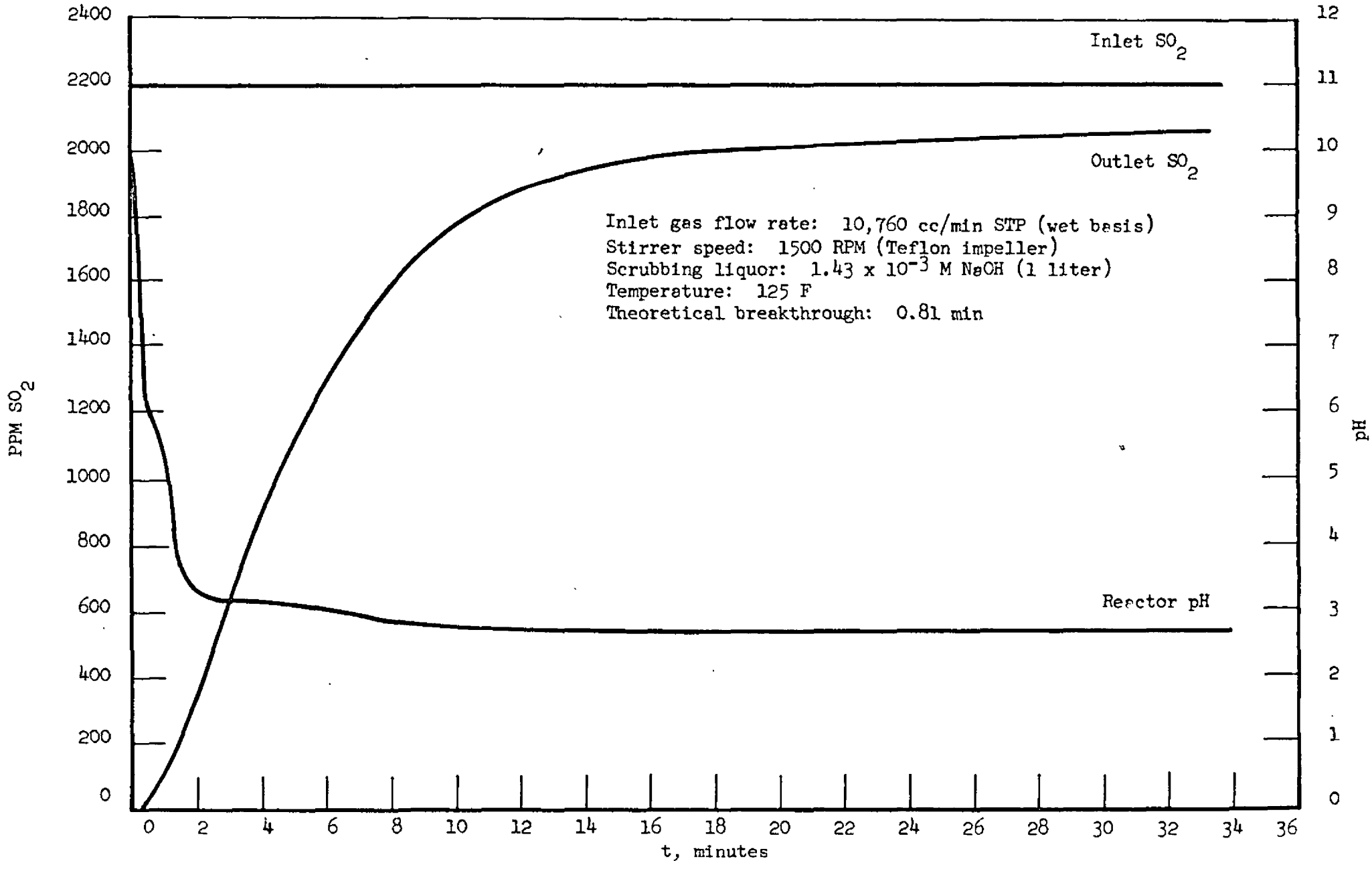


FIGURE 4. SO_2 UPTAKE, RUN A.

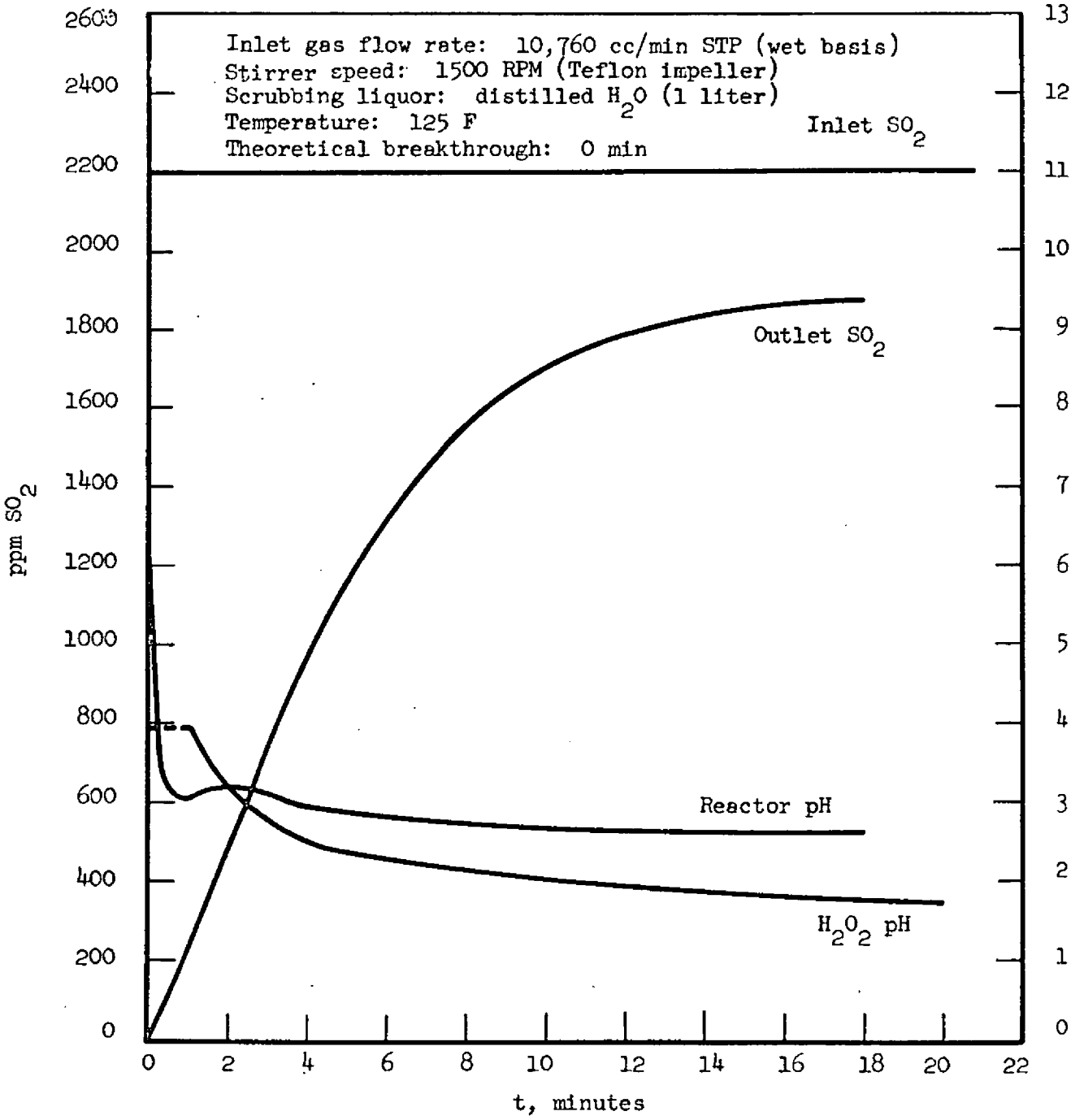


FIGURE 5. SO_2 UPTAKE, RUN B.

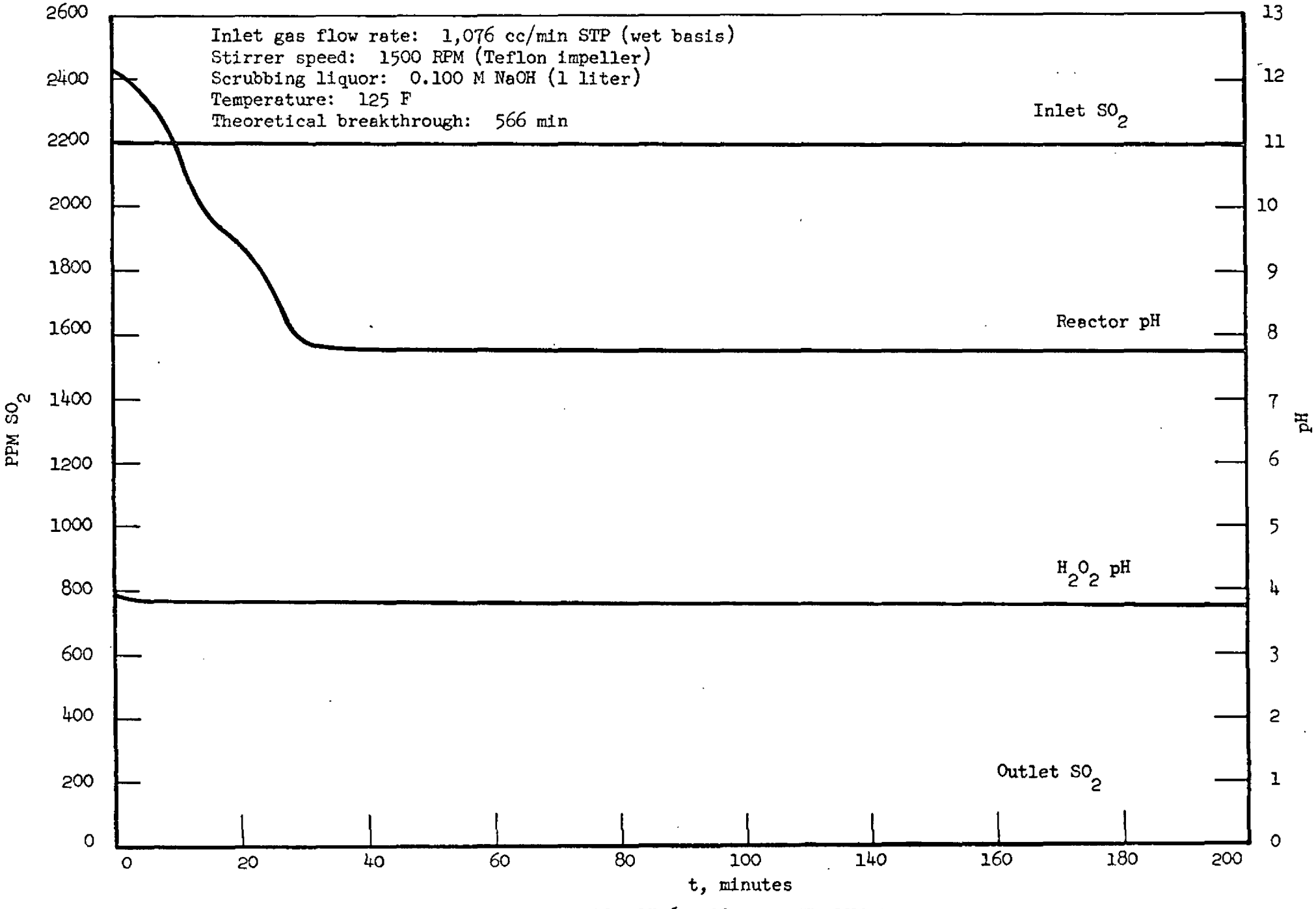


FIGURE 6. SO_2 UPTAKE, RUN 1.

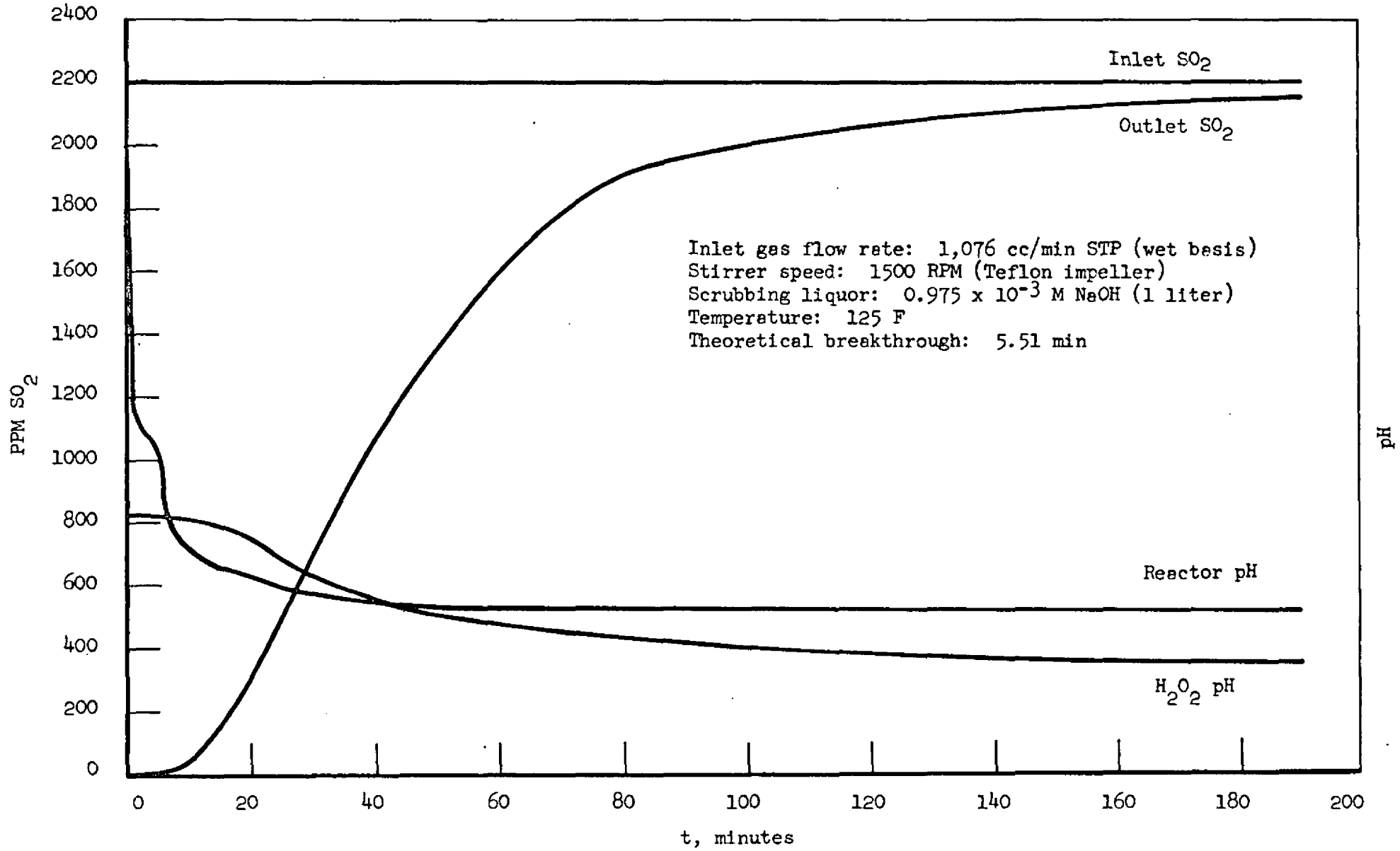


FIGURE 7. SO_2 UPTAKE, RUN 2.

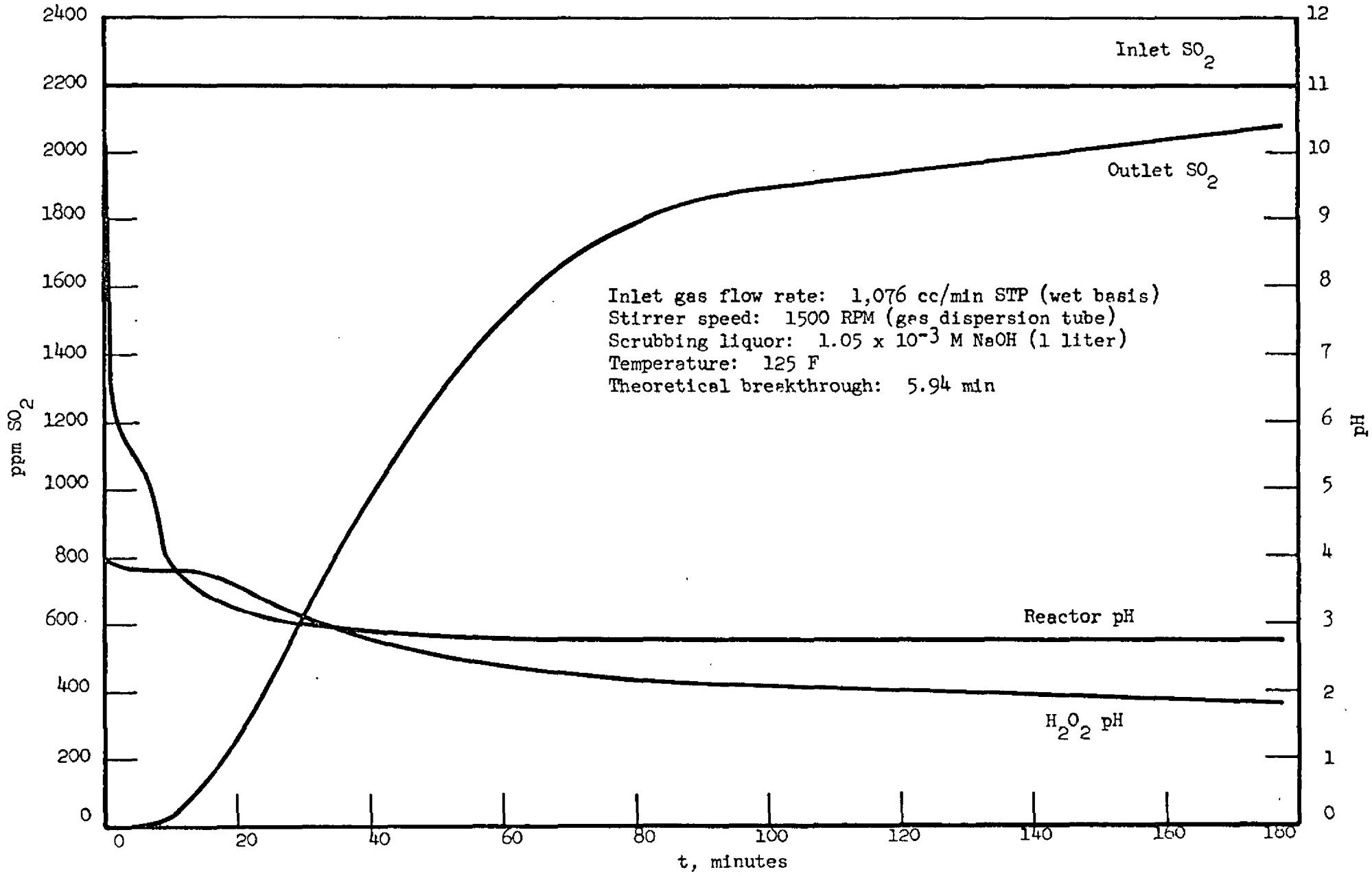


FIGURE 8. SO_2 UPTAKE, RUN 2A.

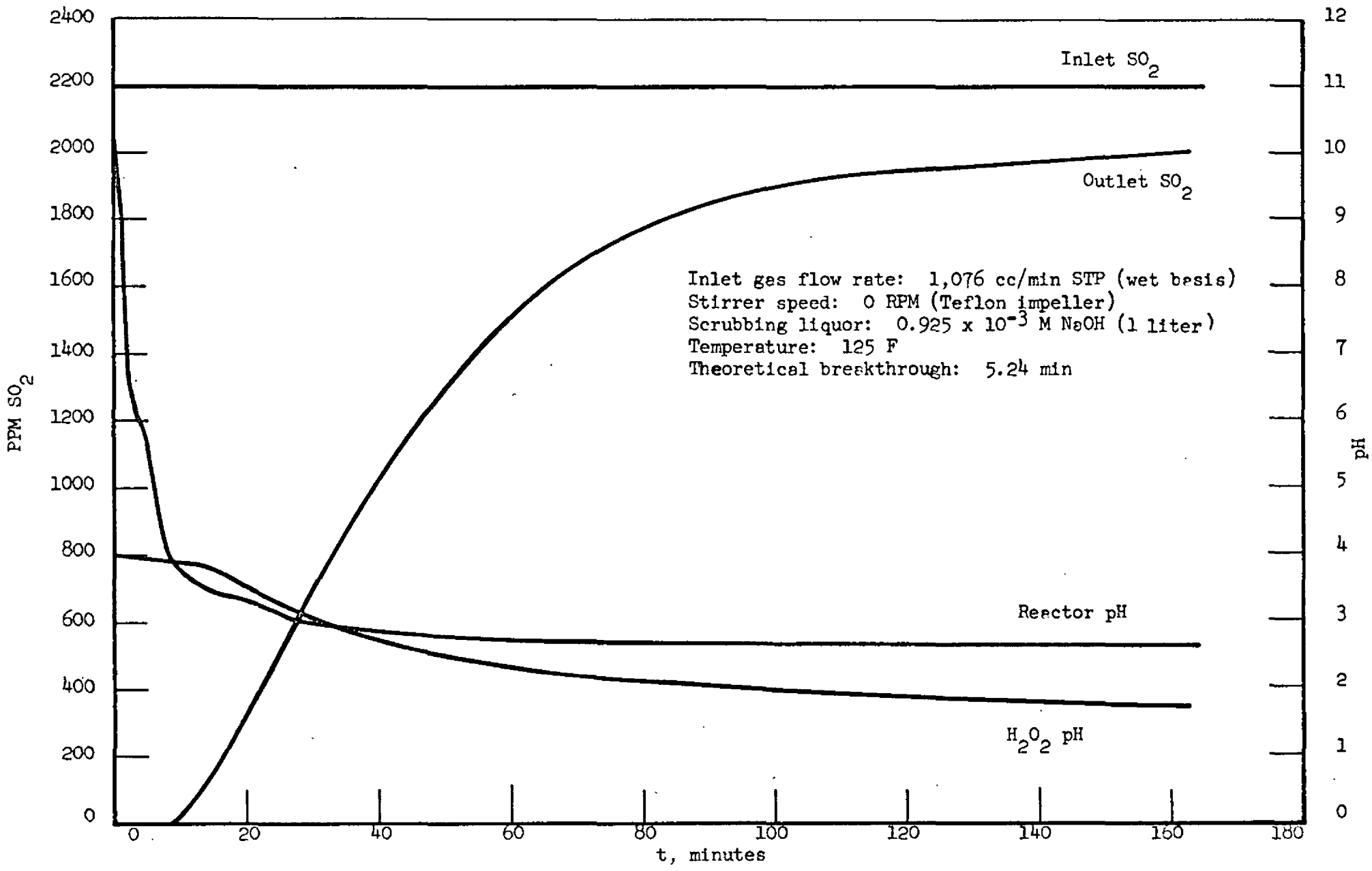


FIGURE 9. SO_2 UPTAKE, RUN 3

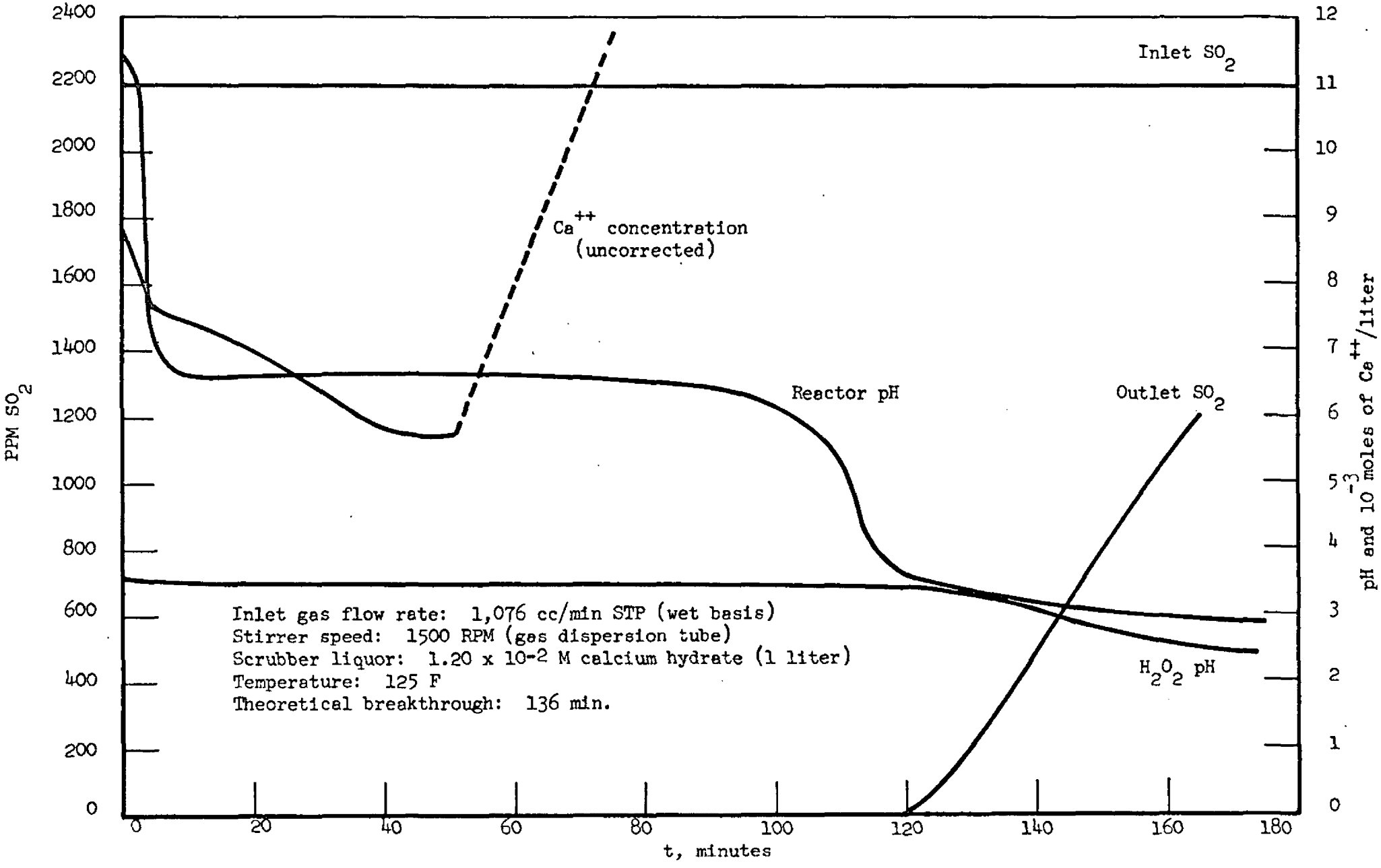


FIGURE 10. SO_2 UPTAKE, RUN 4.

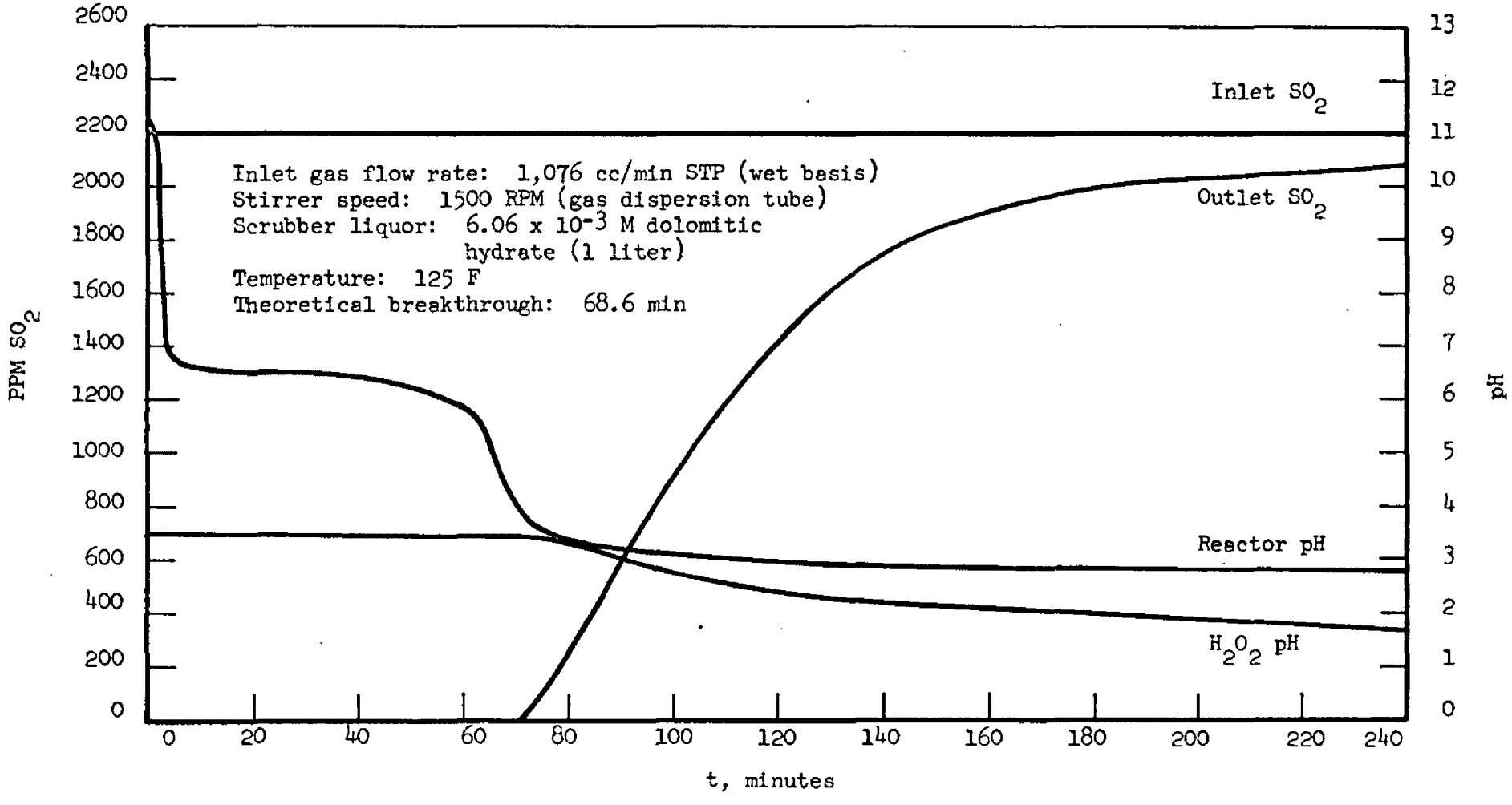


FIGURE 11. SO_2 UPTAKE, RUN 5.

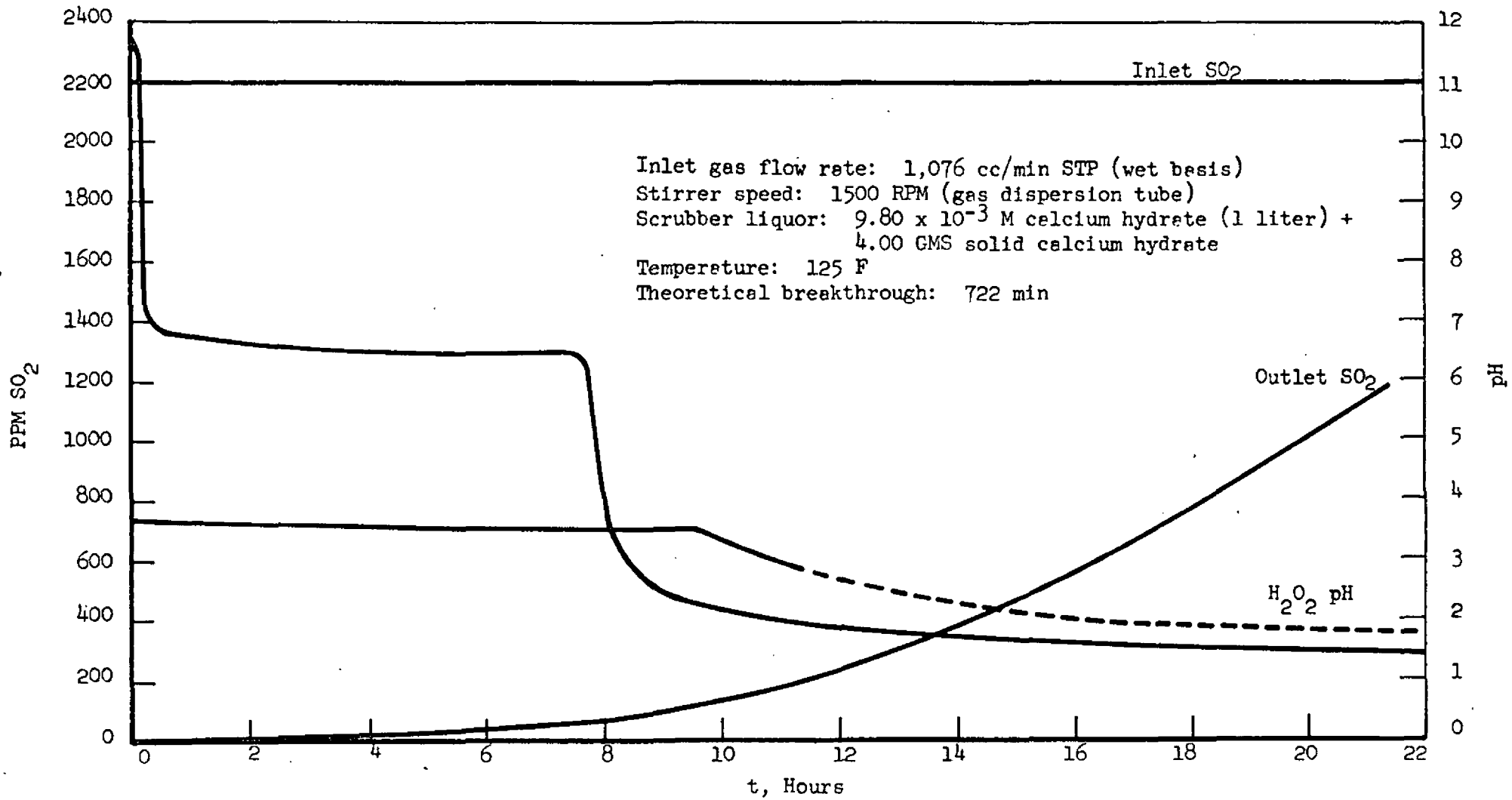


FIGURE 12. SO_2 UPTAKE, RUN 6

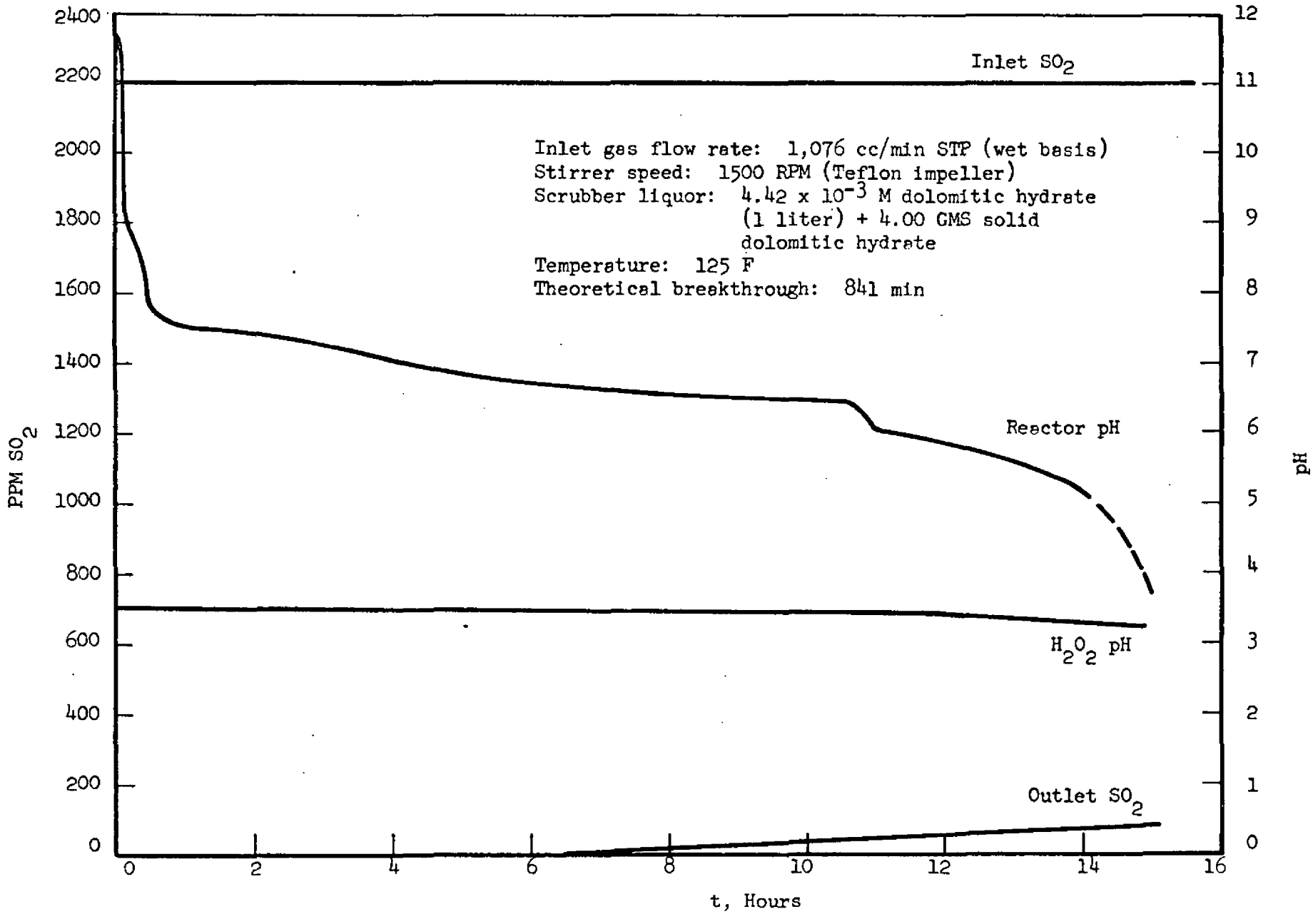


FIGURE 13. SO_2 UPTAKE, RUN 7.

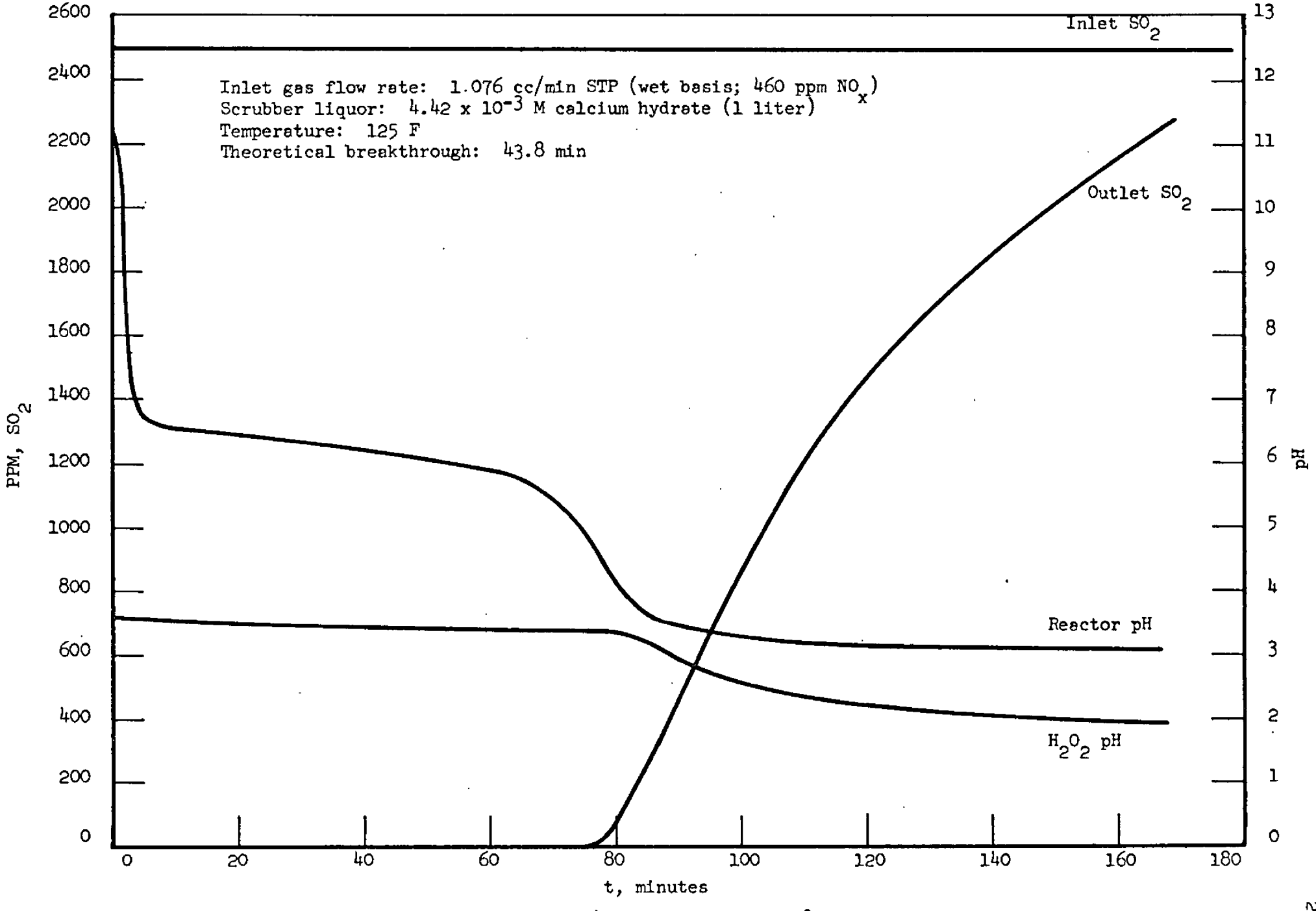


FIGURE 14. SO_2 UPTAKE, RUN 8

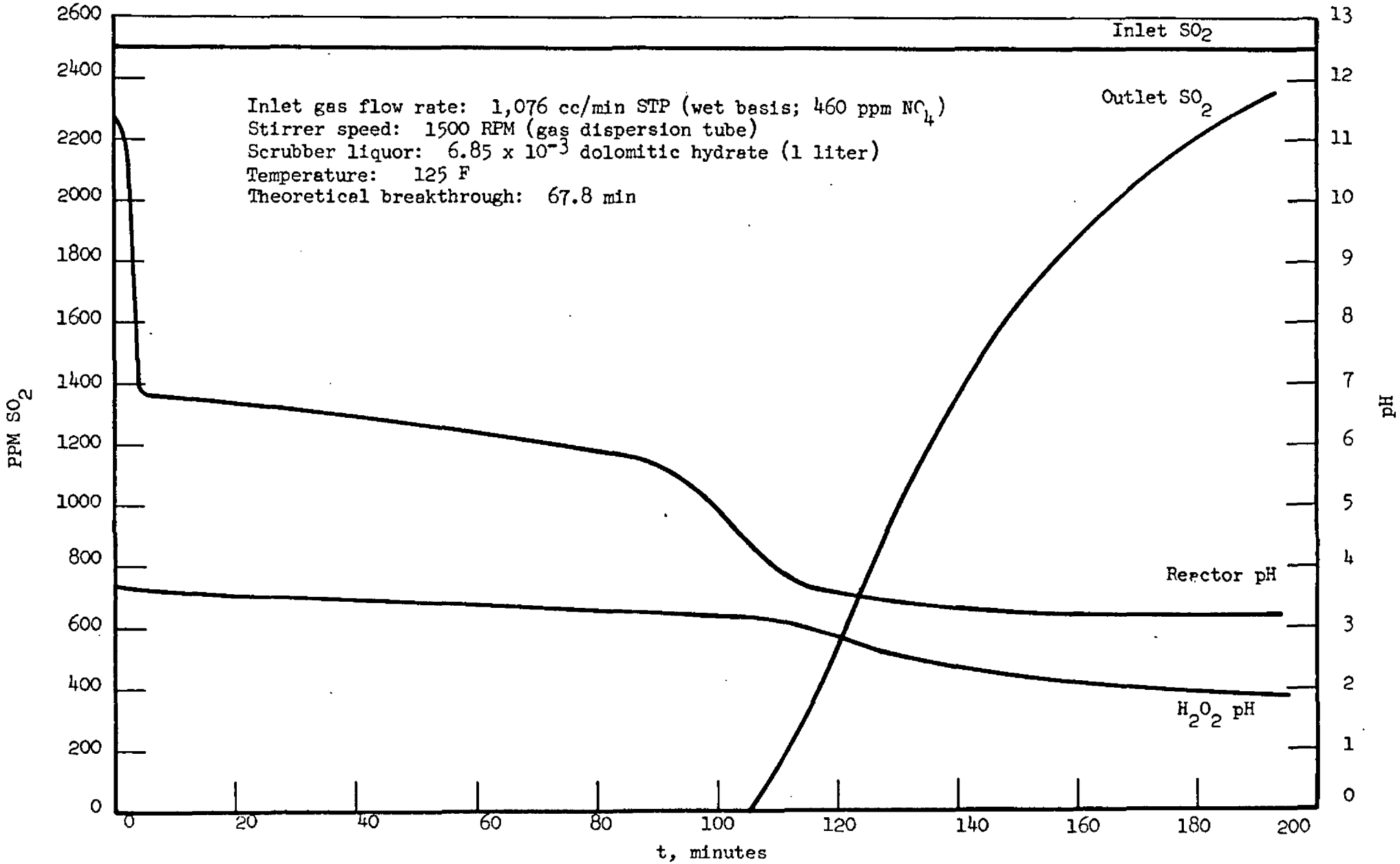


FIGURE 15. SO_2 UPTAKE, RUN 9.

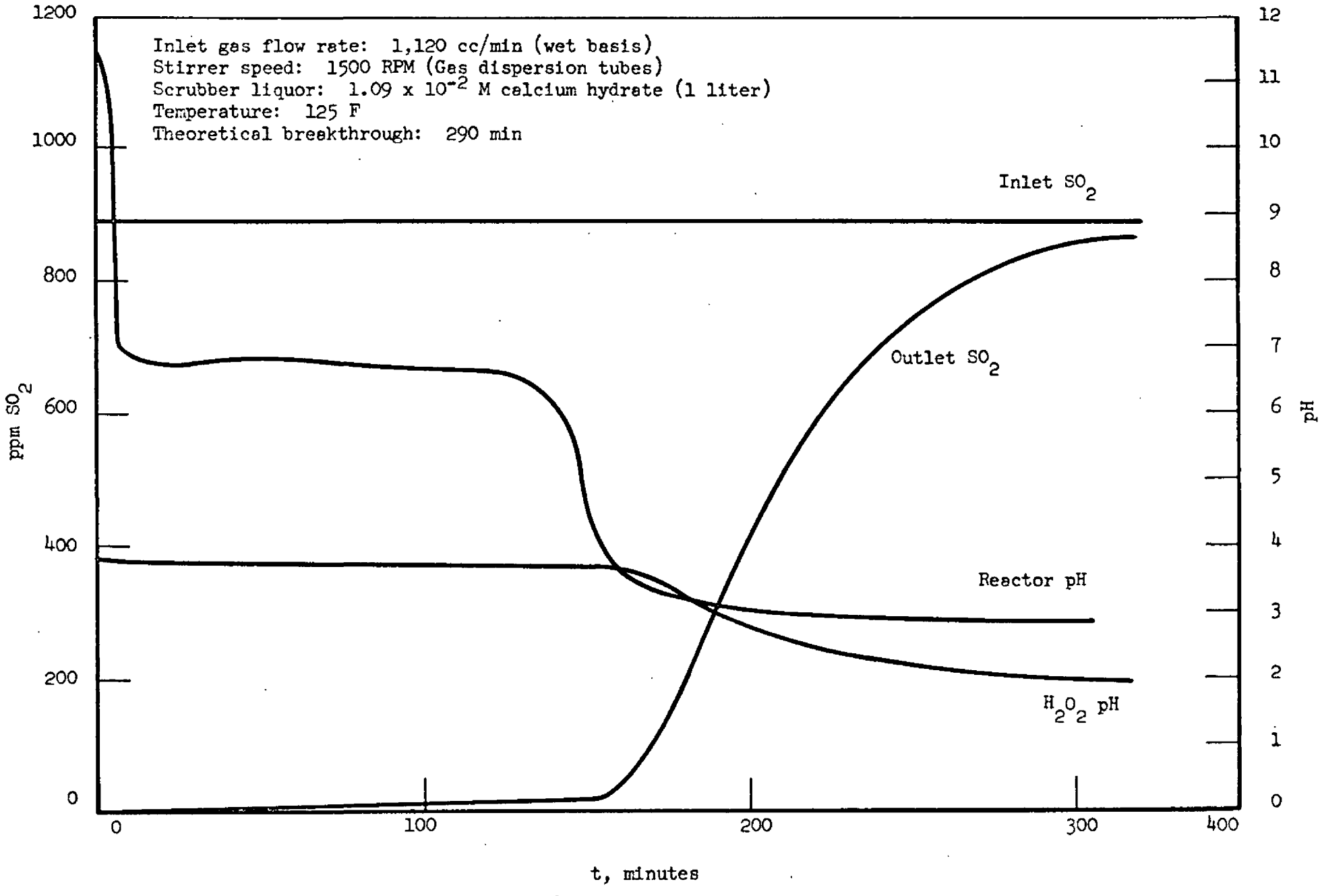


FIGURE 16. SO_2 UPTAKE, RUN 12.

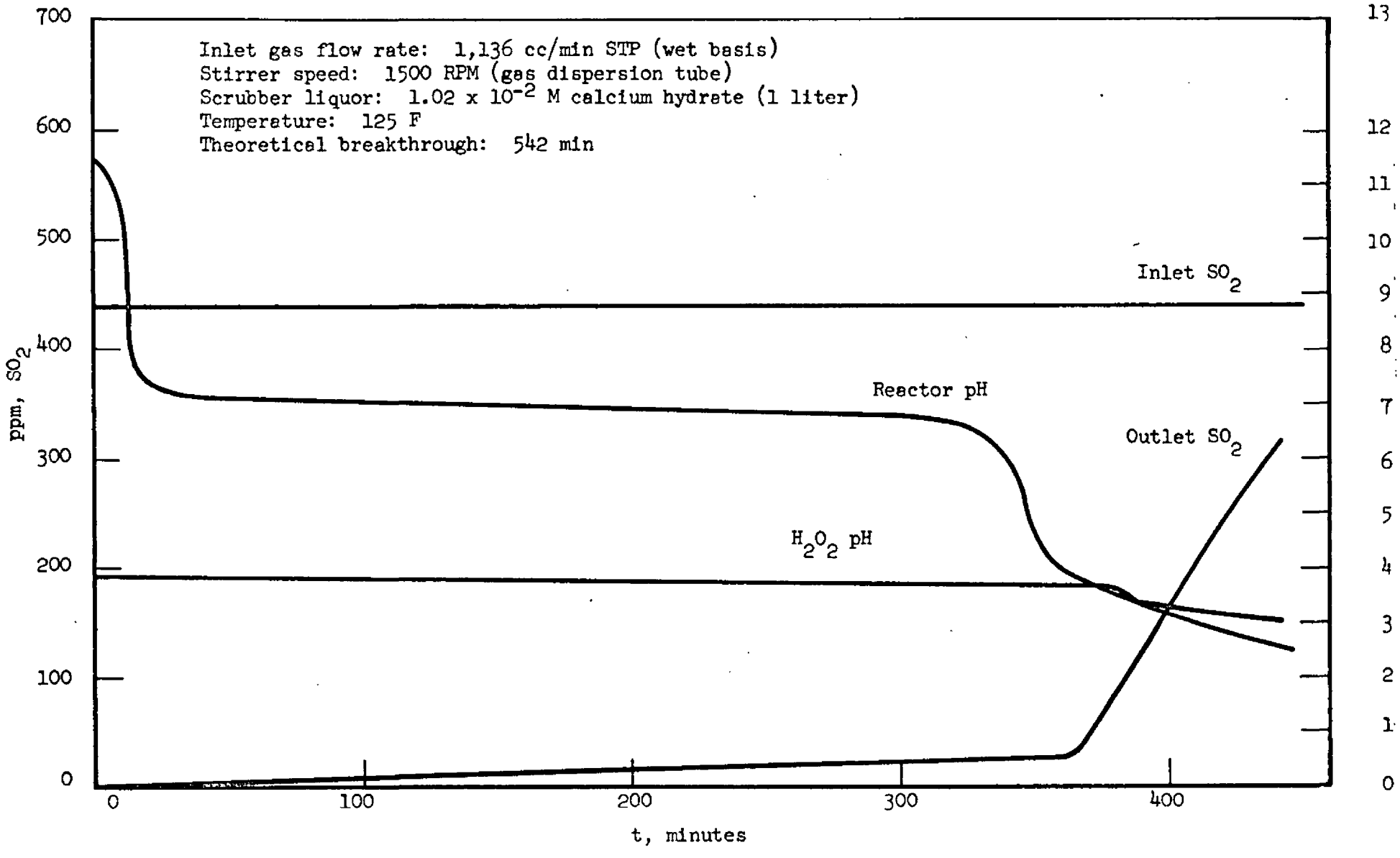


FIGURE 17. SO_2 UPTAKE, RUN 13.

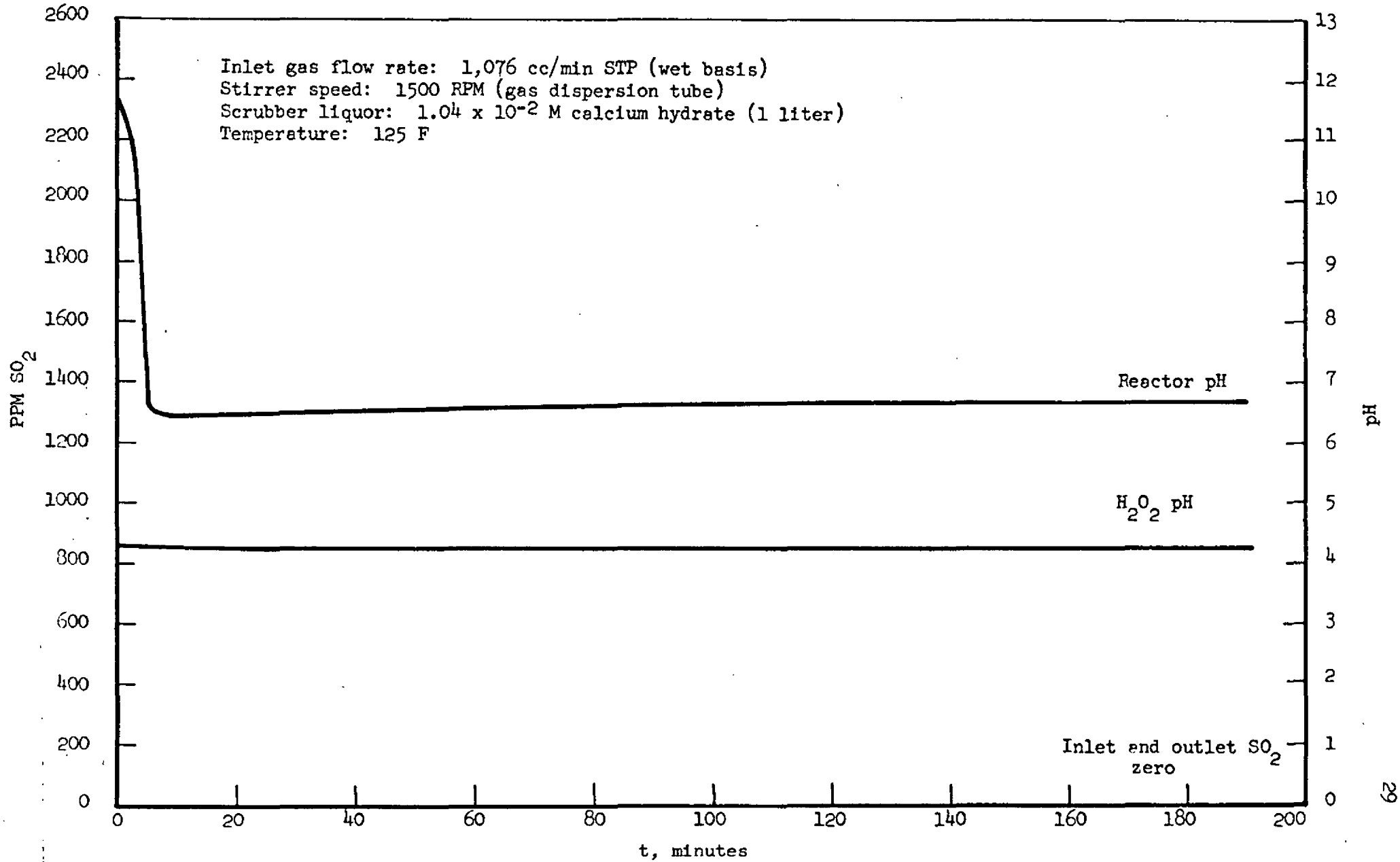


FIGURE 18. CO_2 UPTAKE, RUN 14.

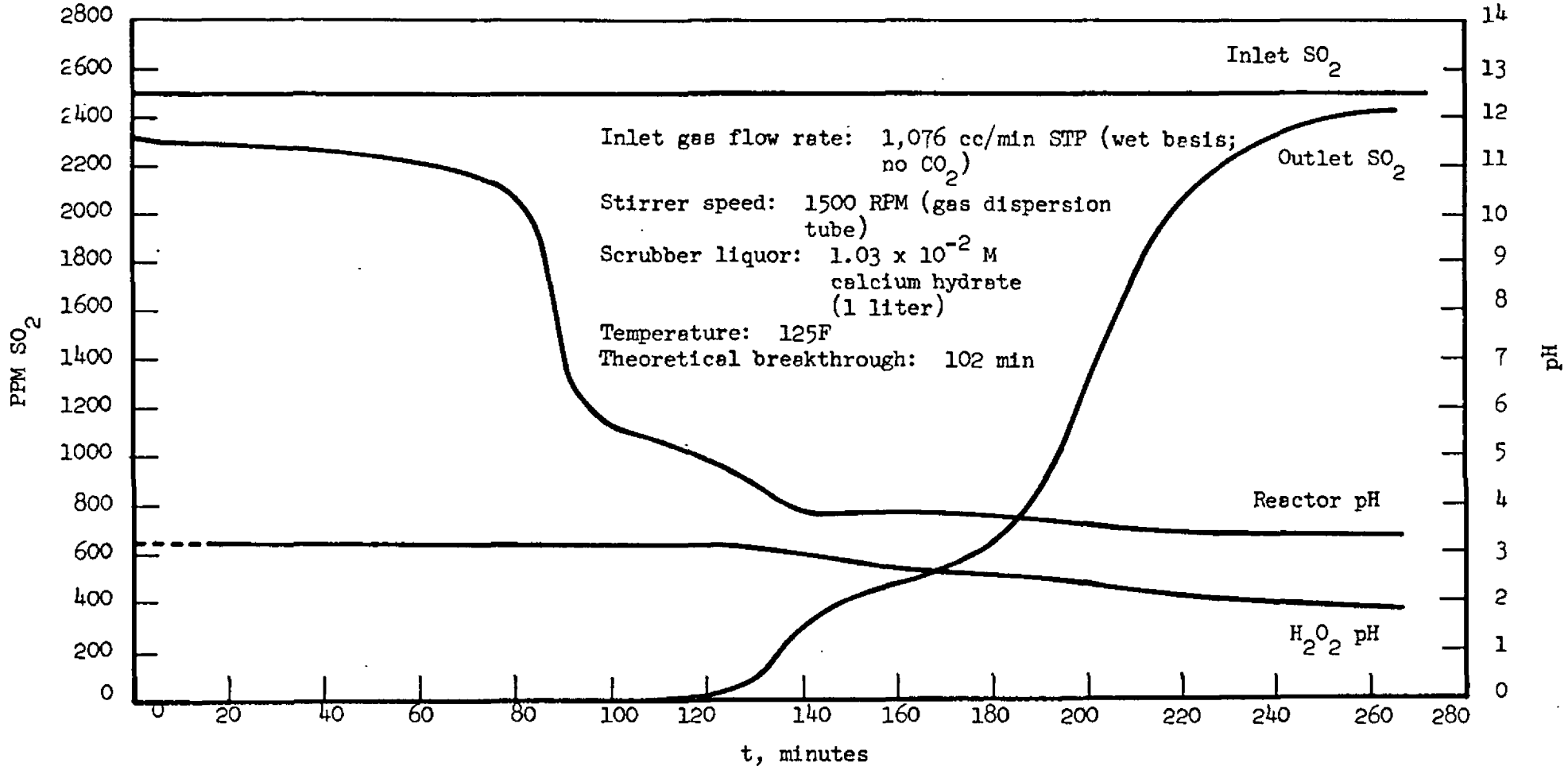


FIGURE 19. SO_2 UPTAKE, RUN 15.

the SO_2 concentrations are estimated to be accurate to ±20 percent. This latter error was caused by experimental difficulties which will be discussed later.

The breakthrough time for SO_2 was also reflected by a sharp decrease in the reactor pH and by decreasing pH in the H_2O_2 scrubber. In the simulated flue gas not containing NO_x, breakthrough of SO_2 occurred at a liquor pH in the range 3-4; with NO_x, the range was 4-5.

The scrubber liquors used in this study included distilled water, NaOH solutions, and lime solutions. The lime solutions were prepared by saturating H_2O with calcium hydrate* or dolomitic hydrate** in a well-stirred beaker for about 24 hours at 125°F and filtering out the excess solids. In the case of Run 8, the liquor was stirred for 66 hours prior to use. The lower calcium concentration of this liquor is probably due to reaction with CO_2 from the air, resulting in the precipitation of $CaCO_3$. Chemical analysis of the dolomitic solutions by atomic absorption revealed that there was no magnesium in solution, indicating that MgO does not readily hydrate and dissolve. Therefore, the dolomitic hydrate apparently was a mixture of $Ca(OH)_2$ and MgO in a 1:1 mole ratio; the mole ratio was calculated from the chemical analysis of the limestone material used to prepare the hydrate (see Appendix). Thus, the only scrubbing liquor that contained magnesium was the one in Run 7, for which 4 grams of solid dolomite hydrate was added to the reactor just before start of the run.

Some of the chemical reactions that can occur between the flue gas and the various scrubber liquors can be represented as follows:

---

* Supplier's notation for hydrated high-calcium lime.

** Supplier's notation for hydrated lime derived from dolomitic limestone.

$$SO_2 + H_2O = H_2SO_3 \quad (1)$$

$$NaOH + H_2SO_3 = NaHSO_3 + H_2O \quad (2)$$

$$2NaOH + H_2SO_3 = Na_2SO_3 + 2H_2O \quad (3)$$

$$Ca(OH)_2 + H_2SO_3 = CaSO_3 + 2H_2O \quad (4)$$

$$Ca(OH)_2 + CO_2 = CaCO_3 + H_2O \quad (5)$$

$$CaCO_3 + H_2SO_3 = CaSO_3 + H_2O + CO_2 \quad (6)$$

$$MgO + H_2SO_3 = MgSO_3 + H_2O \quad (7)$$

$$MgO + CO_2 = MgCO_3 \quad (8)$$

$$MgCO_3 + H_2SO_3 = MgSO_3 + H_2O + CO_2 \quad (9)$$

Reactions involving NO_x complicated further an already complex situation in Runs 8 and 9, where this component was present. In Run 14, the absence of SO_2 eliminated reactions (1), (4), and (6), and in Run 15, the absence of CO_2 eliminated reactions (5) and (6). Reactions (7), (8), and (9) are applicable only in Run 7.

It is postulated that the time until breakthrough of SO_2 in the outlet gas represents the time until exhaustion of reactant in the scrubber liquor, and that the increasing segment of the SO_2-concentration curve represents the effect of mass transfer on the dissolution of SO_2 in the liquor. The theoretical breakthrough time can be calculated from the following equation:

$$t_B = \frac{M^o}{qC^o\ r} \quad (10)$$

where

t_B = theoretical breakthrough time, min

M^o = initial amount of reactant in scrubber liquor, moles

q = inlet gas flow rate, cm^3 per min

C^o = concentration of SO_2 in inlet gas, moles per cm^3

r = moles of reactant consumed per mole of SO_2 consumed.

The term r can best be understood by comparing reactions (2) and (3). In reaction (2) r has a value of 1 and the reaction product is $NaHSO_3$, while in reaction (3) r has a value of 2 and the reaction product in Na_2SO_3. Theoretical break-through times were calculated for each run by using the value for r appropriate to the sulfite rather than the bisulfite reaction product (r = 1 and 2, respectively, for $Ca(OH)_2$, and NaOH solutions). It is recognized that continued sorption after the breakthrough point probably involves formation of bisulfite, but the effect of this reaction on the equilibrium partial pressure of SO_2 was not explicitly considered. In the case of Runs 6 and 7, where solid lime was added to the scrubber liquor, the breakthrough times were calculated by assuming that all of the solid material would eventually dissolve. Experimental breakthrough times were obtained from the curves of SO_2 concentration in the outlet gas versus time and are compared with the theoretical breakthrough times in Table 2. In some cases the agreement is within experimental error and in other cases the agreement is poor; the breakthrough time comparison is discussed for each run in the following paragraphs.

Runs A and B were performed at a gas flow rate of 10 liters per minute, with 10^{-3} M NaOH and distilled water, respectively, as scrubbing liquors. Difficulties were encountered in interpreting the data from the SO_2 analyzer because of

excessive pressure drop needed for the high flow rate. Consequently, all other runs were performed at a flow rate of 1 liter per minute. In Run A, it was impossible to determine the experimental breakthrough time accurately, but it was less than one minute. This compared favorably with the theoretical breakthrough time of 0.81 min. Except for the slight break in the curve at the start of Run A, Runs A and B exhibited the same shape of curve for SO_2 concentration, indicating that, once the NaOH reactant is exhausted, the scrubber liquor behaves the same as distilled water at this low concentration of reaction product.

Runs 1, 2, 2A, and 3 were performed with NaOH solutions as the scrubbing liquor. The concentration in Run 1 was 10^{-1} M while in the other runs it was 10^{-3} M. The theoretical breakthrough time for Run 1 is 566 min and, since the run proceeded for only 180 min, no breakthrough would be expected to occur, as indeed was the case. In Runs 2 and 2A, the experimental and theoretical breakthrough times agreed very well, indicating that the reaction product was indeed Na_2SO_3. In Run 2A, a gas dispersion tube, resulting in somewhat smaller gas bubbles, was used for stirring, rather than the Teflon impeller. The SO_2 concentration curves were about the same for both runs, indicating that the mass transfer rate is not a strong function of bubble size. In Run 3, the Teflon impeller was used but the stirring motor was not turned on; however, the SO_2 concentration curve was still about the same as in Run 2, for which the stirring speed was 1500 rpm. This observation was taken to indicate negligible resistance to mass transfer in the liquid phase. In Run 3, the experimental breakthrough time was greater than the theoretical breakthrough time, possibly indicating the formation of some $NaHSO_3$.

Runs 4 and 5 were performed with saturated solutions of calcium hydrate and dolomitic hydrate, respectively, as the scrubbing liquors. There was very good agreement between the experimental and theoretical breakthrough times for both of these runs. The calcium ion electrode was used in Run 4, in an attempt to monitor the Ca^{++} concentration continuously. However, as the pH of the liquor decreased, the calcium ion electrode output became erratic and increased rapidly, thus negating its usefulness.

Runs 6 and 7 were duplicates of Runs 4 and 5, except that 4.00 gms of calcium hydrate or dolomitic hydrate was added to the respective liquors immediately prior to the start of each run. Difficulty was encountered because of pressure buildup caused by clogging of the gas dispersion tube in Run 6, so that the Teflon impeller was used in Run 7. However, even the relatively large holes (1/16-in diameter) in the Teflon became clogged with solid material during the course of the run, and the run had to be terminated because of excessive pressure buildup in the system. At the conclusion of Runs 6 and 7, both liquors contained a solid crystalline material that was grossly different in appearance from the solid hydrates that were added to the liquors. The crystalline materials were not analyzed, but it is assumed that they are $CaSO_3$ and $MgSO_3$. The experimental breakthrough times in both runs were significantly lower than the theoretical times, indicating that the crystalline material may have deposited around some of the solid hydrate particles, thus preventing their further reaction with SO_2. Also, the presence of solid particles added another resistance to the reaction mechanism in the form of finite rate of dissolution of the hydrates. This added resistance was not accounted for theoretically. However, the breakthrough times were only about 30 percent lower than expected.

Runs 8 and 9 were also duplicates of Runs 4 and 5, except that 450 ppm of NO_x was present in the flue gas. The presence of NO_x caused the infrared-analyzer readings to drift upward with time and, consequently, made it more difficult to interpret the results. However, the experimental breakthrough times were 50 to 70 percent longer than the theoretical times.

Runs 12, 13, and 14 were similar to Run 4, except that the SO_2 concentration in the inlet gas was lowered to 890, 440, and 0 ppm, respectively, from the 2,200 ppm in Run 4. The CO_2 concentration was decreased and the H_2O concentration was increased in the simulated flue gas for Runs 12 and 13 because of limitations in the cylinder gases available. The experimental breakthrough times were about 40 percent lower than the theoretical times in Runs 12 and 13. Probable experimental error can account for only about a 25 percent difference. At first glance it appears that the lower CO_2 concentration might offer an explanation for the discrepancy. However, in Run 15, in which no CO_2 was present, there was excellent agreement between the experimental and theoretical breakthrough times. Therefore, it is difficult to explain the discrepancy between the breakthrough times for Runs 12 and 13, especially in light of the results from the other runs. The reactor pH-versus-time curve for Run 14, in which no SO_2 was present, indicates rapid formation of $CaCO_3$, followed by attainment of the carbonate equilibrium at a pH of about 6.6.

The absence of CO_2 in Run 15 had a significant effect on the shape of the outlet SO_2 concentration curve. Soon after breakthrough, the curve tended to level off at about 500 ppm of SO_2 at a pH of 3.8 and then began increasing and asymptotically approached a value close to the inlet concentration.

Analytical Model for the Wet Lime-SO_2 Scrubbing Process

An attempt has been made to fit the data to an analytical model based on chemical reaction followed by dissolution controlled by gas-phase mass transfer. The model is only a first attempt at an analytical description of these experiments. For simplicity, it was assumed that the chemical-reaction and mass-transfer aspects of this problem can be uncoupled and treated independently. The chemical-reaction portion of the model has already been discussed in terms of experimental and theoretical breakthrough times for SO_2 concentration in the gas leaving the scrubber. The increasing portion of the SO_2 concentration curve has been treated in terms of a gas-phase resistance to mass transfer present in a thin film at the surface of each gas bubble passing through the scrubber liquor. A material balance for SO_2 in the scrubber liquor in the reactor leads to the following equation:

$$\frac{dC_1}{dt} + K\,C_1 = \frac{K}{H}\,C_g \qquad (11)$$

where

C_1 = unreacted SO_2 concentration in scrubber liquor, moles per liter

C_g = SO_2 concentration in outlet gas, moles per liter of dry gas

H = Henry's law partition coefficient at liquor saturation with SO_2, C_g^o/C_1^o

C_g^o = SO_2 concentration in outlet gas at liquor saturation with SO_2, moles per liter of dry gas

C_1^o = unreacted SO_2 concentration in scrubber liquor at liquor saturation with SO_2, moles per liter

t = time, min

K = system constant having units of min^{-1} defined by

$$K = \frac{6\ k_g\ q\ L\ H}{v\ d\ V_1} \tag{12}$$

where

k_g = gas-phase mass transfer coefficient, cm per min

q = gas flow rate, cm^3 of dry gas per min

L = average path length traveled by a gas bubble in the liquor, cm

v = average velocity of gas bubble, cm per min

d = average diameter of a gas bubble, cm

V_1 = volume of liquor, cm^3.

A material balance for SO_2 over the entire system yields

$$q\ C_g^o = q\ C_g + V_1 \frac{d\ C_1}{dt} \tag{13}$$

where

C_g^o = SO_2 concentration in inlet gas (equal to the previous C_g^o) moles per liter of dry gas.

From the definition of the breakthrough time,

$$C_g\ (t = t_B) = 0 \tag{14}$$

so that, at $t = t_B$, Equation (13) becomes

$$\left.\frac{d\ C_1}{dt}\right|_{t=t_B} = \frac{q\ C_g^o}{V_1} \tag{15}$$

Equations (11) and (13) can be solved simultaneously for C_l and C_g yielding

$$C_l = \frac{C_g^o}{H} - \frac{q\, C_g^o}{\alpha\, V_l}\, \epsilon^{\alpha(t-t_B)} \quad (t \geq t_B) \tag{16}$$

and

$$C_g = C_g^o\, [1 - \epsilon^{-\alpha(t-t_B)}] \quad (t \geq t_B) \tag{17}$$

where

$$\alpha = \frac{K}{1 + \frac{K\, V_l}{q\, H}}\,. \tag{18}$$

From Equation (17)

$$\ln\left(1 - \frac{C_g}{C_g^o}\right) = -\,\alpha(t-t_B). \tag{19}$$

Therefore, a plot of $\ln\left(1 - \frac{C_g}{C_g^o}\right)$ versus $(t-t_B)$ should yield a straight line with a slope equal to $-\,\alpha$. A comparison of the experimental data with the analytical model is shown in Figure 20 for Runs 2A and 5. Considering the assumptions involved, such as constant bubble diameter and constant residence time for the bubbles in the liquor, the agreement between experiment and theory is good. It is interesting to note the similarity between the data for Runs 2A and 5. The experimental parameters are the same for these runs, but different scrubbing liquors were used (0.975×10^{-3} M NaOH in Run 2A and 6.06×10^{-3} M dolomitic hydrate in Run 5), resulting in different breakthrough times. However, as far as the dissolution portion of the model is concerned, the only difference between the runs would be different partition coefficient (H) for 10^{-3} M Na_2SO_3 and 6×10^{-3} M $CaSO_3$. Evidently, at these low concentrations, the partition coefficients are about the same, and about equal to that for distilled water.

The value of α for Runs 2A and 5 is approximately 2.76×10^{-2} min^{-1} as obtained from the slope of the line in Figure 20. This value of α, together

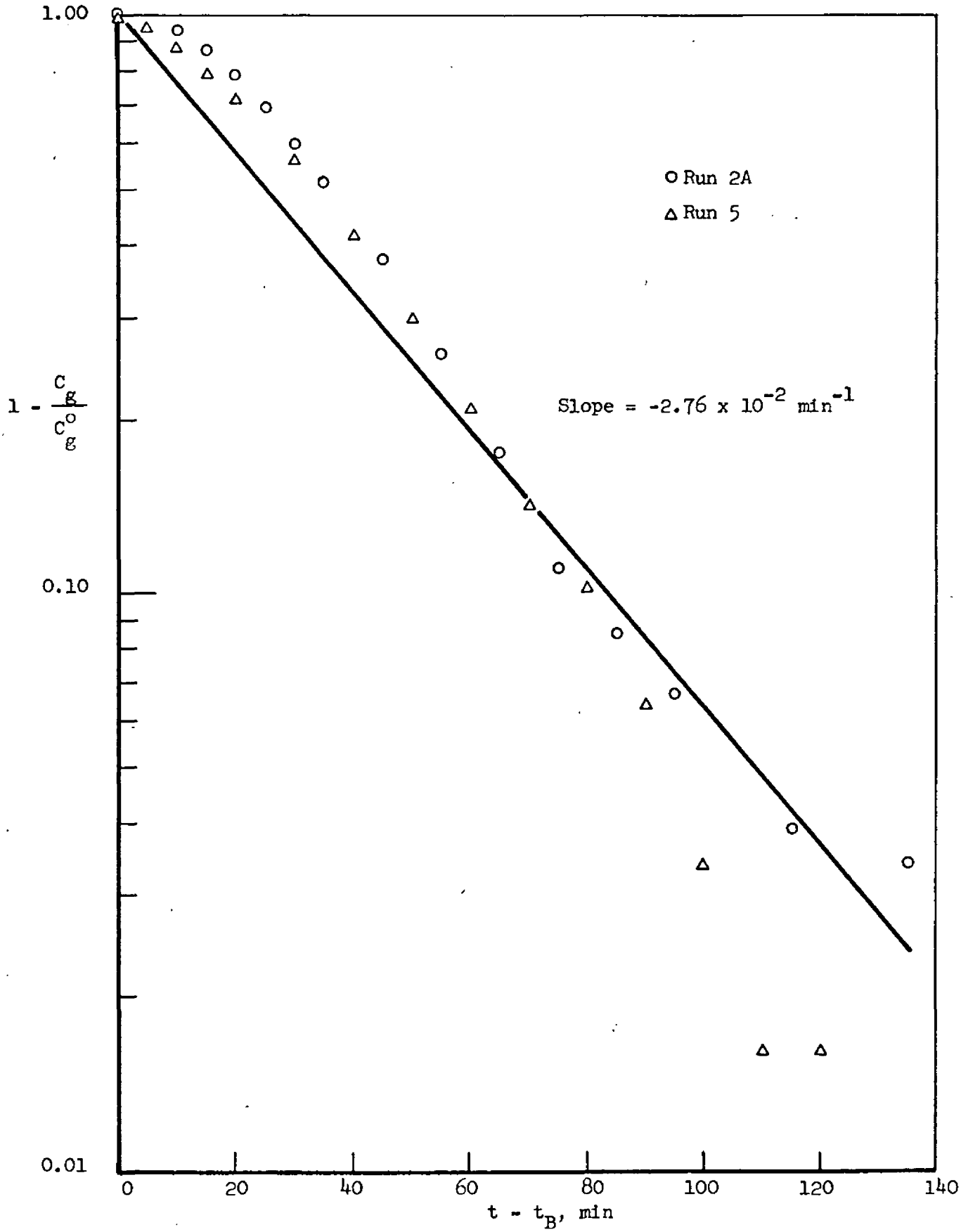


FIGURE 20. COMPARISON OF EXPERIMENTAL DATA WITH ANALYTICAL MODEL FOR SO_2 UPTAKE BY SCRUBBING LIQUORS.

with the calculated theoretical breakthrough time of 68.6 min and C_g^o of 2370 ppm of SO_2 on a dry basis, was used to construct the curve of SO_2 concentration in the outlet gas versus time for Run 5 in accordance with Equation (17). A comparison of the experimental data with the calculated curve is shown in Figure 21; the agreement is very good, considering the simplified analytical model used.

It is possible to calculate partition coefficients (H) for each run by graphically integrating the SO_2 concentration curves. Once values of α and H are known, one can calculate K from Equation (18) and, ultimately, the gas-phase mass-transfer coefficient (k_g) from Equation (12) if the average bubble diameter and average residence time for the bubbles in the scrubbing liquor are known. This was not done insofar as such an analysis did not fall within the scope of this work. It must be realized that the parameters in the analytical model are highly dependent on the scrubber design, and that values derived from the current work are not necessarily applicable to other types of scrubbers.

Hydration of Burnt Lime

Apparatus and Procedure

The rates of hydration of burnt limes were determined using apparatus similar to that prescribed for ASTM Test C-110. A sample charge containing one mole of calcium oxide was added to one liter of water (or other appropriate liquor as specified by the Contract) at 125°F in a well-stirred and well-insulated system and the rate of temperature rise in the system was monitored with a thermocouple connected to a recorder. During these runs, solution pH was also monitored.

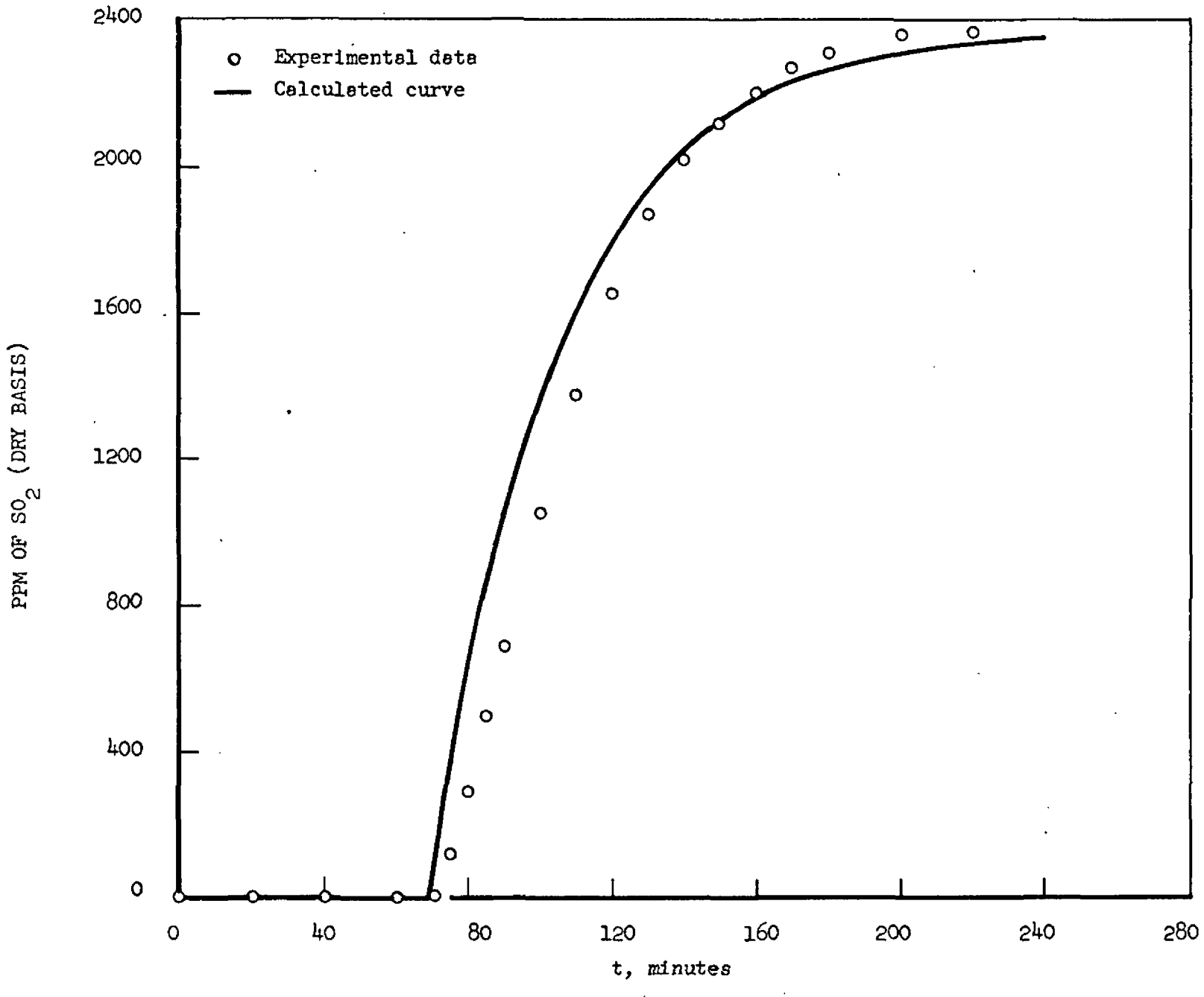


FIGURE 21. COMPARISON OF EXPERIMENTAL DATA WITH CALCULATED CURVE FOR SO_2 CONCENTRATION IN THE OUTLET GAS VS. TIME.

The experimental temperature-rise data were corrected for thermal loss by the system to obtain the true temperature change due to hydration. It was assumed that the thermal loss rate of the system could be represented as

$$\frac{dT}{dt} = -k\,(T_e - T_o)$$

where T_e is the experimentally observed system temperature, T_o is the temperature of an arbitrary heat sink in the system, and k is a constant which includes the heat capacity of the solution, the thermal conductivity of the system walls, geometry of the system, etc. Values of k and T_o were found by determining the thermal loss rate in the absence of hydration reaction at two different values of T_e, and solving the above equation. The corrected temperature change in the system was then calculated as the sum of the observed temperature rise and a correction for thermal loss:

$$\Delta T_c = \Delta T_e + k \int_t (T_e - T_o)dt$$

$$= \Delta T_e + k \sum_i (T_{ei} - T_o)\,\Delta t_i,$$

where the summation is taken over sufficiently small time intervals to keep the effects of local curvature in the temperature-rise curve to a negligible level. In practice, it was found that T_o did not remain constant during a run. The error resulting from this procedure was considered insignificant for runs requiring less than 1 to 1-1/2 hours for completion, but for runs lasting for longer periods of time the error became comparable with observed temperature changes. Therefore, an arbitrary time limit of 83 min (5000 sec) was set for duration of hydration experiments.

All of the samples used in the hydration experiments were supplied by NAPCA. These included limes derived from calcitic and dolomitic limestones which

were prepared with an array of particle sizes and calcination temperatures. The notation used to designate samples is that used in the work statement of the contract: L_{13} is the calcitic lime sample calcined at the lowest temperature and having the largest particle size, and D_{31} is the dolomitic lime calcined at the highest temperature and having the smallest particle size. A listing of specific particle sizes and calcination temperatures is given in Table A-1 of the Appendix. Analyses of the original limestones are given in Table A-2 of the Appendix.

Results

Curves showing the observed temperature rise versus time for the various samples investigated are shown in Figures 22 through 31. For both L_{33} and D_{33} there was very little apparent difference between hydration in tap water and hydration in saturated lime water. However, with partially sulfated L_{33} (Fig. 31), hydration in lime water was severely limited, giving a temperature rise of only 0.7°F in the first 300 seconds. Hydration runs were also performed using L_{33} and D_{33} and a liquid phase consisting of a saturated Ca,Mg - SO_3,SO_4 liquor (Fig. 30). With these runs there was a rapid initial temperature rise of about 5°F followed by extremely slow increase over a period of several hours. As with the partially sulfated lime, the rate was too slow to be defined. Presumably the initial temperature rise was due to reaction of the sulfite-sulfate liquor with the lime. The reaction product probably coated the lime particles and prevented hydration. In fact, there was a strong tendency for agglomeration of the reacted lime, with resultant formation of large clumps (up to 1 cm in diameter) of solids.

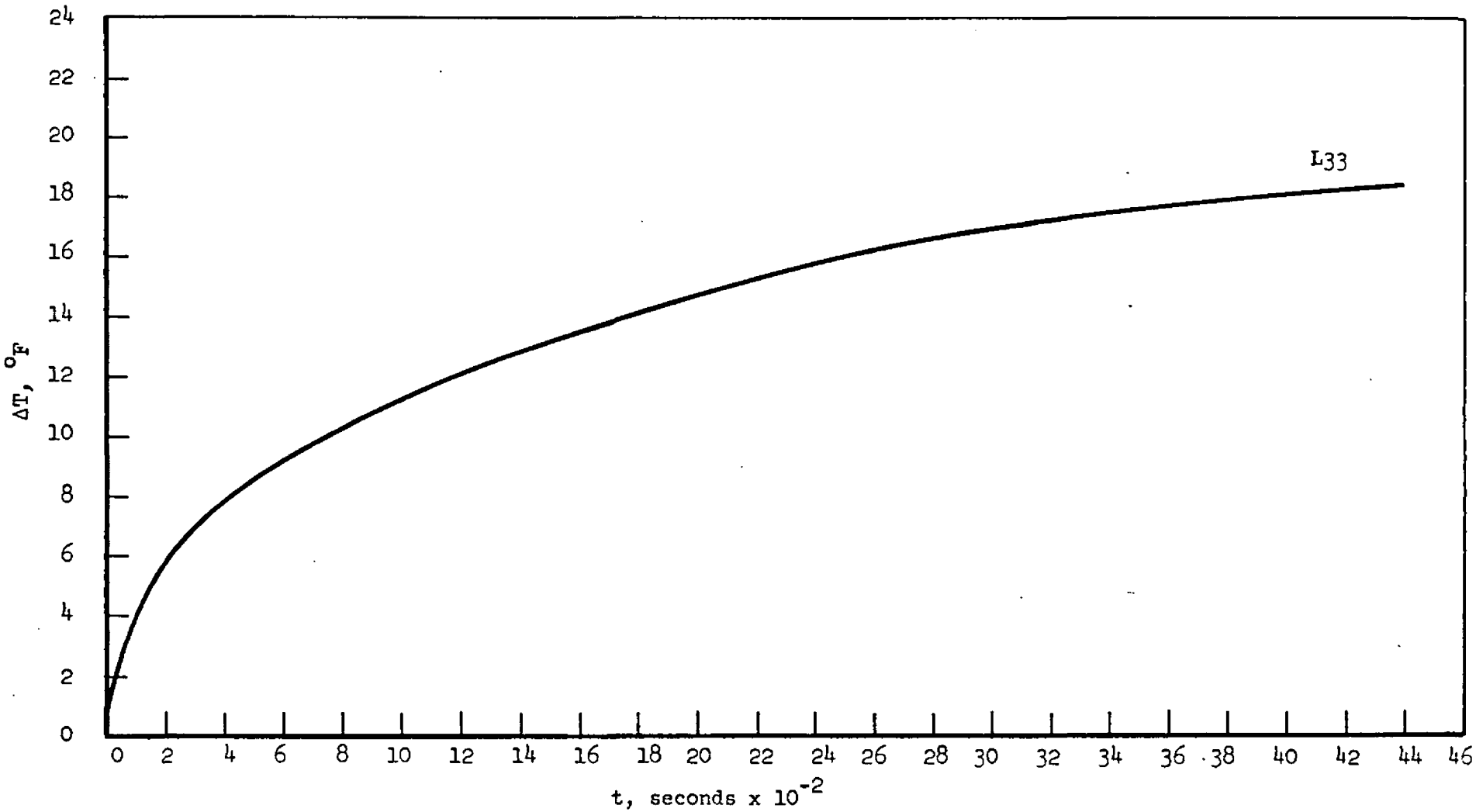


FIGURE 22. HYDRATION OF LIME IN WATER.

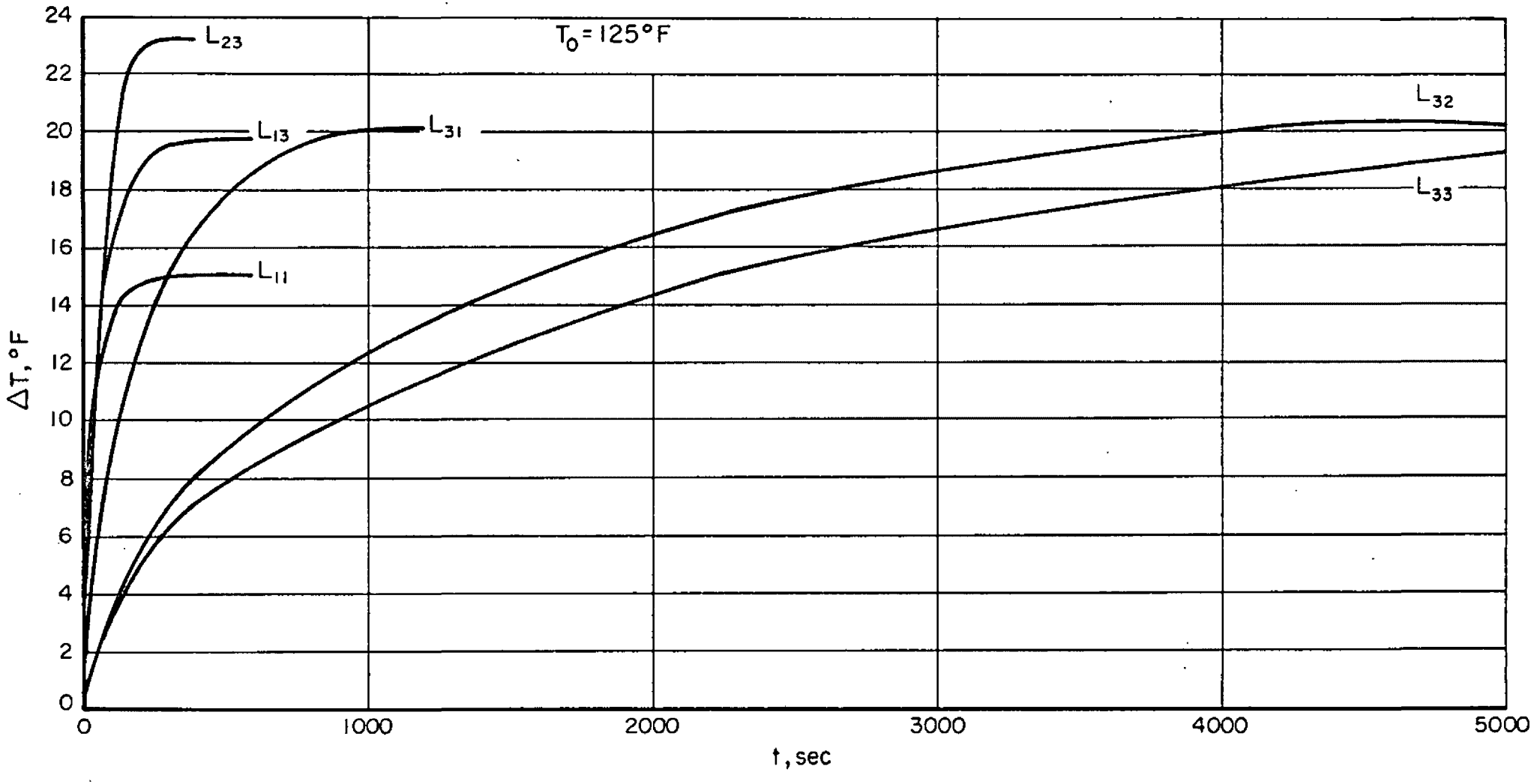


FIGURE 23. HYDRATION OF LIMESTONE-BASED LIMES IN SATURATED LIME WATER.

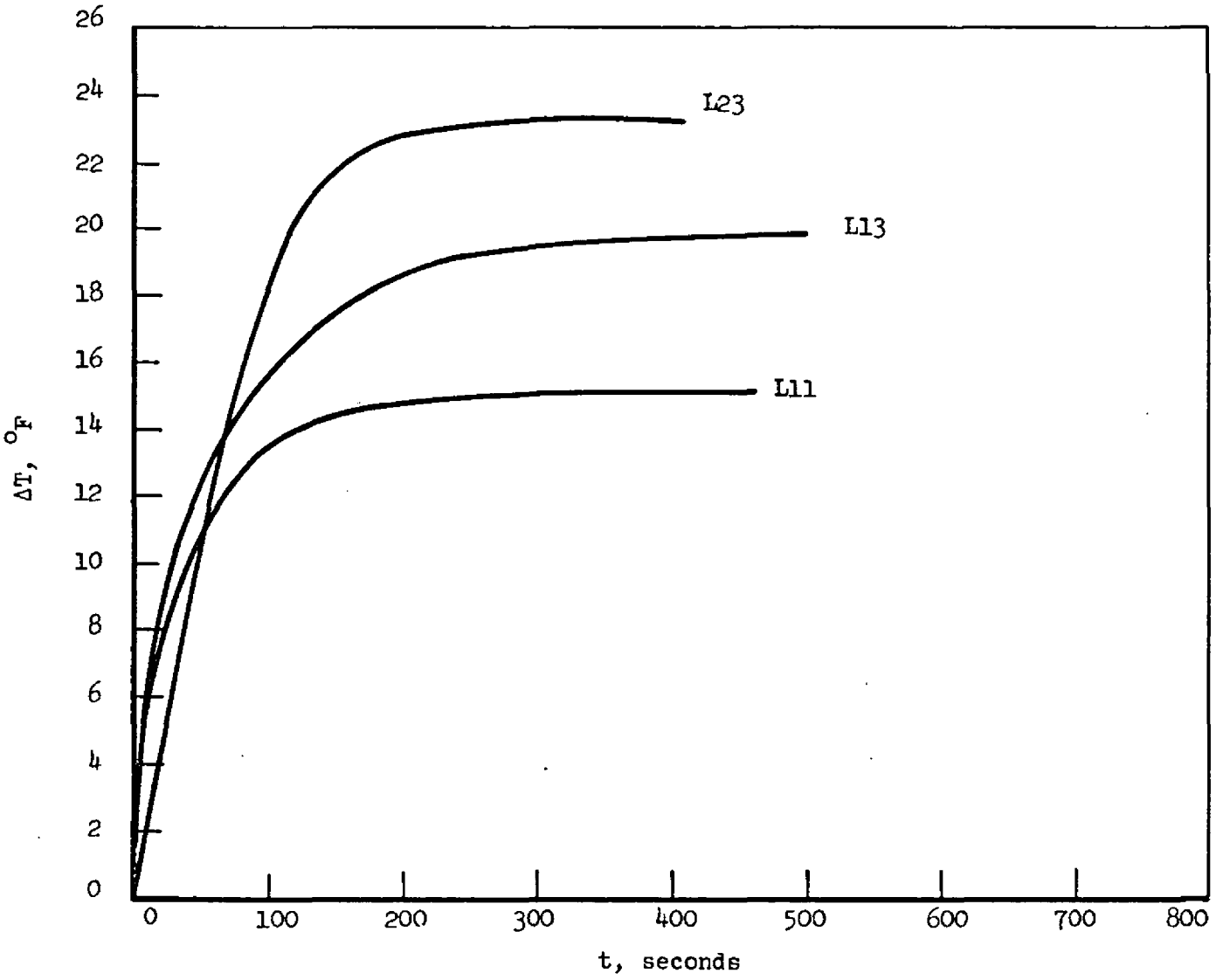


FIGURE 24. HYDRATION OF HIGH CALCIUM LIMES IN SATURATED LIME WATER.

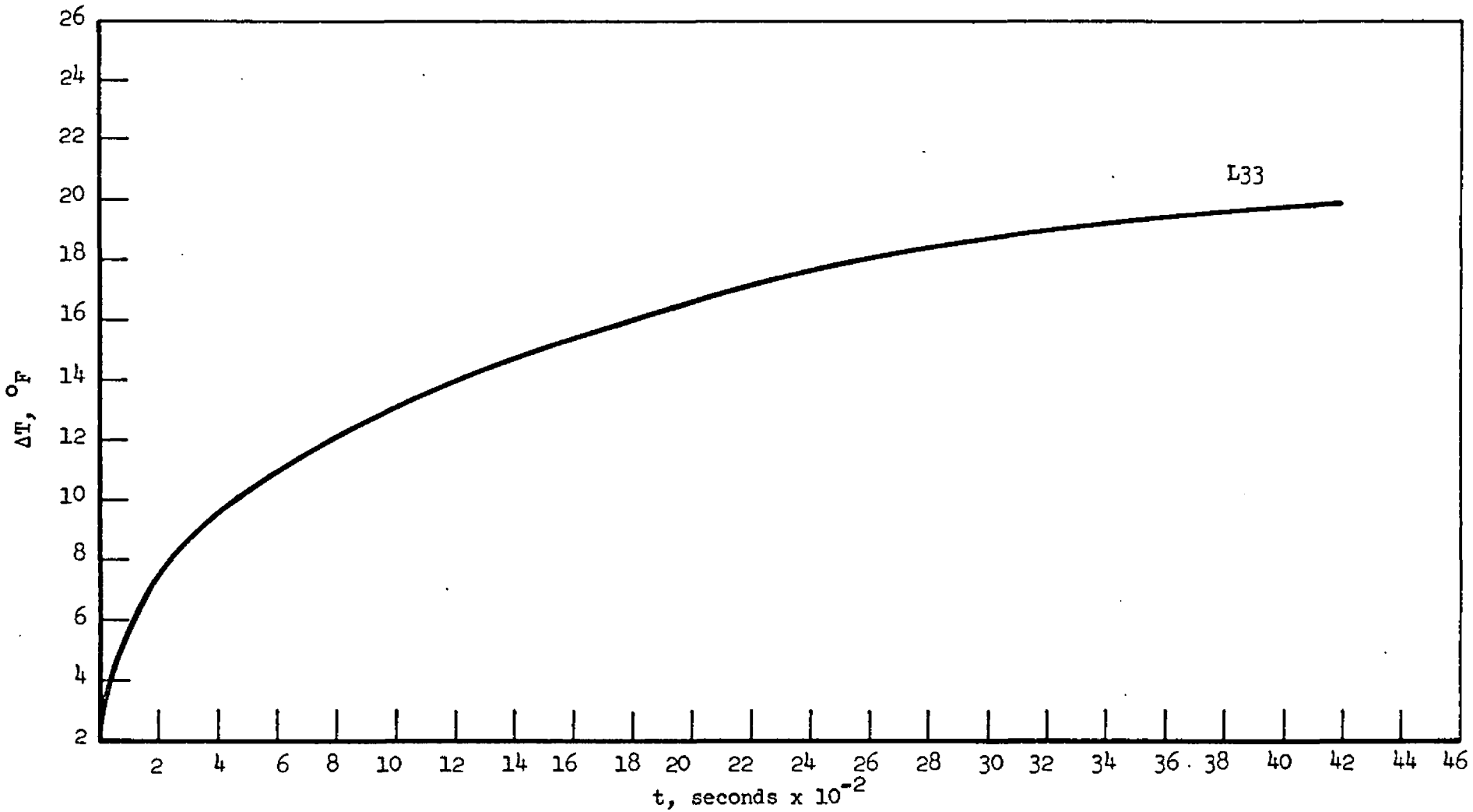


FIGURE 25. RERUN OF HYDRATION OF HIGH CALCIUM LIME IN LIME WATER.

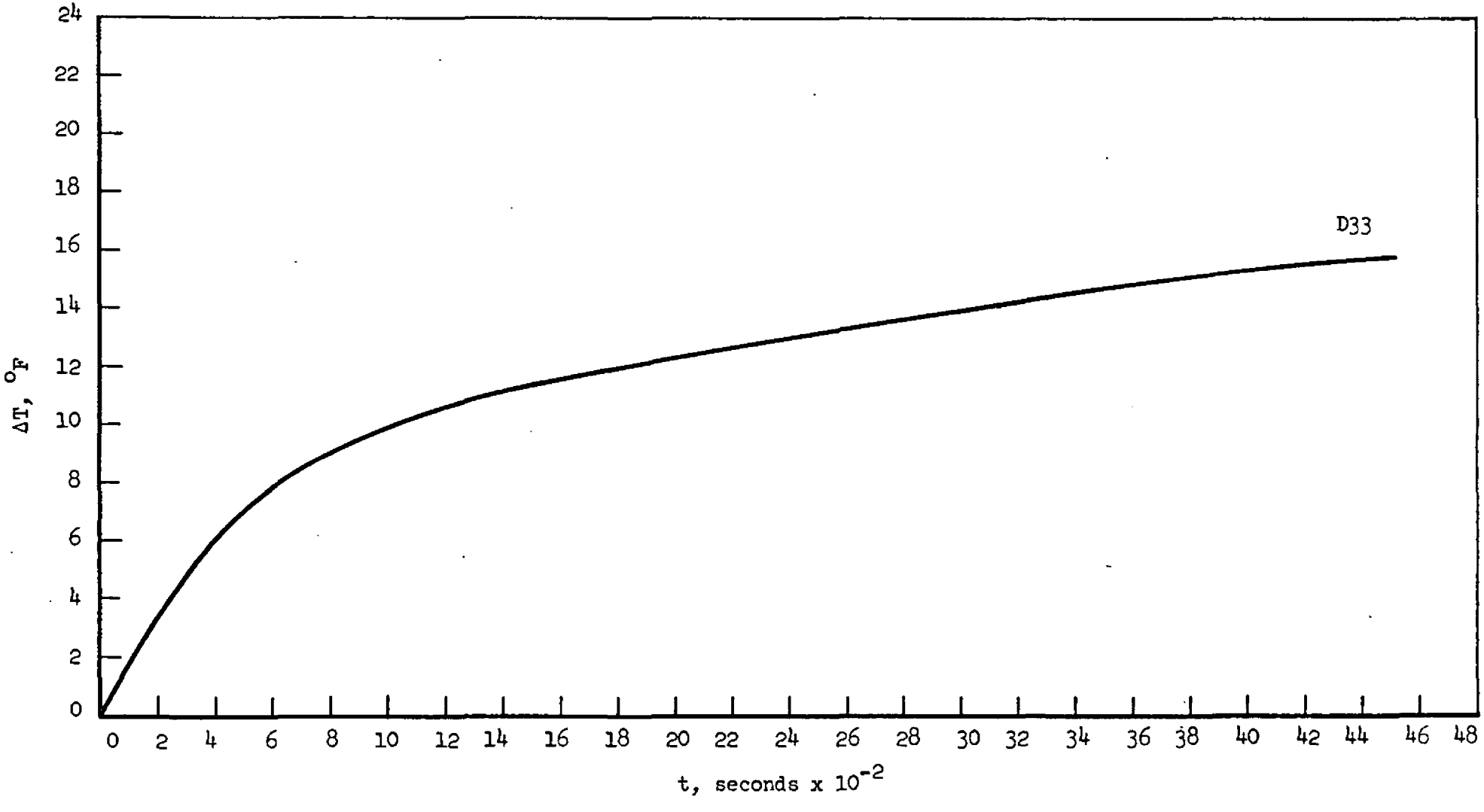


FIGURE 26. HYDRATION OF DOLOMITIC LIME IN WATER.

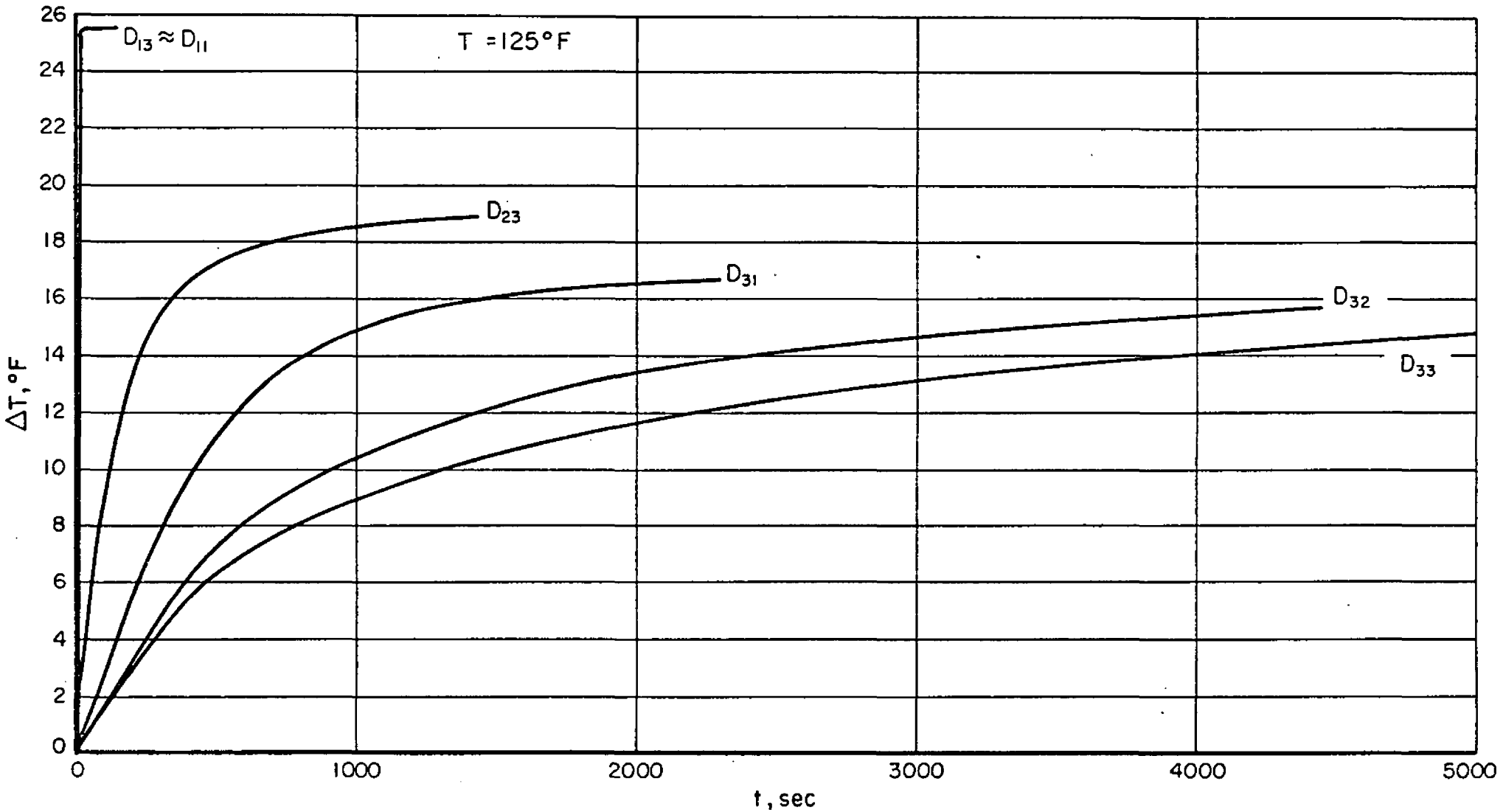


FIGURE 27. HYDRATION OF DOLOMITE-BASED LIMES IN SATURATED LIME WATER.

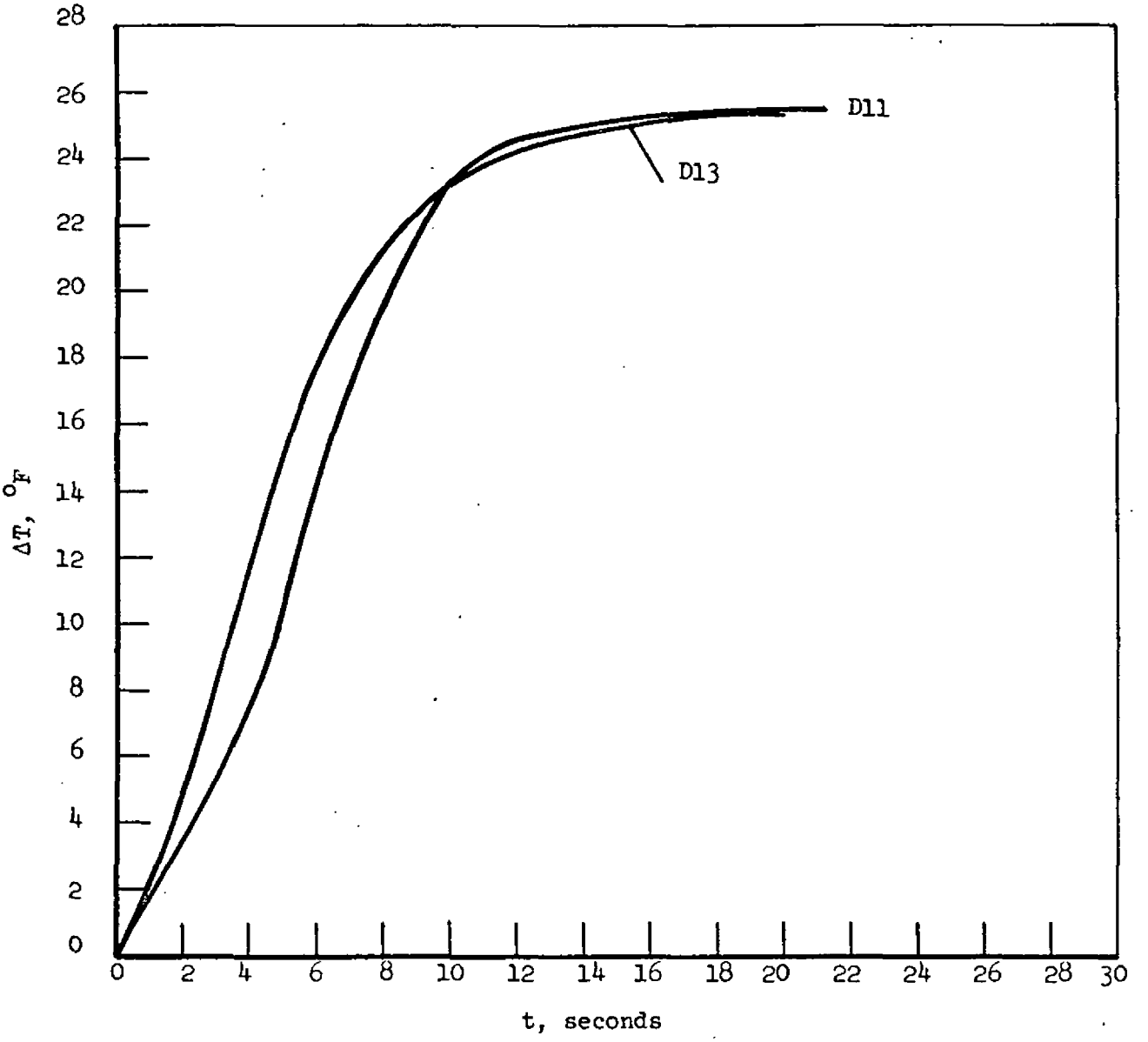


FIGURE 28. HYDRATION OF DOLOMITIC LIMES IN SATURATED LIME WATER.

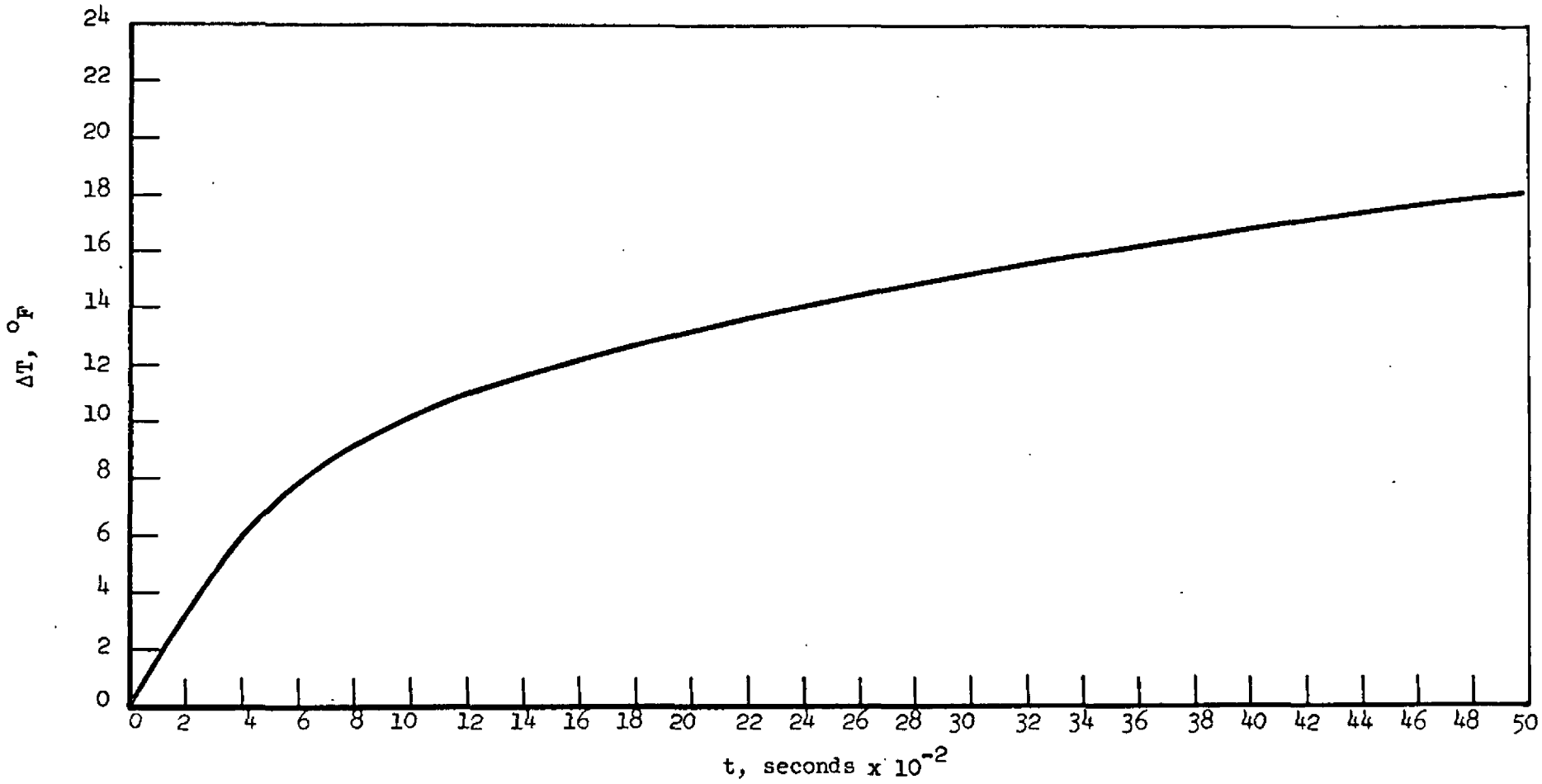


FIGURE 29. RERUN OF HYDRATION OF DOLOMITIC LIME IN LIME WATER.

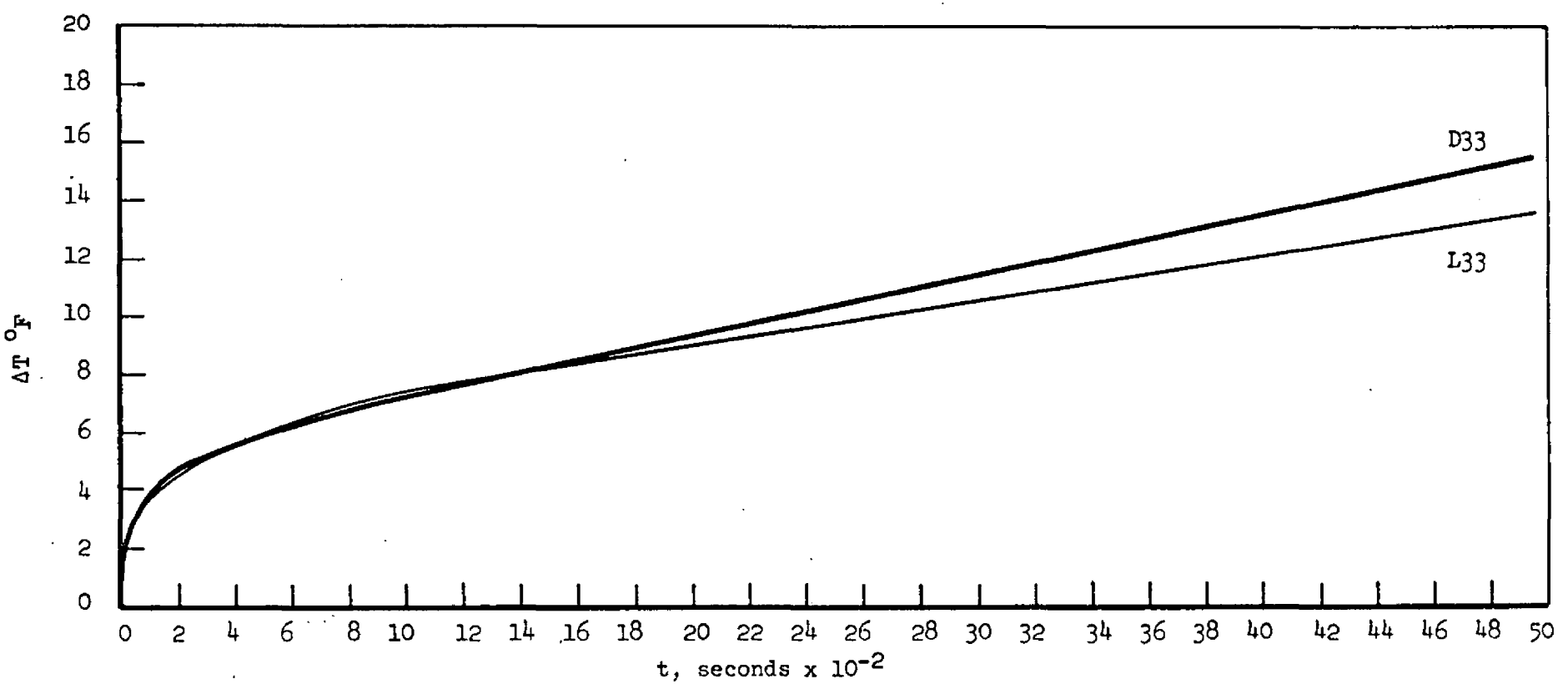


FIGURE 30. HYDRATION OF LIME IN SATURATED SOLUTION OF $MgSO_4$, $CaSO_4$, $MgSO_3$, $CaSO_3$ AT 125°F.

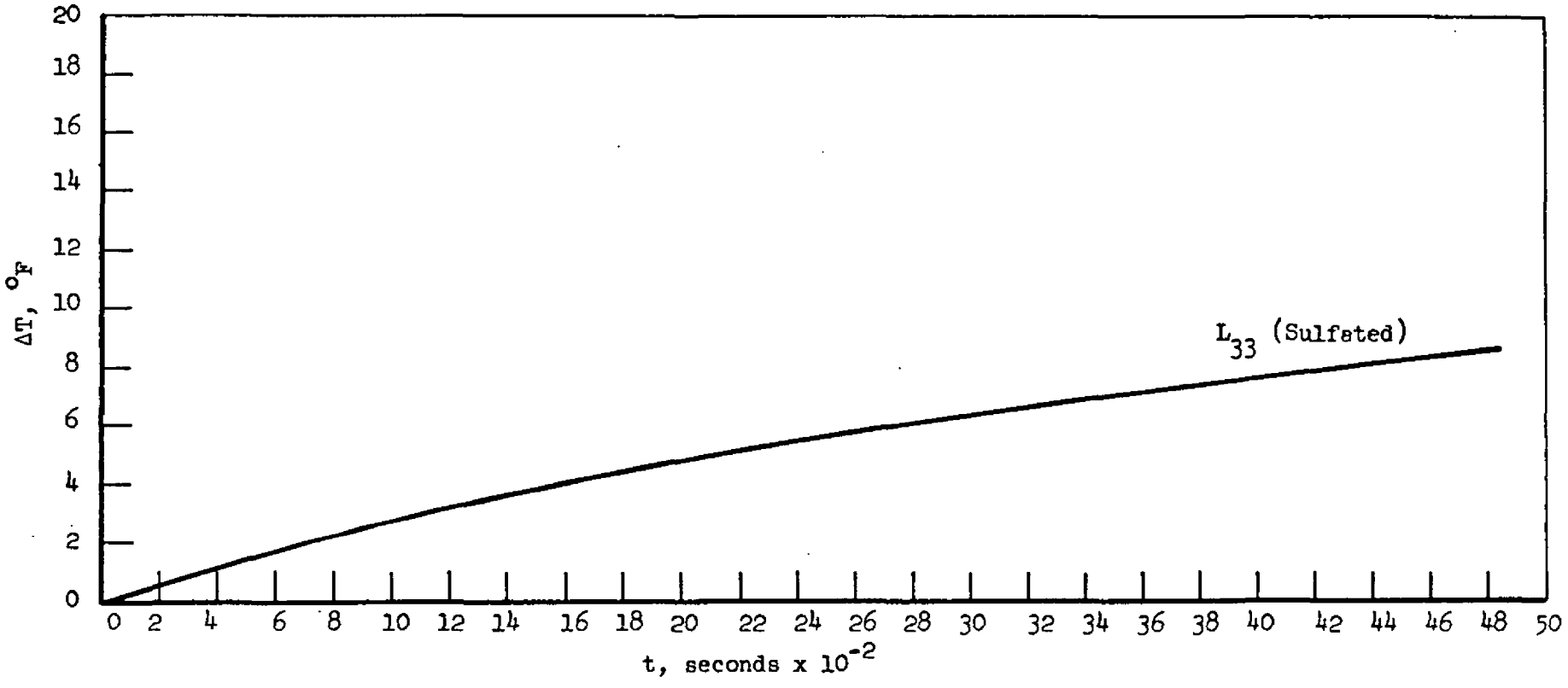


FIGURE 31. HYDRATION OF SULFATED LIME IN LIME WATER.

The data shown in Figures 23 and 27 illustrate distinct trends in the dependence of hydration rate on particle size and calcination temperature. With the dolomitic limes, increasing particle size or increasing calcination temperature clearly decreases the rate of hydration. With the calcitic-based limes, a similar trend was observed. However, the data for L_{11} and L_{13} are considered suspect since a considerable amount of uncalcined stone was found in these samples. This material was a different color from the bulk of the lime and evolved gas when reacted with HCl. With L_{11}, it is estimated that 30 to 40 percent of the sample was uncalcined. For the remaining calcite-based materials, increased particle size or calcination temperature decreases the hydration rate.

It should be noted that, for the limestone series, with only one sample, L_{23}, did the total temperature change approach the theoretical value for reaction of one mole of calcium oxide in one liter of water, 23.4°F. This may be due to incomplete calcination of the particles, or the rate of reaction in the later stages of hydration may have been too slow to be detected. With the dolomitic limes, the temperature change for two samples, D_{11} and D_{13}, exceeded the value of 23.4°F, indicating that some of the magnesium oxide in the samples may have been hydrated in these experiments. Upon calcination of the carbonate, magnesium oxide sinters quite rapidly and becomes resistant to hydration. It is therefore expected that contribution to the temperature rise by hydration of magnesium oxide would occur only with the relatively soft-burned dolomitic limes.

Boynton* suggests that the rate of hydration of a lime is controlled largely by the permeance of the lime to water and the rate of diffusion of water

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* R. S. Boynton, "Chemistry and Technology of Lime and Limestone", Interscience Publishers, New York, (1966), p 297.

through the layer of hydrated lime which is formed around the particles during the initial stages of the reaction. This type of mechanism is consistent with the results of the current work. Figure 32 shows a plot of $1 - (1 - F)^{1/3}$ versus time (F = fraction of lime reacted) for D_{23}. Such a plot should yield a straight line if the reaction is chemically controlled;* a curve of the type shown is indicative of control by diffusion within the particles. It is reasonable, then, that formation of a sulfate coating, either by exposure of the lime to SO_2 prior to contact with the hydrating liquor, or by reaction between the lime and sulfate or sulfite in the liquor, might further inhibit permeation of water into the lime.

Dissolution

Procedure

The rates of dissolution of hydrated calcite- and dolomite-based hydrated limes were studied in water and in a liquor saturated with $CaSO_3$, $CaSO_4$, $MgSO_3$, and $MgSO_4$. Certain of the solutions were also saturated with CO_2 at a partial pressure of 77 torr. In these experiments, a two-gram charge of hydrated lime was added to a well-stirred isothermal vessel containing one liter of solvent (water or sulfite-sulfate liquor), and the pH and calcium-ion activity were monitored continuously using appropriate electrodes. Calcium ion was detected using an Orion liquid-liquid junction-type electrode which was specific to calcium.

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* O. Levenspiel, "Chemical Reaction Engineering", Chapter 12, John Wiley and Sons, Inc., New York, 1962.

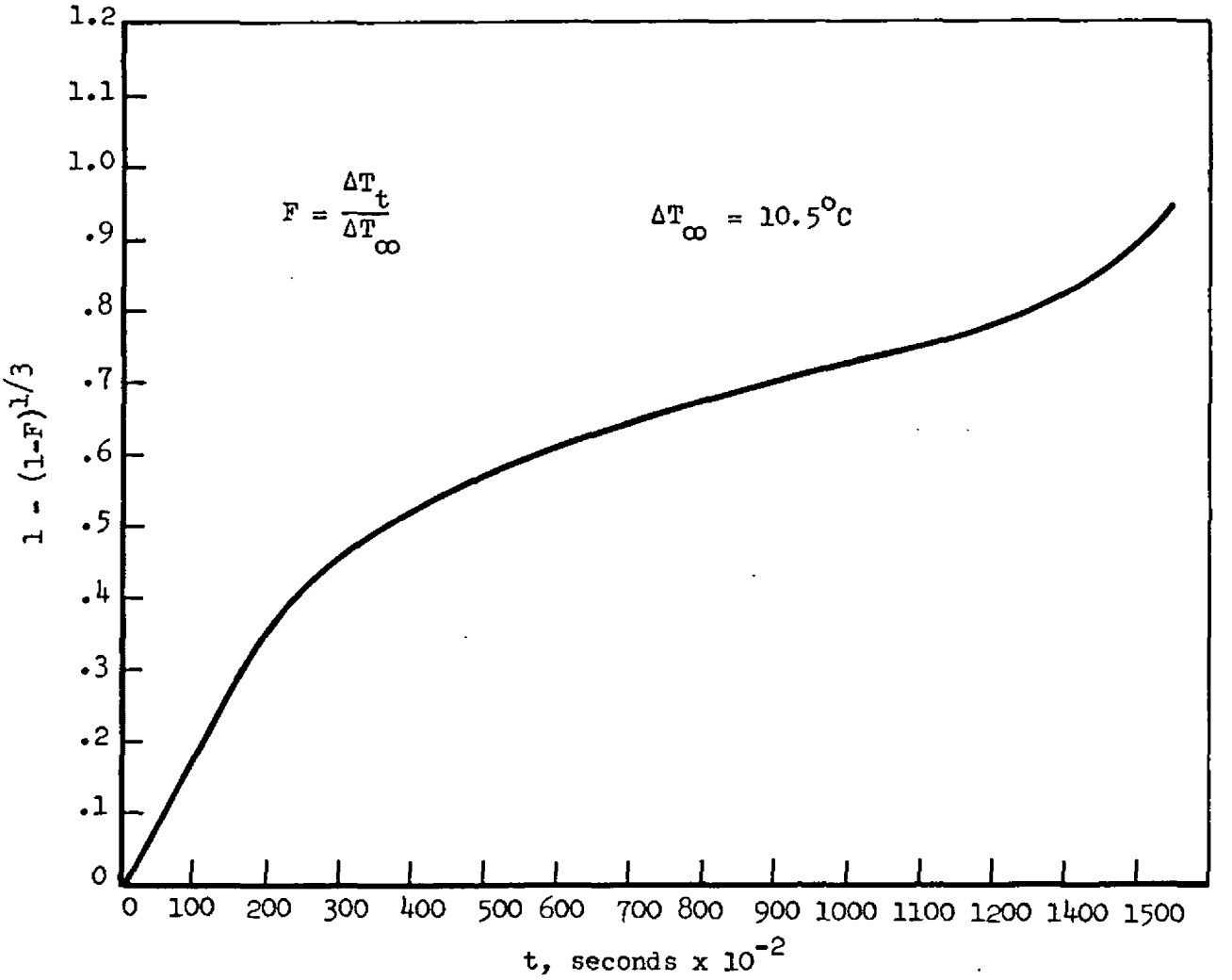

FIGURE 32. HYDRATION OF D_{23}.

With most of the runs, dissolution was essentially complete within a few tens of seconds, and except for the case of dissolution in tap water, the calcium ion activity in solution did not change appreciably during the experiments.

Results

Data summarizing the essential characteristics of the dissolution experiments are shown in Table 3. In those experiments involving the saturated sulfite-sulfate solutions as the solvent, only the OH-activity changed during the experiment. This is probably due to precipitation of sulfite or sulfate on the surface of the lime, i.e.,

$$Ca(OH)_2\ (s) + SO_x^{=} \rightarrow CaSO_x\ (s) + 2OH^- \quad .$$

As in the hydration experiments involving the use of the sulfite-sulfate liquor, there was a strong tendency for agglomeration of the lime particles. Even with tap water as the solvent, the dissolution of calcium was inhibited significantly by contaminants in the water; the calcium ion activity never became as high as would be predicted on the basis of the observed OH^- activity.

Rates cited in Table 3 are average initial rates of dissolution computed by dividing the half-time for reaction into the OH^- activity change up to that point. The rate of dissolution in tap water was significantly greater than that in the liquor. The rate of dissolution in the liquor was further suppressed by the presence of CO_2. The latter fact could be due to deposition of carbonate as well as sulfate on the surface of the particles. The rate of dissolution of the dolomitic lime did increase by an order of magnitude when the temperature was increased from 55 to 125°F. The presence of fly ash lowered the calcium ion activity, but had only a minor effect on the apparent rate of dissolution.

TABLE 3. DISSOLUTION OF HYDRATED LIMES

Hydrated Lime	Solvent	T, °F	pOH		pCa		$t_{1/2}$, sec[b]	Rate[c]
			Initial	Final	Initial	Final		
Dolomite	Tap water	55	6.72	1.47	3.35	2.47	16	1×10^{-3}
Dolomite	Liquor[d]	55	6.45	4.69	2.76	2.76	15.5	4.2×10^{-8}
Limestone	Liquor	55	6.58	4.76	2.43	2.43	7.8	1×10^{-6}
Dolomite	Liquor	125	6.85	5.88	1.80	1.80	1.3	4.5×10^{-7}
Dolomite	Liquor + CO_2[e]	125	7.78	5.88	1.65	1.68	11.5	5.6×10^{-8}
Limestone	Liquor + CO_2	125	7.84	6.03	1.65	1.65	18.5	2.5×10^{-8}
Limestone	Liquor + fly ash[f]	125	7.01	6.44	2.68	2.68	1.8	4.6×10^{-8}

(a) One liter at 77 F.

(b) Time required to reach one-half final OH^- reactivity.

(c) Average rate = net change in OH^- activity/2 $t_{1/2}$, moles/liter-sec, for 2 grams of $Ca(OH)_2$.

(d) Saturated solution of $CaSO_4$, $CaSO_3$, $MgSO_4$, $MgSO_3$.

(e) P_{CO_2} = 77 torr.

(f) 5 grams fly ash per liter of solution.

As in the case of hydration, the rate of dissolution of lime appears to be severely limited when a layer of reaction product can form around the lime particles. This inhibition of hydration and dissolution may well be the major factor in reducing the efficiency of utilization of lime in an SO_2 scrubber which receives the lime in particulate form.

Analysis of Liquors

The compositions of saturated sulfite-sulfate-carbonate solutions were determined at 55, 90, and 125°F. These solutions were prepared by addition of amounts of the components considerably in excess of the published solubilities in water. After thorough mixing for a period of several hours, the solutions were filtered at temperature, and were analyzed for Ca^{++}, Mg^{++}, $SO_3^{=}$, $SO_4^{=}$, $CO_3^{=}$, HCO_3^{-}, and pH. Standard procedures were used in the chemical analyses; calcium was determined atomic absorption, magnesium by gravimetry as the pyrophosphate, sulfite by iodimetry, sulfate by gravimetry as the barium salt, and carbonate and bicarbonate by double-endpoint titration using phenolphthalein and methylorange indicators. Results of these determinations are shown in Table 4. As can be seen from the Table, the solutions are essentially magnesium sulfate solutions.

Analyses were also made of selected liquors recovered from the SO_2-sorption experiments. These analyses were carried out using procedures similar to those listed above, with the exception that atomic absorption was employed to verify the absence of magnesium in the spent liquors. Results of these analyses are shown in Table 5.

TABLE 4. COMPOSITION* OF SULFITE-SULFATE-CARBONATE LIQUORS

Lime Additive	T^oF	Ca^{++}	Mg^{++}	$SO_3^=$	$SO_4^=$	$CO_3^=$	HCO_3^-	pH
Limestone	55	0.03	4.97	0.40	19.3	0.50	0.25	8.90
Dolomite	55	0.03	4.90	0.15	19.1	0.18	0	8.75
Limestone	90	0.03	6.11	0.43	23.5	0.43	0	8.30
Dolomite	90	0.03	6.18	0.16	24.1	0.16	0.16	8.10
Limestone	125	0.04	6.07	0.37	24.0	0.26	0.11	7.85
Dolomite	125	0.03	6.13	0.056	24.1	0.10	0.04	7.65

* Weight percent.

TABLE 5. COMPOSITION* OF SPENT LIQUORS

Run No.	Ca^{++}	Mg^{++}	$SO_3^{=}$	$SO_4^{=}$	$CO_3^{=}$	HCO_3^{-}
4	0.247	0	0.079	1.34	0	0
5	0.167	0	0.073	0.92	0	0
12	0.243	0	0.076	1.29	0	0
13	0.235	0	0.063	1.09	0	0
14	0.082	0	0	<0.1	0	0.23
15	0.315	0	1.00	0.69	0	0

* grams per liter.

CONCLUSIONS

Although it is difficult to draw meaningful conclusions from one-of-a-kind type experiments, the following facts have been brought to light as a result of this program.

1. Under the experimental conditions employed, the wet lime-SO_2 scrubbing process can be represented by an analytical model based on chemical reaction until exhaustion of reactant, followed by dissolution controlled by gas-phase mass-transfer. For the scrubber investigated experimentally in this program, there is little or no SO_2 in the outlet gas from the scrubber until the reactant is exhausted. The SO_2 concentration in the outlet gas then increases and approaches the inlet gas concentration asymptotically.

2. The reaction product between SO_2 and the scrubbing liquor at the breakthrough point is approximately represented by the sulfite rather than the bisulfite.

3. The presence of solid lime caused serious clogging of the gas inlet openings to the experimental scrubber. The SO_2 breakthrough time is slightly reduced, presumably because of coating of the limestone particles by sulfite (or sulfate) crystals. This observation suggests that full-scale scrubber operation might be expected to experience both scaling and reduced utilization of any undissolved solids present in the scrubber liquor.

4. Uptake of CO_2 causes the rapid initial drop in the pH of the scrubber liquor during a run (by formation of $CaCO_3$), but appears to have little or no effect on the SO_2 breakthrough time.

5. For the SO_2 uptake runs with slurries of hydrated material, breakthrough occurred significantly before the reactant was exhausted, indicating solid-liquid mass transfer as a limiting step under these conditions.

6. The presence of NO in the flue gas significantly increases the ratio of observed to calculated breakthrough times. It has been suggested that oxidation of sulfite to sulfate is the cause of this effect.

7. Rates of hydration of burnt limes are controlled by diffusion of water into the particles and hence are decreased by overburning of the lime or use of large particles. The effect of particle size on hydration rate is apparently much stronger for hard-burned than for soft-burned lime.

8. Deposition of sulfate on the lime hinders the hydration process.

9. Deposition of sulfate or carbonate on the lime hinders the dissolution of hydrated lime.

10. The process of dissolution can be accelerated by increasing the solution temperature.

RECOMMENDATIONS

The current experimental work is largely of an exploratory nature, and, as such, suggests several areas of need for better understanding and development of the limestone SO_2 wet-scrubbing process.

The results of the current experiments indicate that lime in particulate form reacts readily with various sulfur species or carbonate in solution to yield a coating which inhibits utilization of the bulk of the lime. Fine grinding of the lime might alleviate this problem to some extent. However, because of the observed tendency for particles to become cemented together

forming large clusters, a high degree of utilization of the lime may not be possible as long as the lime is admitted to the scrubber in particulate form. It is therefore recommended that further consideration be given to the importance of particle size in the overall scrubbing process. It is further recommended that consideration be given to the possibility of predissolving the lime, or limestone, in the feed water to the scrubber through the use of excess CO_2 or other solubilizing agents.

Further development is also needed in the area of modeling of the overall reaction system. The model given in this report is only a first attempt at description of the scrubbing process, and as such does not give adequate representation of the mechanical and chemical factors involved. For instance, the dependence of the equilibrium partial pressure of SO_2 on solution composition is not explicit in the model given. Also, a detailed analysis of these data will yield only rudimentary information on the various mass transfer resistances in this system, which may not be directly applicable to large-scale systems.

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The data on which this report is based are recorded in Battelle Laboratory Record Books No. 21754, pp 1-42, and No. 26980, pp. 1-57.

APPENDIX

IDENTIFICATION AND COMPOSITION OF SAMPLES

TABLE A-1. IDENTIFICATION OF HYDRATION SAMPLES

Sample	Type	Particle Size (mesh range)	Calcination Temperature °F
D_{11}	Dolomitic	-325	1700
D_{13}	Dolomitic	-100 + 200	1700
D_{23}	Dolomitic	-100 + 200	2200
D_{31}	Dolomitic	-325	2700
D_{32}	Dolomitic	-200 + 325	2700
D_{33}	Dolomitic	-100 + 200	2700
L_{11}	Calcitic	-325	1700
L_{13}	Calcitic	-100 + 200	1700
L_{23}	Calcitic	-100 + 200	2200
L_{31}	Calcitic	-325	2700
L_{32}	Calcitic	-200 + 325	2700
L_{33}	Calcitic	-100 + 200	2700

TABLE A-2. CHEMICAL ANALYSES OF LIMESTONES*

Component	Dolomitic Limestone	High Calcium Limestone
CaO	30.39**	54.40
MgO	21.54	0.48
SiO_2	1.05	1.22
Fe_2O_3	0.28	0.19
Al_2O_3	0.10	0.44
Loss on ignition (1000°C)	46.63	43.13

* Supplied by G&WH Corson, Inc.

** Weight percent.