

Recovery of Sulfur Dioxide as Dilute Sulfuric Acid

Catalytic Oxidation in Water Solution

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In agreement with the results of Johnstone (1) it has been found possible to recover sulfur dioxide from waste gases as dilute sulfuric acid. Mixtures of sulfur dioxide and air are bubbled through water containing manganese sulfate as catalyst. Thirty per cent acid is readily produced, but the reaction ceases at about 40 per cent acid. In a glass column with a fine porous plate at the bottom, through which the gas is introduced, rates of absorption several times higher than those reported by Johnstone are obtained. The concentration of catalyst, temperature, gas composition, rate of gas flow, and depth of absorbing solution are studied as

affecting the rate of absorption. The capacity of the apparatus is compared for batch as against continuous operation. Other experiments show that the rate of absorption per unit volume is greater with a fine porous plate than with a coarse plate. The rates of absorption per unit volume in both a small and a large packed tower are much lower than those in the glass column with porous plate bottom. The catalyst is susceptible to poisoning by minute amounts of certain substances. In this connection, water from several sources, refinery gases containing sulfur dioxide, and various materials of construction were tested.

IN THE treatment of petroleum fractions with sulfuric acid incident to refining, sulfur dioxide is liberated. While the actual daily amount of the gas liberated in any one refinery is not large compared, for instance, with the daily amount discharged in the stack gases from a large power station burning coal, nevertheless the amount generated in the acid-treating equipment and in the subsequent blowing of the oil to remove dissolved sulfur dioxide is such as to present a disposal problem. In some refineries the gases from the treating and the blowing equipment are piped to the tall stacks of the power plant and disposed of by dilution, as in the coal-burning power stations. If this is not done, the sulfur dioxide escaping to the air sets up unpleasant conditions in the adjacent parts of the refinery and accelerates corrosion of nearby steel structures.

The problem of sulfur dioxide recovery in a refinery is rendered somewhat difficult by the facts that the gases ordinarily must be collected from a number of pieces of equipment, and that both the volume of gas and the sulfur dioxide content vary greatly from time to time. Observed variations in the sulfur dioxide content in one instance were from 12 to 0.6 per cent sulfur dioxide. The average concentration in this case was about 2 per cent sulfur dioxide. The present paper describes experimental work exploring the possibility of converting sulfur dioxide in waste gases to dilute sulfuric acid through catalytic oxidation in water solution.

PREVIOUS WORK

It has long been known that the oxidation of sulfur dioxide in water solution is catalyzed by the ions of various metals. Recently Johnstone (1) studied this reaction in the hope of utilizing it for the removal of sulfur dioxide from the stack gases of central power stations. His experiments indicated that it was possible to recover sulfur dioxide as dilute sulfuric acid of such strength as to make the possibility attractive, since 30 per cent acid ordinarily can be concentrated at a profit. However, his experiments showed low rates of absorption, and low efficiencies in the larger apparatus. In the work described in the present paper, it was found possible to attain much higher rates of absorption, thereby increasing

the capacity of the absorption apparatus to a reasonably high value.

PRELIMINARY EXPERIMENTS

The first experiments were carried out in a small glass column 2.2 cm. (0.87 inch) inside diameter and 100 cm. (39 inches) high. The column was packed with 5-mm. (0.2-inch) glass beads to a height of 81 cm. (32 inches), and was jacketed with a glass tube of larger diameter, through which water at controlled temperature could be circulated. A thermometer was placed inside the column to indicate the temperature. Sulfur dioxide and air were passed separately through flowmeters, and then mixed just before entering the bottom of the column. The scrubbed gas leaving the top of the column was passed through two small absorption tubes containing sodium hydroxide solution, in which the sulfur dioxide escaping the main column was caught. The rates of gas flow were held constant throughout a given run, with the exception of run 24.

The absorbing solution, of which 100 cc. were placed in the column, was prepared from distilled water, concentrated sulfuric acid, and the salt used as catalyst. The reagents were of c. p. grade. The time required for making the individual experiments was shortened in the majority of cases by starting with a solution already containing 20 per cent sulfuric acid.

At the end of the run the sulfuric acid solution was drained out of the column, and the column then rinsed with distilled water. The amount of sulfuric acid produced during the run was determined by titration of the solution and wash water with standard alkali. Precaution was taken to boil the solution before titrating, to remove dissolved sulfur dioxide, although ordinarily this was probably an unnecessary refinement. The percentage sulfuric acid produced was calculated from the titration on the basis of 100 cc. final volume. The quantity of sulfur dioxide escaping the column was determined by titration of the sodium hydroxide solution from the absorption tubes.

The first experiments showed at once that absorption and catalytic oxidation of sulfur dioxide were possible in solutions already containing 20 per cent sulfuric acid. Manganese salts were found to be excellent catalysts, the same results being obtained with either the sulfate or the nitrate. Ferrous sulfate also acted as a catalyst, but, in agreement with Johnstone, the rate of absorption was much less than with manganese. Manganese sulfate was therefore used as the catalytic salt in all of the subsequent runs.

A summary of some of the results obtained is given in

TABLE I. PRELIMINARY EXPERIMENTS IN SMALL COLUMN PACKED WITH GLASS BEADS

RUN	Mn %	TEMP. ° C.	TOTAL GAS VELOCITY Cm./sec.	SO ₂ IN ENTERING GAS		LENGTH OF RUN Hours	H ₂ SO ₄		SO ₂		EFFI- CIENCY ^a %	RATE OF ABSORPTION Grams/hr
				Flowmeter %	Calcd. %		Initial %	Final %	Absorbed in column Grams	Escaping Grams		
9	0.40	30	0.44	10.0	10.3	3.82	20.1	21.8	1.47	5.22	22	0.38
10	0.40	30	0.88	5.0	5.70	5.27	20.1	24.1	3.43	6.85	33	0.65
11	0.40	30	4.40	1.0	1.21	6.54	20.1	27.7	6.80	6.71	50	1.04
12	0.40	30	2.20	2.0	2.35	5.72	20.1	26.4	5.43	6.15	47	0.95
13	0.40	50	2.20	2.0	2.55	2.87	20.0	24.0	3.48	2.82	55	1.21
14	0.40	60	2.20	2.0	2.43	4.95	20.0	27.0	6.23	4.14	55	1.26
15	0.40	70	2.20	2.0	2.41	5.47	20.0	28.3	7.35	4.04	65	1.34
16	1.00	30	2.20	2.0	2.47	6.25	20.0	30.3	9.38	3.99	70	1.50
17	0.04	30	2.20	2.0	2.43	6.09	19.5	28.0	5.65	7.16	44	0.93
18	0.20	30	2.20	2.0	2.49	6.17	19.5	27.0	6.63	6.59	50	1.07
19	0.40	30	2.20	2.0	2.47	4.71	19.5	26.4	6.03	4.01	60	1.28
20	0.02	30	2.20	2.0	2.49	5.12	19.5	24.4	4.29	6.70	39	0.84
21	0.01	30	2.20	2.0	2.41	1.95	19.5	20.7	0.99	3.06	24	0.51
24	0.04	50	2.18	1.5-0.6	1.27	40.0	0.0	39.0	33.0	10.3	76	0.84
29	0.04	30	1.10	2.0	2.24	2.07	34.0	34.6	0.69	1.31	35	0.33

^a Percentage SO₂ absorbed.

Table I. The total gas velocity is here expressed as centimeters per second, which is the total number of cubic centimeters of gas measured at standard conditions supplied per second as read from the flowmeters, divided by the cross-sectional area of the column in square centimeters. The percentage sulfur dioxide in the entering gas is given both as indicated by the flowmeters, and as calculated from the total amount of sulfur dioxide absorbed in both the column and the sodium hydroxide tubes. The difference is believed to be due to errors in the flowmeter readings, since the actual flow of sulfur dioxide was very small.

The experiments of Table I also gave indication of the effect of temperature and of catalyst concentration. Runs 12-15 showed that the rate of absorption increased with temperature over the range covered. Runs 16-21, from which Figure 1 is plotted, indicated that the rate of absorption increased continuously with increase in catalyst concentration from 0.01 to 1.00 per cent manganese. However, the optimum concentration of catalyst was indicated to be in the vicinity of 0.02 to 0.04 per cent manganese, since further increase in catalyst concentration above this amount did not greatly increase the rate of absorption.

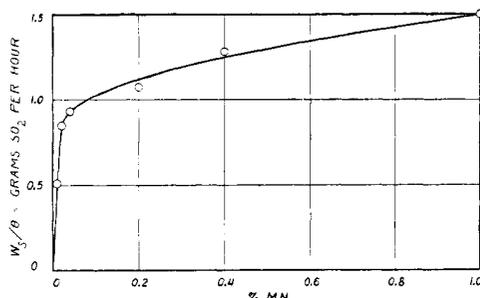


FIGURE 1. VARIATION IN ABSORPTION RATE WITH CATALYST CONCENTRATION

Run 24 was long, starting with distilled water containing 0.04 per cent manganese. The course of the reaction was followed by replacing the solution in the sodium hydroxide absorbing tube at intervals with fresh solution, and titrating the solution drawn off. In this way the rate at which sulfur dioxide was escaping the main column was determined over short intervals. The efficiency of absorption tended to fall as the concentration of sulfuric acid increased. For this reason the rate at which sulfur dioxide was supplied was decreased at intervals during the run, in order to maintain a high efficiency. The average efficiency of absorption for the entire run was 76 per cent. In 40 hours 39 per cent sulfuric acid was reached, but at this point practically none of the sulfur dioxide was being absorbed in the main reaction tube. It was concluded that the maximum concentration of sulfuric acid which could be produced was about 40 per cent. Run 29, starting with 34 per cent sulfuric acid, also

showed that relatively lower rates of absorption were obtained at higher acid concentrations.

EXPERIMENTS IN LARGE GLASS COLUMN WITHOUT PACKING

A further study of the fundamentals of the process was undertaken on a somewhat larger scale.

The apparatus used is shown diagrammatically in Figure 2, and consisted of a glass tube, *D*, 9.25 cm. (3.64 inches) inside diameter by 183 cm. (72 inches) long, mounted in a vertical position. A circular section was cut from a fine porous plate (Filtros grade E) of the proper diameter just to fit inside the glass tube, and 3.8 cm. (1.5 inches) thick. The pores around the circumference of this section were sealed with wax of high melting point. The porous plate and a glass reducing fitting were attached to the bottom of the column by means of a rubber sleeve, *E*. A wax plug, *I*, was prepared for the top of the column, through which passed the gas discharge tube, *H*, and a smaller glass tube, *F*, for withdrawing samples of the liquid. Thermometer *G* and calibrated flowmeters *A* and *B* were provided. The gas mixture was passed through wash bottle *C*, where it was washed and brought to about 60 per cent relative humidity by sulfuric acid of the proper strength.

The gas leaving the column was sampled at intervals through tube *J*. The gas sample was drawn through the small absorption tube, *K*, packed with glass beads. The gas leaving tube *K* was measured by means of the wet meter, *L*. The composition of the exit gas was determined by drawing gas through the system until a known quantity of standard sodium hydroxide solution in tube *K* was rendered neutral to phenolphthalein, and noting the wet meter readings.

No provision was made in this apparatus for controlling the temperature. The over-all reaction was strongly exothermic, and the temperature of the absorbing solution was raised considerably above room temperature by the heat generated. The rate of reaction, in general, increased with temperature. However, the temperature rise was limited by the evaporation of water from the hot solution, and by the loss of heat to surroundings. The maximum temperature reached in any of the present experiments was 65° C. (149° F.). The volume of water evaporated ordinarily was approximately balanced by the increase in volume due to production of sulfuric acid, so that the volume of absorbing solution did not change greatly in any one run.

Both batch and continuous runs were made in this apparatus. In the batch runs, as in the preliminary experiments, the absorbing solution was placed in the column and allowed to remain until the end, the concentration of sulfuric acid increasing throughout the run. In the continuous runs a solution containing a given concentration of sulfuric acid, plus the catalyst, was placed in the column at the start; at intervals during the run, solution was drawn off through tube *F*, and water containing the same concentration of catalyst was added to the column at such a rate as to maintain an approximately constant concentration of sulfuric acid in the column throughout the run.

Most of the runs were carried out at efficiencies in the vicinity of 80 to 90 per cent. The general procedure was to

set the air rate at the desired value and then to adjust the sulfur dioxide rate so that about 90 per cent of the sulfur dioxide supplied was being absorbed. In the batch runs, as in run 24 of Table I, it was necessary to decrease the sulfur dioxide rate as the runs progressed. The experiments were thus carried out at constant absorption efficiency

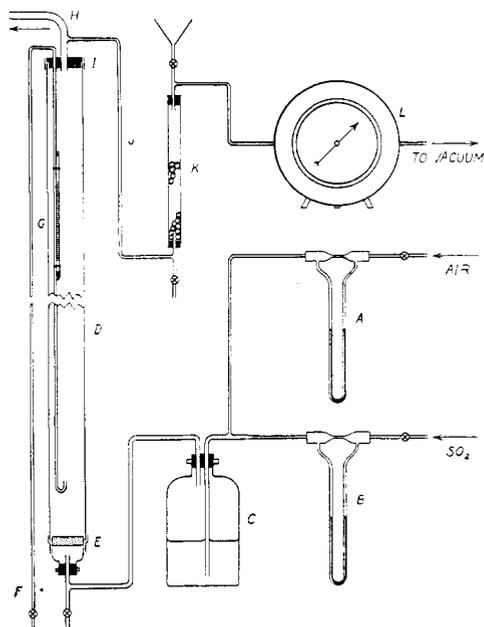


FIGURE 2. DIAGRAM OF APPARATUS

rather than at constant gas composition. If this had not been done, either low absorption efficiencies would have been obtained at the higher acid concentrations, or, as in Johnstone's experiments, efficiencies of practically 100 per cent would have been observed at the start and over a considerable part of the runs. In the latter case practically no absorption would be taking place in the upper part of the column, and capacity coefficients could not be calculated. A few runs were made at low efficiencies to determine the effect of an excess of sulfur dioxide, and in one run nitrogen was added to the gas mixture, using an additional flowmeter, in order to demonstrate the effect of decreasing the oxygen partial pressure.

TREATMENT OF EXPERIMENTAL DATA

The experimental results are presented in terms of the rate of absorption, W_s/Θ (weight of sulfur dioxide absorbed per unit time), and of the capacity per unit volume, or capacity coefficient, $W_s/\Theta V$ (weight of sulfur dioxide absorbed per unit time per unit volume). In order to interpret the results, it is desirable to set up a theory as to the mechanism of the process. The simplest theory, and the one suggested by Johnstone, is that both the sulfur dioxide and the oxygen are absorbed from the gas into the liquid by diffusion through surface films, and that the two dissolved gases then react, this reaction being catalyzed by the manganese ion. Whether or not this mechanism is correct, it has been found adequate to account for the experimental results here obtained.

Of the two gases, the rate of absorption of oxygen by stirred water is known to be much slower than that of sulfur dioxide at equal partial pressures (4). Even at the relative partial pressures used in the experiments, the potential rate of absorption of oxygen must be considerably lower than that of sulfur dioxide. In the absence of a catalyst the oxidation of the dissolved sulfur dioxide is known to be a slow reaction. The preliminary experiments showed that the over-all rate

increased rapidly with the concentration of catalyst up to a certain optimum concentration, and only slowly thereafter. This behavior may be explained by the assumption that below the optimum concentration of catalyst the over-all rate is limited by the rate of oxidation and therefore increases greatly with the catalyst concentration. As the optimum concentration of catalyst is approached, however, the concentration of dissolved oxygen becomes small, and the rate of absorption of oxygen thus approaches its maximum possible value, which would be reached if the dissolved oxygen were actually reduced to zero concentration. Above the optimum concentration of catalyst, the potential rate of oxidation is so great that the rate of absorption of oxygen becomes the factor limiting the over-all rate, which therefore increases only slightly as the catalyst concentration is increased further.

Of the present experiments, nearly all were carried out at catalyst concentrations in excess of the optimum, since this case is the more important from a practical point of view. It is then evident that the rate of absorption of sulfur dioxide was limited by the rate of absorption of oxygen. For the absorption of oxygen, the equation may be written (3):

$$W_o/\Theta = K_o a V (\Delta P_{av.})$$

where W_o/Θ = weight of oxygen adsorbed per unit time

K_o = absorption coefficient for oxygen

a = interfacial area per unit volume

V = active volume of apparatus

$(\Delta P_{av.})$ = mean driving force, defined as av. difference between partial pressure of oxygen in gas phase and partial pressure of oxygen in equilibrium with liquid

This equation indicates that the rate of absorption of oxygen, and hence the rate of absorption of sulfur dioxide, per unit volume of the absorption apparatus, is dependent only upon the values of K_o , a , and $(\Delta P_{av.})$. Factors which may affect the absorption coefficient, K_o , are temperature, concentration of sulfuric acid, and rates of flow of gas and liquid. The interfacial area, a , in the type of apparatus

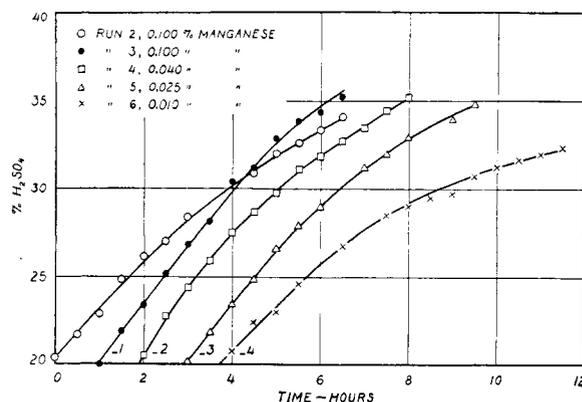


FIGURE 3. RATE OF INCREASE OF ACID CONCENTRATION AT DIFFERENT CONCENTRATIONS OF CATALYST

used here, will depend upon the size and number of bubbles per unit volume. This in turn will depend upon the porosity of the plate and the rate of flow of gas, and to a lesser extent upon the temperature, the concentration of sulfuric acid, and possibly other factors.

The partial pressure of oxygen in equilibrium with the liquid will depend upon the particular dynamic equilibrium existing under the given experimental conditions. Obviously, for reaction to proceed, a certain concentration of dissolved oxygen must be present in the liquid phase. However, when a considerable excess of catalyst is present, the concentration of dissolved oxygen must be very small. Under this condi-

TABLE II. DATA OF TYPICAL RUN

ELAPSED TIME	TEMP.	AIR RATE	SO ₂ RATE	Gas VELOCITY	SO ₂ IN Gas Entering	SO ₂ IN Gas Leaving	H ₂ SO ₄	EFFICIENCY ^a	W _s /θ	W _s /θV
Hours	° C.	Cc./sec.	Cc./sec.	Cm./sec.	%	%	%	%	Grams/hr.	Grams/hr./active liter
0	28	250	27.8	4.15	10.0	0.0	0	100	285	32.5
0.5	46	205	27.8	3.45	12.0	1.4	3.2	90	260	29.5
1.0	57	175	27.8	3.00	13.8	1.8	6.3	89	255	29.0
1.5	63	170	27.8	2.95	14.2	2.7	9.5	83	235	27.0
2.0	65	170	23.6	2.90	12.3	1.7	11.7	88	215	24.5
2.5	66	160	23.6	2.75	12.9	2.1	14.2	86	210	23.5
3.0	65	170	23.6	2.90	12.3	2.3	16.7	83	200	23.0
3.5	64	170	20.2	2.85	10.7	1.4	18.7	88	185	21.0
4.0	63	170	20.2	2.85	10.7	1.7	20.3	86	180	20.5
4.5	62	170	20.2	2.85	10.7	1.8	22.1	85	175	20.0
5.5	60	175	15.8	2.85	8.4	0.1	24.7	99	160	18.5
6.0	59	175	15.8	2.85	8.4	1.0	26.3	89	145	16.5
6.5	58	185	15.8	3.00	7.9	1.4	27.7	84	135	15.5
7.0	57	185	15.8	3.00	7.9	1.9	29.0	78	125	14.5

^a Percentage SO₂ absorbed.

TABLE III. BATCH RUNS IN LARGE GLASS COLUMN WITHOUT PACKING

RUN	Mn %	TEMPERATURE		VOL. OF SOLN. Liters	ACTIVE VOL. Liters	AV. GAS VELOCITY Cm./sec.	SO ₂ IN ENTERING GAS		AV. O ₂ IN ENTERING GAS %	LENGTH OF RUN Hours	H ₂ SO ₄		AV. EFFICIENCY ^a %	W _s /θV		
		AV. ° C.	MAX. ° C.				Initial %	Final %			Initial %	Final %		10% H ₂ SO ₄	20% H ₂ SO ₄	30% H ₂ SO ₄
2	0.100	49	56	6.0	8.7	3.3	9.1	3.4	19.6	6.5	20.3	34.3	89	..	22	12
3	0.100	50	52	6.3	10.8	4.1	7.0	2.4	19.9	5.5	20.0	35.2	86	..	18	11
4	0.040	52	56	6.0	8.7	3.4	8.6	3.7	19.6	6.0	20.5	35.2	91	..	23	13
5	0.025	51	56	6.0	8.7	3.4	8.6	2.8	19.7	6.5	20.2	34.8	91	..	22	13
6	0.010	44	50	6.1	8.7	3.5	9.1	2.3	19.7	7.5	20.7	32.4	90	..	21	6.7
23	0.100	58	66	6.0	8.7	3.0	14.2	7.9	18.6	7.0	0.0	29.5	88	27	20	15
29	0.100	50	55	6.0	8.7	3.9	15.7	6.6	18.6	7.5	0.0	23.6	64	22	17	..
30	0.100	46	49	6.0	8.7	3.9	18.2	10.2	17.9	7.0	0.0	19.5	45	15
31	0.100	44	48	6.0	8.7	3.4	9.0	4.0	9.7	7.5	0.0	16.7	83	12
32	0.100	50	56	6.0	8.7	3.8	11.0	8.1	18.9	3.0	0.0	13.7	81	28

^a Percentage SO₂ absorbed.

tion the equilibrium partial pressure of oxygen may be neglected, and (ΔP_{av}) may be assumed equal to the average partial pressure of oxygen in the gas phase.

Since in the present paper interest centers upon the absorption of sulfur dioxide, it has been preferred to use the quantity $W_s/\theta V$ rather than K_o or $K_o a$. No attempt was made to determine the interfacial area, a , although a rough estimate for one particular instance is made below. By stoichiometry:

$$W_s/\theta V = 4 W_o/\theta V = 4 K_o a (\Delta P_{av})$$

Actually, since the gas mixture was made up from air plus a much smaller proportion of sulfur dioxide, the average partial pressure of oxygen was approximately constant at 0.19 atmosphere in all the experiments, except the single run in which nitrogen was also added to the inlet gas stream. Hence, with the one exception:

$$W_s/\theta V = 0.75 K_o a \text{ (approx.)}$$

The units used will be grams, hours, liters, and atmospheres. (To convert to pounds, hours, cubic feet, and atmospheres, divide $W_s/\theta V$, $\bar{W}/\theta V$, or $K_o a$, by 16.0.)

To illustrate the treatment of the experimental results, run 23 is selected as typical of batch operation. The observed data are given in Table II, and in condensed form in Table III. In making this run, 6.0 liters of water containing 0.10 per cent manganese were placed in the column, filling it to a depth of 89 cm. (35.0 inches). The air and sulfur dioxide rates were adjusted to the values shown in Table II (all gas volumes are given for standard conditions). The air rate was such as to hold the level of the foaming liquid constant at a depth of 130 cm. (51.2 inches). The active volume during operation was therefore 8.75 liters.

The calculations may be illustrated by taking the observations one-half hour after the start of the experiment. The superficial gas velocity was calculated by dividing the total gas velocity (233 cc. per second) by the cross-sectional area (67.3 sq. cm.), giving 3.46 cm. per second. The percentage sulfur dioxide in the entering gas was 12.0 per cent, in the exit gas, 1.4 per cent. Hence the efficiency of absorption was:

$$100 \left(\frac{12.0}{88.0} - \frac{1.4}{98.6} \right) / \left(\frac{12.0}{88.0} \right) = 90\%$$

The rate of absorption of sulfur dioxide was then 25.0 cc. per second, or $W_s/\theta = 260$ grams per hour. Dividing the latter by 8.75 liters, $W_s/\theta V$ is calculated to be 29.5 grams per hour per liter active volume.

The rate of absorption may also be calculated from the liquor analyses. An increase in concentration from 0 to 3.2 per cent sulfuric acid represents the absorption of 128 grams of sulfur dioxide; from 3.2 to 6.3 per cent, 129 grams. The average rate of absorption at one-half hour after the start of the experiment was thus 257 grams per hour, which checks the rate calculated from the gas analyses. The agreement was not always as close as this, however, a difference of about 10 per cent being the average. In the tables, W_s/θ and $W_s/\theta V$ are given as calculated from the gas analyses only.

In the above example the total volume occupied by the gas bubbles was obviously 2.75 liters. During operation of the column the gas bubbles were distributed throughout the whole volume of the solution and averaged perhaps 0.50 cm. (0.20 inch) in diameter. Using this roughly estimated figure it is possible to calculate the values of K_o and a , although the calculation indicates order of magnitude only. The value of a so calculated is 3800 sq. cm. per liter of active volume (120 sq. ft. per cu. ft.). Since the value of $W_s/\theta V$ above was 29.5, $K_o a = 39$, and $K_o = 0.01$ gram hour per sq. cm. per atmosphere. This, although very approximate, appears to be a reasonable value.

BATCH RUNS

The batch runs are summarized in Table III. $W_s/\theta V$ is given at three different acid concentrations only. However, the data are presented more completely in Figures 3-6. In Figures 3 and 5, for convenience in plotting, each successive curve is displaced toward the right by an interval of one hour.

Runs 2 to 6, inclusive (Figures 3 and 4), were made at a series of catalyst concentrations, the other experimental conditions being substantially constant. The results show

that approximately the same rates of absorption were obtained with catalyst concentrations of 0.100, 0.040, and 0.025 per cent. Only when the catalyst concentration was decreased to 0.010 per cent manganese was the rate of absorption obviously lessened. Of the four catalyst concentrations tried, the optimum thus appeared to be 0.025 per cent manganese.

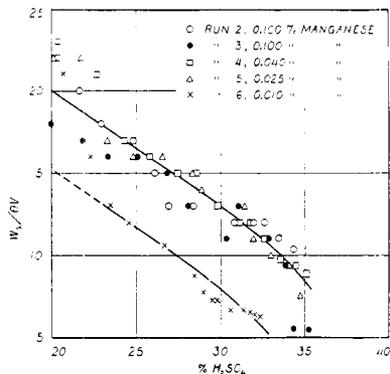


FIGURE 4. VARIATION IN RATE OF ABSORPTION PER UNIT VOLUME WITH ACID CONCENTRATION AT DIFFERENT CONCENTRATIONS OF CATALYST

The results of runs 23 and 29-32 are plotted in Figures 5 and 6. Run 23 best illustrates the manner in which the rate of absorption decreased as the concentration of sulfuric acid increased. In this run the efficiency of absorption was maintained at an average value of 88 per cent. In runs 29 and 30 the average efficiencies fell to 64 and 45 per cent, respectively, as a result of increasing the rate of supply of sulfur dioxide. Not only did the increase in partial pressure of sulfur dioxide not cause a corresponding increase in the rate of absorption, but a decrease actually resulted. This decrease cannot be explained on the basis of decreased oxygen partial pressure, since this was nearly constant for the set of runs. It would appear that a large excess of sulfur dioxide actually hinders the absorption of oxygen. The scattering of the points for runs 29 and 30 in Figure 6 was caused by

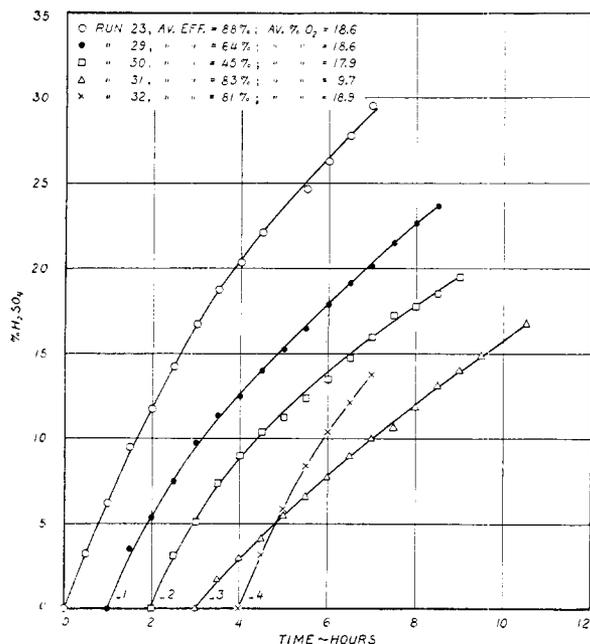


FIGURE 5. RATE OF INCREASE OF ACID CONCENTRATION

failure to maintain a constant efficiency. However, the effect of decreasing the efficiency, on the average, is plainly evident.

In run 31, by adding nitrogen to the entering gas, the partial pressure of oxygen was approximately halved. Comparison with run 23 shows that the rate of absorption decreased about in proportion to the decrease in oxygen partial pressure, as would be expected when the rate of absorption of oxygen was the limiting factor. Run 32 was a check run made under approximately the same conditions as run 23. Excellent agreement in absorption rates was obtained.

The batch runs as a whole showed much higher rates of absorption, as compared with the preliminary experiments and with Johnstone's results. For example, in run 23 only 7 hours were required to build up an acid concentration of 29 per cent as compared with 40 hours for 39 per cent acid in the preliminary experiments (run 24, Table I), and 58 hours for 35 per cent acid according to Johnstone's results. The capacity per unit volume of the absorption apparatus was thus increased to a reasonably high value.

CONTINUOUS RUNS

A summary of the continuous runs is given in Table IV. Most of the runs were of too short duration for the liquor rate to be accurately established. In Runs 24-26, however, the liquor rate was fixed (solution was added to and withdrawn from the column in the amount of 500 cc. at half-hour intervals), and the concentration of solution drawn off from the column was a variable to be determined.

Runs 19 and 20, Table IV, were made to study the effect of varying the volume of absorbing solution and the rate of gas flow, upon the rate of absorption. Since the apparatus was of constant cross section, changing the volume of absorbing solution was equivalent to changing the depth of the solution over the porous plate. The runs made at each of three different gas rates are plotted in Figure 7, in which W_s/θ is plotted vs. the volume of solution used, the volumes being 2.0, 4.0, and 6.0 liters. The corresponding depths of solution (standing) were 29.8 cm. (11.7 inches), 59.5 cm. (23.4 inches), and 89.3 cm. (35.2 inches), respectively. As might be ex-

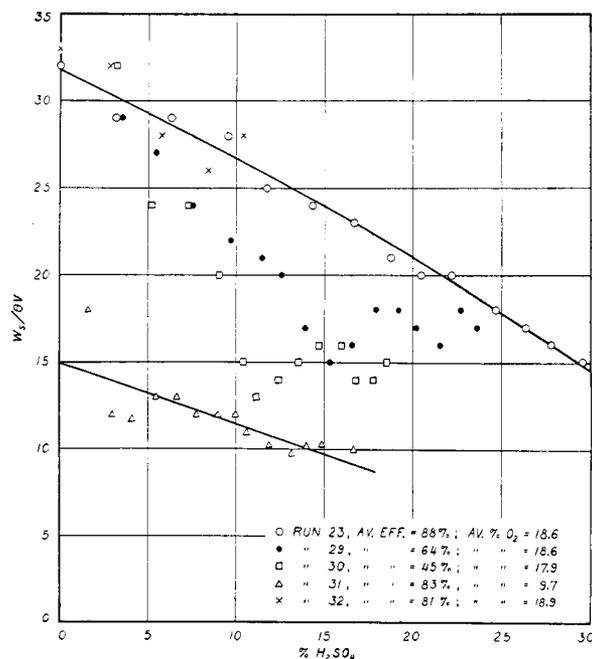


FIGURE 6. VARIATION IN RATE OF ABSORPTION PER UNIT VOLUME WITH ACID CONCENTRATION

TABLE IV. CONTINUOUS RUNS IN LARGE GLASS COLUMN WITHOUT PACKING

RUN	Mn %	TEMP. ° C.	VOL. OF SOLN. Liters	ACTIVE VOL. Liters	GAS VELOCITY Cm./sec.	SO ₂ IN	LENGTH OF RUN Hours	LIQUOR RATE Liters/hr.	H ₂ SO ₄		EFFICIENCY ^a %	W _s /θ Grams/ hr.	W _s /θV Grams/hr./ active liter
						ENTERING GAS %			Entering	Leaving			
20d	0.040	41	2.0	2.56	2.1	2.9	1.0	..	0.0	29.0	78	34	13
20e	0.040	40	2.0	3.00	3.1	2.8	1.0	..	0.0	28.8	76	47	16
20f	0.040	40	2.0	3.43	4.0	2.8	1.0	..	0.0	29.1	63	48	14
20g	0.040	44	4.0	4.90	2.1	4.0	0.5	..	0.0	30.7	82	49	10
20b	0.040	46	4.0	5.65	3.1	3.9	1.5	..	0.0	30.7	81	70	12
20a	0.040	46	4.0	7.00	4.1	3.9	1.5	..	0.0	31.7	83	93	13
19c	0.040	44	6.0	6.65	1.2	5.1	1.0	..	0.0	30.1	91	39	5.9
19b	0.040	47	6.0	7.35	2.2	5.1	1.0	..	0.0	29.7	84	65	8.9
19a	0.040	52	6.0	8.75	3.2	5.4	1.0	..	0.0	30.1	97	117	13
19d	0.040	46	6.0	10.1	4.2	5.9	1.0	..	0.0	29.9	85	146	14
24	0.040	54	3.0	5.1	3.7	10.0	5.5	1.00	0.0	18.0	59	151	30
25	0.040	50	3.0	5.1	3.6	6.1	7.0	1.00	18.0	28.0	62	93	18
26	0.040	42	3.0	5.1	3.4	2.5	7.5	1.00	27.6	31.4	82	49	9.6

^a Percentage SO₂ absorbed.

pected, the rate of absorption (at constant efficiency) was found to be proportional to the volume of solution used. It follows that the depth of solution required for a given efficiency of absorption is proportional to the rate at which sulfur dioxide is supplied, or, for a given rate of gas flow, to the percentage of sulfur dioxide in the entering gas.

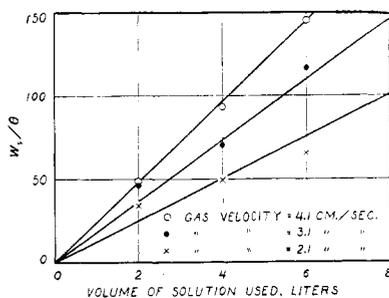


FIGURE 7. VARIATION IN RATE OF ABSORPTION WITH VOLUME OF SOLUTION IN COLUMN

During operation of the column, the active volume of the solution was increased considerably by the gas bubbles in suspension. This is shown by Figure 8, in which the ratio of the active volume during the run to the actual volume of solution used is plotted vs. the gas rate. This ratio is shown to be the same for different volumes of solution. Consequently, it follows that the rate of absorption is proportional, not only to the volume of solution used, but also to the active volume, V , during the run. It also follows that the value $W_s/\theta V$ is independent of the active volume of the apparatus.

The data of Table IV indicate that, for a given volume of solution, the rate of absorption, W_s/θ , increases in proportion to the gas rate, as shown in Figure 7. Since the active volume increases much more than in proportion to the gas rate, as shown in Figure 8, it follows that $W_s/\theta V$ increases much less than in proportion to the gas rate. This is shown in Figure 9, which indicates that it probably was not advantageous to use a gas rate in excess of 3 to 4 cm. per second (5.9 to 7.9 cu. ft. per sq. ft. per minute).

The disadvantage of continuous as compared with batch operation is that the absorbing solution in the column must be maintained at the concentration of the product which it is desired to draw off. Since the rate of absorption is lower at the higher concentrations of sulfuric acid, the average capacity of a given apparatus would be considerably less in continuous than in batch operation. Obviously this disadvantage may be partly overcome by multistage continuous operation. The three runs, 24-26, are indications of what may be accomplished by three-stage operation, the runs approximating the first, second, and third stages, respectively, of a continuous system. Here the gas entering the first stage

contained 10.0 per cent sulfur dioxide, 6.1 per cent entering the second stage, and 2.5 per cent entering the third stage. The over-all efficiency of absorption of sulfur dioxide was 97 per cent, corresponding to 0.4 per cent sulfur dioxide in the exit gas. The concentration of acid leaving the first stage was 18.0 per cent, leaving the second stage, 28.0, and leaving the last stage, 31.4. The total rate of absorption of sulfur dioxide, calculated from the gas analyses, was 293 grams per hour, of which 51 per cent was absorbed in the first stage, 32 in the second, and 17 in the third. Since the total active volume of the three stages was 15.3 liters, $W_s/\theta V$ for the entire system averaged 19.2. This compares with a value of about 13.0 for single-stage continuous operation, and an average value of about 23.0 for batch operation.

Runs 24-26 were analogous to a three-stage system in which the gas and liquid were passed through the stages in parallel flow. Countercurrent flow of the gas and liquid was not tried, but the fact that the rate of absorption depended upon the oxygen partial pressure indicated that little advantage would result from countercurrent operation, since the oxygen partial pressure was nearly constant. For example, in the above runs the decrease in sulfur dioxide partial pressure from 0.100 to 0.004 atmosphere was accompanied by a decrease in the oxygen partial pressure only

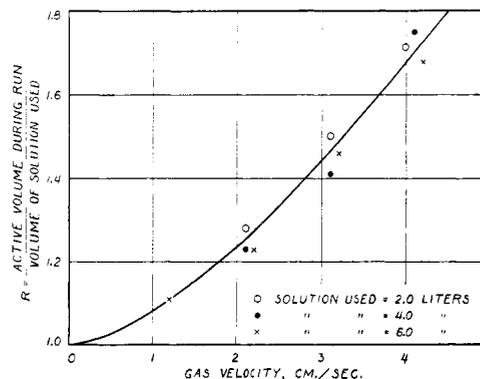


FIGURE 8. INCREASE IN ACTIVE VOLUME WITH GAS VELOCITY

from 0.189 to 0.166 atmosphere (dry basis). Thus it would appear that, when there is a large excess of oxygen, it should make little difference for continuous multistage operation whether the gas and liquid flow in parallel or in countercurrent.

OTHER EXPERIMENTS

A few experiments were performed in a galvanized iron tank 1 foot (30.5 cm.) square by 3 feet (91.4 cm.) deep, fitted with a standard 1 foot square porous plate as a false bottom. The inner walls of this tank were protected by a coating of

wax of high melting point. With a fine porous plate (Filtros grade E), rates of absorption comparable to those in the large glass column were obtained. With a coarse porous plate (Filtros grade A), much lower rates, comparable to those obtained by Johnstone, were observed.

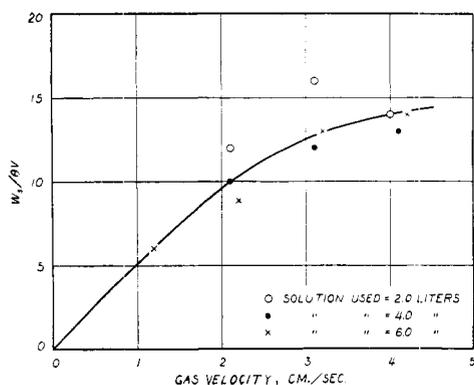


FIGURE 9. INCREASE IN RATE OF ABSORPTION PER UNIT ACTIVE VOLUME WITH GAS VELOCITY

Several experiments were also made in an attempt to carry out the absorption in a packed tower, with the solution trickling down over the packing in the usual way. Both a glass column packed with glass beads, and a large column constructed of 61-cm. (24-inch) sewer tile and packed with 7.6-cm. (3-inch) spiral tile packing were used. In the glass column packed with glass beads, the values of $W_a/\Theta V$ obtained were of the order of magnitude of one-tenth of those in the bubble column with porous plate bottom. In the large tile column extremely poor rates of absorption were obtained.

The advantage of the type of apparatus in which the gas stream is broken up into fine bubbles and bubbled up through the liquid will bear emphasis. As compared with a tower packed with any of the usual commercial materials, a much greater area of contact per unit volume of the apparatus is obtained. Also, much higher rates of absorption per unit interfacial area may result from the greater disturbance of the liquid film in the case of the bubble tower (2).

Throughout the work it was necessary to take precautions to prevent contamination of the solutions and possible poisoning of the catalyst. It became evident that minute quantities of certain substances, if dissolved in the water used, would slow up the catalyzed reaction or stop it completely. Thus the preliminary experiments were all carried out with carefully distilled water. It was subsequently found that river water which had been prepared for power house use by filtration and zeolite treatment was equally as good as distilled water, and this water was used in the experiments in the large glass column.

Experiments in which the laboratory apparatus was moved into the refinery and operated on gases taken directly from the agitators and separators showed that these gases contained no constituents interfering with the catalysis.

The immersion of pieces of acid-proof brick, wood, or sheet lead in the absorbing solution caused a decrease in the rate of reaction. The effect of lead was small and appeared to depend upon the area exposed. Wood protected with asphalt paint had no effect. Pieces of the sewer tile and tile packing used in the large packed tower, when powdered and extracted with the solution, were found to inhibit the reaction. This may have accounted in part for the extremely poor rates of absorption observed in the large tower, although it is believed that the poor contact resulting from the use of the large packing was sufficient explanation in itself.

The effect of a number of metallic ions was investigated by tests in which salts of the metal were added to an absorbing solution containing 0.04 per cent manganese. As reported by Johnstone, copper ions were found to have an inhibiting effect. However, the effect was small at low concentrations; 20 p. p. m. of copper reduced the rate of absorption in 30 per cent sulfuric acid by 50 per cent. Mercury ions also inhibited the reaction. Ions having no effect were antimony, arsenic, chromium, cobalt, lead, magnesium, molybdenum, nickel, vanadium, and zinc. The fact that lead when added as a salt had no effect was interesting in view of the above results with sheet lead. Many tests were made to establish the effect of iron salts. Ferric iron at a concentration of 5 p. p. m. had no effect, but at 25 p. p. m. the rate of reaction was reduced by 70 per cent. Ferrous iron temporarily inhibited the reaction, but apparently was soon oxidized to the ferric state.

In case the process were carried out on a large scale, care should be used in selecting materials of construction that would withstand the dilute sulfuric acid produced and at the same time not have an adverse effect upon the catalyst. It is suggested that lead-lined pumps could be used for handling the liquid, and that suitable tanks with porous-plate false bottoms could be constructed of concrete with a mastic asphalt lining.

CONCLUSIONS

1. The experiments have verified Johnstone's results in so far as they have demonstrated that sulfur dioxide and oxygen may be absorbed simultaneously from a gas stream by water containing manganese ions as catalyst, to produce dilute sulfuric acid.
2. The rate of absorption decreases as the concentration of sulfuric acid increases, and the maximum strength that can be produced is about 40 per cent acid.
3. For gas mixtures of sulfur dioxide with an excess of air, the optimum concentration of catalyst is in the vicinity of 0.025 per cent manganese. Below the optimum concentration, the over-all rate is limited by the rate of oxidation, and therefore increases greatly with the concentration of catalyst. Above the optimum concentration, the rate of absorption of oxygen becomes the factor limiting the over-all rate, which therefore increases only slightly as the catalyst concentration is increased further.
4. When the rate of absorption of oxygen is the limiting factor, the over-all rate is substantially proportional to the oxygen partial pressure. The sulfur dioxide partial pressure has little effect, although it appears that an excessive supply of sulfur dioxide actually causes a decrease in the over-all rate.
5. The reaction is strongly exothermic, and during operation the temperature of the absorbing solution is raised by the heat generated. The rate of absorption increases with the temperature.
6. The type of apparatus in which the gas stream is subdivided by means of a porous plate and bubbled up through the liquid permits relatively high rates of absorption per unit volume, by reason of the tremendous interfacial area of contact and the rapid renewal of the liquid film. Greater absorption rates per unit volume are obtained by using a fine porous plate instead of a coarse plate.
7. The depth of solution over the porous plate required for high efficiencies of absorption is not great; the depth required for a given efficiency is proportional to the rate at which sulfur dioxide is supplied.
8. The rate of absorption increases with the gas rate, but, since the active volume also increases, the rate of absorption per unit volume tends to approach a maximum.

9. The capacity of a given apparatus in producing, for example, 30 per cent sulfuric acid is smaller in single-stage continuous operation than in single-stage batch operation. Multistage continuous operation approaches batch operation in capacity per unit volume.

10. The manganese catalyst is susceptible to poisoning by minute amounts of certain impurities in the water used. However, river water, filtered and zeolite-softened, is equally as good as distilled water, at least in this instance. Apparently gases containing sulfur dioxide given off in petroleum refining contain no substances which adversely affect the catalyst. Contact with certain materials may inhibit the reaction, so that in case the process is carried out on a

large scale, care must be used in selecting materials of construction.

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New Method of Producing Hydrogen Sulfide and Thiosulfates

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IN THE ammonia-soda process, corrosion of the equipment in contact with the process liquors is largely prevented or controlled by the presence of sulfide ion which apparently forms a protective coating of an iron sulfide. As the sulfides usually occurring in the crude ammonia are at times insufficient for this purpose, a source of sulfides, independent of the use of crude ammonia, is very desirable to allow control of the sulfide concentration and hence of the corrosion.

Sodium sulfide is costly for this purpose. The usual process of forming hydrogen sulfide by heating sulfur with oil is unsatisfactory and gives an inferior product. Investigation of the liquid hydrogen sulfide market reveals no source available at a price justifying its purchase for this use. While there are large quantities of by-product hydrogen sulfide available, the cost of concentrating, purifying, packaging, and shipping increases the price to a high figure even in large quantities. This article will not be concerned with the recovery of hydrogen sulfide from these sources.

A search of the literature revealed no really satisfactory method which would produce the gas at a low cost, so the process (25) described below was devised. It has the advantages of allowing the production of hydrogen sulfide, if desired, at a pressure sufficiently high so that liquefaction can be accomplished without mechanical compression, and of producing a valuable by-product.

PREVIOUS METHODS

FROM SULFUR. The processes starting with elementary sulfur, in general, consist in either directly combining it with free hydrogen, with or without a catalyst, or reacting the sulfur with a hydrocarbon, or the like, which, in effect, yields hydrogen for combination with the sulfur. Some of the processes are quite complicated.

Sulfide has long been known to be essential in controlling corrosion in the ammonia-soda process. The literature reveals no satisfactory method of producing hydrogen sulfide for this purpose. A new process for its production under pressure from sulfur and alkali has been worked out. If desired, this pressure may be sufficiently high to allow direct liquefaction without further compression mechanically. As a co-product, either thiosulfate or sulfate of the alkali used is produced. Satisfactory service is given by steel as a material of construction.

In 1918 Ikeda and Iwamura (21) patented the reaction of hydrogen and sulfur vapor at 500° to 600° C. in the presence of copper or other metallic sulfides as catalyzers. Ikeda (20) in 1920 modified the process by using fuel gas in place of hydrogen. The gases formed contained carbon oxysulfide which was converted into hydrogen sulfide and carbon dioxide by magnesium hydroxide and water. Bacon (2) in 1929 patented a process for passing hydrogen into molten sulfur

with agitation at 250° to 300° C. and 5 to 10 atmospheres. The same year the Société d'études et réalisation "Ereal" (33) obtained a similar patent in Belgium, with the modification of adding more hydrogen and passing over activated charcoal to convert the entrained sulfur vapor. Any sulfur remaining after catalysis was removed by washing with ammonium sulfide. Gutehoffnungshütte Oberhausen (13) in 1929-30 patented a process for reacting sulfur, or a substance containing or yielding sulfur, with steam at 350° C. and a pressure above 15 atmospheres.

The production of hydrogen sulfide by heating paraffin, flowers of sulfur, and shredded asbestos was known as early as 1832 (5). Hanley (15) in 1921 published a description of a sulfur and oil method of making hydrogen sulfide, Bindschedler and Rugeley (4) in 1925 patented the distilling and refluxing of hydrocarbon oils with sulfur at temperatures of 200° to 400° C. and passing the gas through charcoal to free it from mercaptan products. In 1927 I. G. Farbenindustrie (19) obtained patents on heating sulfur or certain sulfur compounds under pressure with hydrogen, carbon monoxide, formic acid, or formates under certain conditions. Devaux (7) in 1930 patented a process for heating sulfur at normal pressure with hydrocarbons of high molecular weights, which do not boil below 170° C.

Sárvárer Kunstseidenfabrick (31) obtained a patent in 1914