

**Argonne National Laboratory**

**ABSORPTION OF SOME HALOGEN GASES  
FROM AIR BY A LIMESTONE BED  
AND A SPRAY TOWER**

by

**R. C. Liimatainen and M. Levenson**

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# ABSORPTION OF SOME HALOGEN GASES FROM AIR BY A LIMESTONE BED AND A SPRAY TOWER

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## ABSTRACT

An investigation was made to compare the effectiveness of an oölitic limestone bed and that of a spray tower for removal of certain highly toxic halogens and their simple compounds from an air stream. The application may be the treatment of the exhaust ventilation from areas in which these chemicals are employed. Both methods investigated depend upon absorption accompanied by chemical reaction, thus converting the reactive halogens to a readily disposable and innocuous form such as calcium fluoride fines in a limestone bed or soluble potassium fluoride in a spray tower.

The limestone bed gave efficiencies of 99.9 per cent for the removal of hydrogen fluoride at room temperature with 1/8 to 1/4-inch particles of oölitic limestone in a 6-inch packed depth up to a point where 44 per cent of the bed was reacted. The fluorine from interhalogens was absorbed with efficiencies ranging from 87 to 99 per cent; however, both the bromine and chlorine from interhalogens were absorbed, in general, with low efficiencies and capacities (of the order of only pounds per ton of limestone), even with beds up to 5 feet deep. Hydrogen bromide was absorbed with a high efficiency only until 0.5 per cent of the bed was reacted; the efficiency then declined rapidly. Humidification of the air stream resulted in little improvement in the efficiency of bromide absorption. Elemental bromine was not absorbed by the limestone bed. Elemental fluorine was initially absorbed with a high efficiency which rapidly dropped to an efficiency of 60 per cent with less than 0.1 per cent of the bed reacted.

For the spray tower studies, a 5.047-inch diameter tower was employed. Contacting was achieved with a hollow cone spray nozzle through which an aqueous potassium hydroxide solution was pumped cocurrently to the gas stream. Because of the energy imparted to the gas stream by the high-velocity liquid spray, the tower operated under conditions of negligible pressure drop. Efficiencies of absorption ranging from 99.4 to 100 per cent were obtained for hydrogen fluoride and hydrogen bromide. Efficiencies ranging from 97.8 to 99.8 per cent were obtained for elemental bromine and fluorine at contact times of as low as 1.8 seconds. The chlorine, bromine, and fluorine from interhalogens were absorbed with very nearly the same efficiencies; all runs showed efficiencies greater than 90 per cent. Because carbon dioxide is absorbed with efficiencies of the same order of magnitude as those for halogens, the potassium hydroxide in the recycle tank is ultimately converted to potassium bicarbonate. This absorbs bromine at a somewhat slower rate than potassium hydroxide does. The average value of the HTU for the tower, for the absorption of halogens, was 0.6 foot.

## I. INTRODUCTION

An experimental program was undertaken to investigate means of safely and conveniently disposing of certain halogen-bearing materials from an air stream. Specifically, the unit would be required to remove from an exhaust system excessive amounts of hydrogen halides, interhalogens, and elemental halogens which would, if not removed, be discharged into the atmosphere.

Since the permissible level of concentration of halogens in air is very low, a very efficient unit is required. The maximum allowable continuous-exposure concentrations for typical halogen materials are as follows: bromine, 0.5 ppm; hydrogen bromide, 5 ppm; hydrogen fluoride, 1.5 ppm; fluorine, 1 ppm.<sup>1</sup>

Two methods presented in the literature showed sufficient promise to merit further investigation. The first method was that of Hignett and Siegel<sup>2</sup> who employed a bed of oölitic limestone to recover hydrogen fluoride in stack gases from the roasting of rock phosphate. A 4-foot bed packed with 1-1/2 to 1/4-inch particles of oölitic limestone gave efficiencies for the removal of hydrogen fluoride ranging from 71 to 96 per cent. The absorption was accomplished at temperatures ranging from 200 to 900°F. with the aid of recycle to remove the calcium fluoride fines and hence provide fresh reaction surface. They determined that the oölitic variety (the term "oölitic" referring to a large, rather open grain structure) was superior to the non-oölitic (fine grain structure) because the calcium fluoride reaction product held to the parent calcium carbonate less tenaciously. This permitted better removal of the calcium fluoride, which in turn promoted higher efficiencies of absorption.

The second method to achieve removal of halogens was that of absorption by gas-liquid contacting. Burford and Hamilton<sup>3</sup> employed a scrub tower with a spray plate through which an aqueous sodium hydroxide solution was recirculated. Using very low gas velocities and hence long contact times (about 1 minute), they reported essentially quantitative absorption for both fluorine and hydrogen fluoride.

Landau and Rosen<sup>4</sup> reported continuous absorption of fluorine and hydrogen fluoride in a packed tower (using a 5 to 10 per cent sodium hydroxide solution) to an exit gas concentration of less than 3 ppm. They recommended the use of contact times of 1 minute because of the initial rapid formation of  $OF_2$  from the reaction between fluorine and sodium hydroxide and a subsequent slower reaction between the  $OF_2$  and sodium hydroxide yielding sodium fluoride and oxygen.<sup>5</sup> Berly, *et al.*<sup>6</sup> effected the absorption of hydrogen fluoride by means of two successive stages of Saran fiber cells which were wetted by a spray of water, followed by a dry cell, to efficiencies greater than 99 per cent. At an air velocity of 216 ft./min., this unit gave a pressure drop of 4 inches of water.

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The purpose of this study, therefore, was to evaluate the two general methods of limestone absorption and gas-liquid absorption. For the limestone bed, this meant determining whether the absorption of both bromides and fluorides could be accomplished at room temperature with a bed depth which would give both a low pressure drop and a high efficiency. It was desirable, also, that the bed should have a capacity large enough to eliminate recycling.

For the scrub tower, it was deemed desirable to investigate the absorption, particularly of elemental fluorine and interhalogens, at contact times of the order of seconds rather than minutes (since a contact time of 1 minute would require a rather large tower for the average ventilating system).

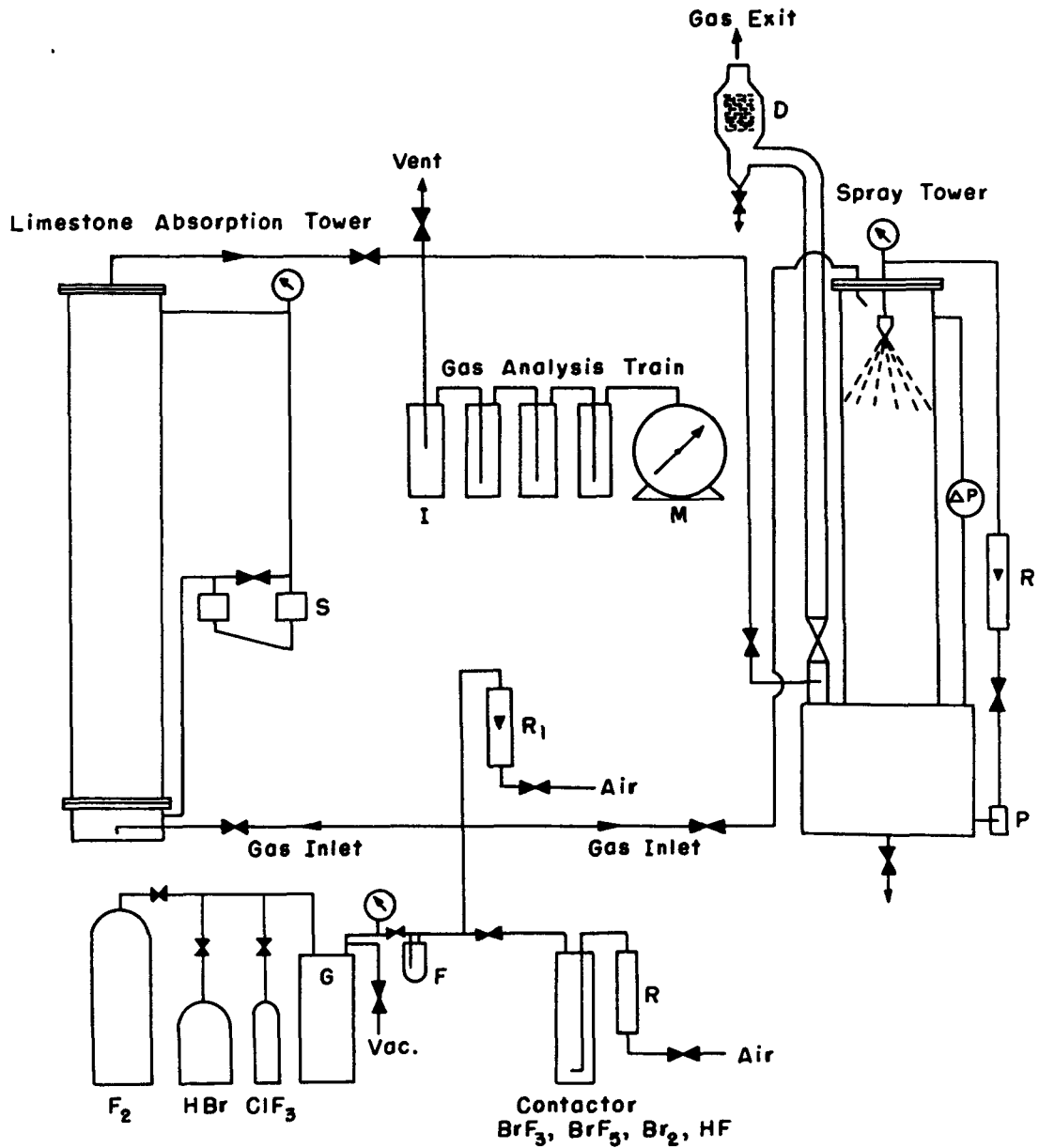
## II. METHOD OF INVESTIGATION

The runs for the absorption of halogens were made at ambient room temperature and at a pressure of approximately 1 inch of mercury above atmospheric. The air used was the low-pressure building supply which is dried by passing through a silica gel bed. Both the limestone and spray absorption towers were constructed of standard 5-inch iron pipe with flanged ends; the heights being 6 and 4 feet, respectively. Figure 1 shows a sketch of the equipment employed in this study. The pressure drop of the limestone bed was measured by an inclined manometer with mercury as the indicating liquid and monochlorotrifluoroethylene oil as the sealing liquid. This unit was calibrated to the nearest 0.05 inch over a range of 0 to 6 inches of water. For each run the limestone absorption tower was charged with a fresh bed of known weight.

The amount and composition of the inlet gas stream were determined by metering separately the air and halogen streams and then combining the two (mixing being accomplished by high-velocity turbulent flow). The air flows were measured with rotameters and corrected for temperature and pressure variations. The quantity of halogen added was determined by one of two methods. For bromine, bromine trifluoride, bromine pentafluoride, and anhydrous hydrogen fluoride, which have relatively low vapor pressures under the conditions employed, a contacting device was used in which a dry air stream was bubbled through the liquid halogen. The temperature was kept constant by pre-heating the air stream to supply the latent heat of vaporization. The loss in weight over a definite time interval gave the amount vaporized into the air stream. For fluorine, hydrogen bromide, and chlorine trifluoride, which were at rather high pressures (60 psig, 350 psig, and 15psig, respectively) in cylinders, it was necessary to fill a metering tank of known volume and from the drop in pressure calculate the amount added. However, for the runs at high inlet concentrations, the quantity of hydrogen bromide and chlorine trifluoride added was determined directly by the weight loss of the



FIGURE 1.  
EQUIPMENT FLOWSHEET.



R. Rotameter

P. Positive Displacement Pump

$\Delta P$ . Inclined Manometer - 1 inch Water Range

D. De-entraining Section;  $250 \mu$  Monel Fibers

M. Precision Wet Test Meter

I. Impingement Tube Trap

S. Seal Pots for Manometer

F. Flow Indicator Employing Monochlorotrifluoroethylene Oil

G. Gas Metering Tank

cylinder. After combination, the air-halogen stream entered a gas distributing section, flowing up through the bed in the limestone absorption tower. For the spray tower, the air-halogen stream entered the top of the tower, flowing down cocurrently with the aqueous potassium hydroxide solution which was used as the absorbing liquid. A Schutte-Koerting hollow cone, 60° spray nozzle with a 3.5-mm-diameter orifice was used to increase the area of contact of the liquid stream.

After passing through either tower, part of the gas stream was sent continuously through a gas analysis train and then metered. The main portion of the exit gas stream was vented. The solutions from the absorption train were then analyzed for halides. From these data the efficiency of absorption was calculated. The analysis for fluoride ion was performed spectrophotometrically using thoron reagent as described by Horton, *et al.*<sup>7</sup> The concentration of bromide ion was determined by a standard Volhard titration. The standard nephelometric analysis for silver chloride was used for the chloride analysis.

### III. RESULTS

#### A. Limestone Bed

The performance of the limestone bed is given in terms of efficiency of absorption as a function of capacity (the capacity is defined as the theoretical fraction of the bed consumed). Mass transfer coefficients were not calculated since the absorption is of the unsteady-state type.

For both a 66-inch bed and a 36.5-inch bed, elemental fluorine was completely removed until 0.02 per cent of the bed was consumed (as determined by the absence of fluorine odor and a negative test with potassium iodide starch paper). After this point, the efficiency declined at a slightly greater rate for the 36.5-inch bed; or, stated differently, an increased capacity results for the deeper bed. These data for the absorption of fluorine are summarized in Table 1. The relationship between capacity and efficiency is plotted in Figure 2. Run B, in which crushed marble (non-oölitic) with a depth of 19 inches was employed, shows a more rapid drop in efficiency despite the larger amount of surface available from the smaller particle size.

Run D in Table 1 shows that, within the limits of analytical accuracy, no absorption of elemental bromine takes place. The per cent of error based on the inlet concentration is 4.9 for Run D1 and 5.1 for Run D2.

A summary of the results obtained for the absorption of hydrogen halides with oölitic limestone is given in Table 2. The general pattern is that of initial absorption at high efficiencies followed by a rapid decrease in efficiency as the thickness of calcium fluoride or bromide film increased. Figure 3 shows the data from Table 2 plotted as the exit fluoride concentration,

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Table 1

ABSORPTION OF ELEMENTAL HALOGENS IN A LIMESTONE BED

Cross-sectional area of bed = 0.139 sq. ft.

Run No.	Air-Mass Velocity lb./hr. (sq. ft.)	Type of Limestone	Particle Size, inches	Bed Depth, inches	Halogen in Air Stream	Average Halogen Content		Efficiency of Absorption, per cent	Per Cent of Bed Reacted	
						Inlet Air, ppm*	Exit Air, ppm		Initially	Finally
A.**		oölitic	1/8-1/4	36.5	fluorine					
1.	68					1990	372	81.3	0	0.094
2.	63	1820	768	57.8	0.094	0.155				
B.		non-oölitic	1/64 ave.	19.0	fluorine					
1.	32					2800	431	84.6	0	0.062
2.	32					3780	2310	38.8	0.062	0.101
3.	32	7120	4800	32.5	0.101	0.143				
C.		oölitic	1/8-1/4	66.0	fluorine					
1.	63					3600	234	93.5	0	0.054
2.	63					4170	970	76.7	0.054	0.103
3.	63	3400	935	72.5	0.103	0.183				
D.		oölitic	1/8-1/4	35.5	bromine					
1.	62					11,720	12,300	0	0	0
2.	62	13,820	14,500	0	0	0				

\*ppm defined as  $\frac{\text{grams halide}}{10^6 \text{ grams air}}$

\*\*For runs A and C, the fluorine was absorbed with 100 per cent efficiency until 0.02 per cent of the bed was reacted.

FIGURE 2.

ABSORPTION OF FLUORINE FROM AN AIR  
STREAM WITH A LIMESTONE BED.

- Run A: 36.5 in. Bed Depth,  $\frac{1}{8}$ - $\frac{1}{4}$  in. Particles - Oölitic
- Run B: 19.0 in. Bed Depth,  $\frac{1}{64}$  in. Particles - Crushed Marble
- Run C: 66.0 in. Bed Depth,  $\frac{1}{8}$ - $\frac{1}{4}$  in. Particles - Oölitic

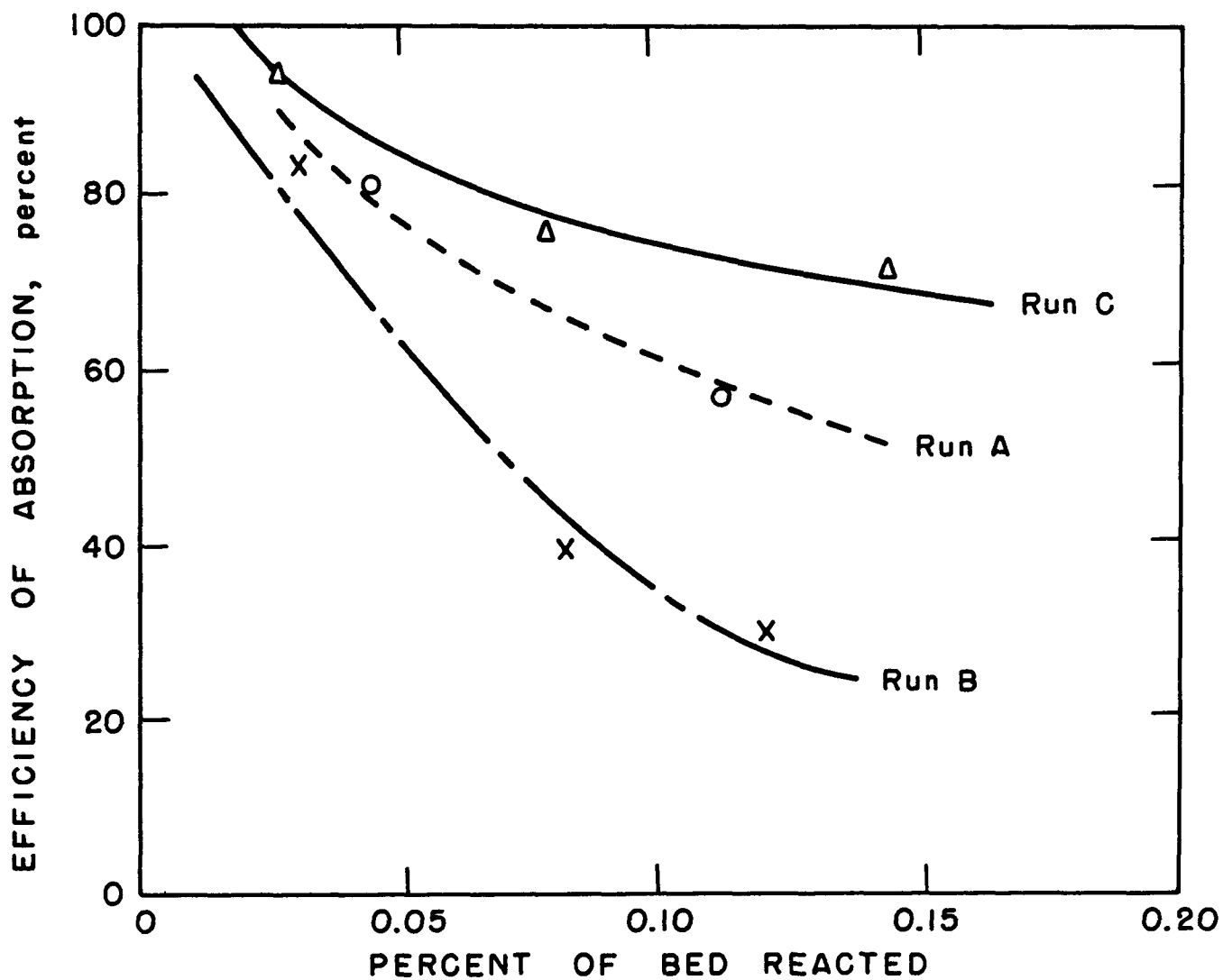


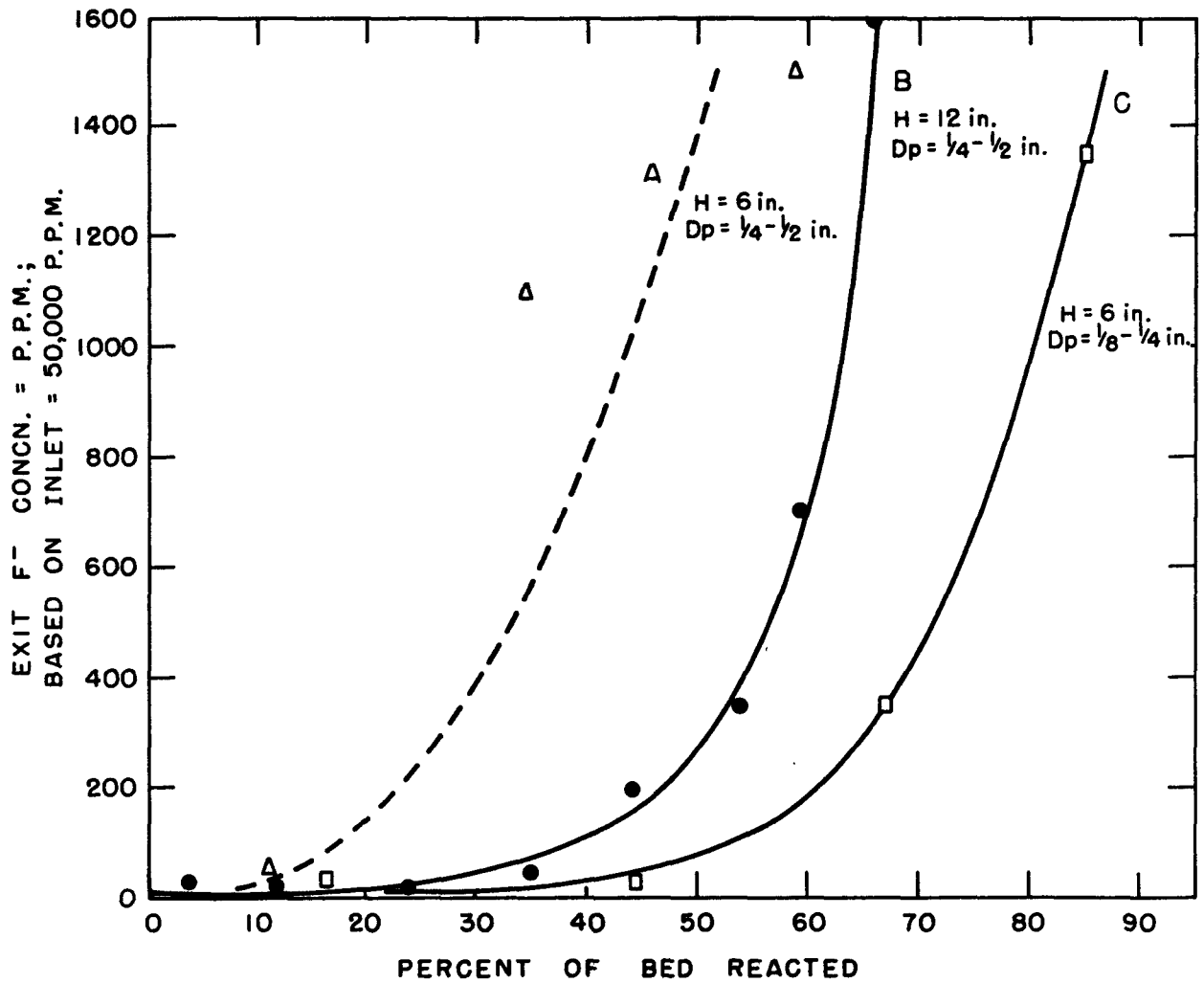
Table 2

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ABSORPTION OF HYDROGEN HALIDES IN AN OÖLITIC LIMESTONE BED

Run No.	Air-Mass Velocity lb./ (hr.) (sq. ft.)	Particle Size, inches	Bed Depth, inches	Halogen in Air Stream	Average Halogen Content		Efficiency of Absorption, per cent	Per Cent of Bed Reacted	
					Inlet Air, ppm	Exit Air, ppm		Initially	Finally
A.		1/4-1/2	6	hydrogen fluoride					
1.	135				54,600	48	99.9	0	21.7
2.	133				94,600	2130	97.8	21.7	47.4
3.	136				55,400	1660	97.0	47.4	69.6
B.		1/4-1/2	12	hydrogen fluoride					
1.	135				48,300	28	99.9 <sup>+</sup>	0	6.5
2.	134				53,500	14	99.9 <sup>+</sup>	6.5	17.1
3.	136				57,500	17	99.9 <sup>+</sup>	17.1	28.9
4.	135				60,300	68	99.9	28.9	40.8
5.	135				53,000	230	99.6	40.8	48.8
6.	137				61,800	453	99.3	48.8	57.0
7.	138				39,200	546	98.6	57.0	62.5
8.	137				33,100	1060	96.8	62.5	69.0
C.		1/8-1/4	6	hydrogen fluoride					
1.	140				78,500	63	99.9	0	32.6
2.	138				80,000	38	99.9	32.6	55.5
3.	138				60,000	419	99.3	55.0	78.3
4.	146				68,000	1830	97.3	78.3	91.7
D.		1/4-1/2	24	hydrogen bromide					
1.	65				27,400	0	100.0	0	0.30
2.	68				25,700	174	99.3	0.30	0.60
3.	66				13,200	1102	91.6	0.60	0.74

FIGURE 3.  
 ABSORPTION OF HYDROGEN FLUORIDE FROM AN  
 AIR STREAM IN A LIMESTONE PACKED TOWER.



referred to a standard feed concentration, versus capacity expressed as the per cent of the bed reacted. Runs A and B compare the absorption for the same particle size but for different bed depths. The plot shows that the 12-inch bed has both a larger capacity and a higher initial efficiency than the 6-inch bed. Any comparison must necessarily be made at some definite level of efficiency. For example, if one takes from Figure 3 an exit fluoride concentration of 250 ppm (corresponding efficiency equals 99.5 per cent), it is seen that the 6-inch bed will continue to absorb hydrogen fluoride at an efficiency greater than 99.5 per cent until 25 per cent of it is reacted, whereas the 12-inch bed will continue to do so until it is 50 per cent reacted. The proportionality between efficiency and capacity is due to the greater time and area of contact for the deeper bed which in turn allows more diffusion through the calcium fluoride film to the reactive calcium carbonate.

By now comparing Curves A and C in Figure 3 it can be seen that the capacity is proportional to the surface area. Since the per cent voids for the two beds are approximately equal, the total surface area varies inversely as particle diameter, assuming a uniform distribution.

Because of the high inlet concentrations employed, the absorption was great enough for the heat of reaction to cause a rise in temperature of the bed of 12°C. The zone of reaction (as indicated by the temperatures along the length of the bed) moved upward as the bed became exhausted.

The results on the absorption of hydrogen bromide are shown in Figure 4. The plot shows that after only 0.5 per cent of the bed is reacted, the efficiency begins to fall rather rapidly even with a 24-inch bed depth.

The results obtained for the absorption of interhalogens are given in Table 3. For bromine trifluoride, the fluoride is absorbed with an efficiency greater than 99 per cent for a bed depth as low as 12 inches. The bromide, however, is absorbed with low efficiencies and capacities even with a rather deep bed of 66 inches as shown in Run D. (It is to be noted that up to the very low capacity of 0.001 per cent of the bed consumed, 100 per cent efficiency was attained for both the bromide and the fluoride absorption. This corresponds to formation of a film thickness of reaction products of less than a micron on the calcium carbonate.) The relationship between efficiency and capacity for the 66-inch bed is shown in Figure 5. The plot illustrates a rapid decline in bromide absorption at a low capacity.

Run D4 (Table 3) shows that increasing the contact time to 30 seconds gives only a slight improvement in the bromide absorption. Run E, in which the air stream was humidified to an average value of 40 per cent, shows only a slight improvement for the bromide absorption. (The efficiencies do not fall into a consistent pattern because of the corrosion which took

FIGURE 4.

ABSORPTION OF HYDROGEN BROMIDE FROM AN  
AIR STREAM WITH A LIMESTONE BED.

24 in. Bed Depth,  $\frac{1}{4}$  -  $\frac{1}{2}$  in. Particles - Oölitic

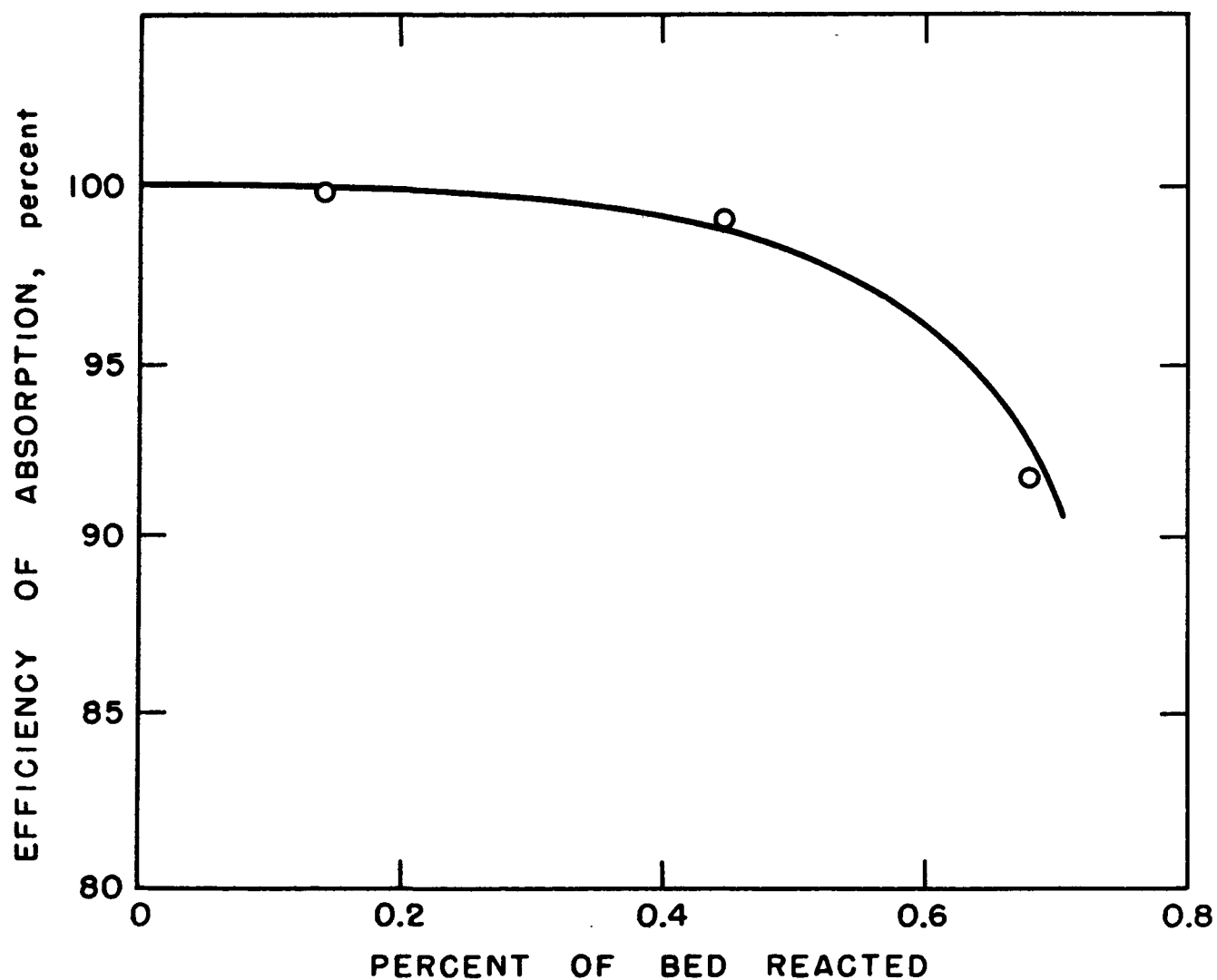




Table 3

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ABSORPTION OF INTERHALOGENS IN AN OÖLITIC LIMESTONE BED

Run No.	Air-Mass Velocity lb./hr. (sq.ft.)	Halogen in Air Stream	Bed Depth,* inches	Average Halogen Content			Efficiency of Absorption, per cent		Per Cent of Bed Reacted	
				Inlet Air, ppm total	Exit Air, ppm		Fluoride	Bromide	Initially	Finally
					Fluoride	Bromide				
A.										
1.	26	bromine trifluoride	12.5	8290	13	4070	99.6	15.9	0	0.116
B.										
1.	62	bromine trifluoride	24.0	2810	5	1130	99.6	31.1	0	0.104
2.	62			2760	2	1210	99.8	24.8	0.104	0.299
3.	66			2333	2	1200	99.8	11.8	0.299	0.515
4.	62			2430	2	1240	99.8	12.7	0.515	0.865
C.										
1.	89	bromine trifluoride	48.0	1662	3	720	99.6	25.8	0	0.062
2.	89			1672	2	823	99.7	15.6	0.062	0.117
3.	84			1168	2	750	99.6	0.0	0.117	0.234
D.**										
1.	89	bromine trifluoride	66.0	2110	10	395	99.0	67.9	0	0.051
2.	88			1804	9	667	98.8	36.7	0.051	0.090
3.	88			1804	7	802	99.1	23.8	0.090	0.128
4.	25			6480	11	2540	99.6	32.8	0.128	0.202
E.***										
1.	66	bromine trifluoride	24	1937	1	31	99.9	97.3	0	0.228
2.	68			2585	2	171	99.8	88.7	0.228	0.310
3.	67			2615	1	573	99.9	62.5	0.310	0.387
4.	83			1888	24	847	97.0	23.0	0.387	0.478
5.	87			2615	2	528	99.8	65.4	0.478	0.708
6.	67			2615	1	785	99.9	48.5	0.708	0.998
F.										
1.	64	bromine pentafluoride	37	21,220	1400	981	87.8	89.9	0	1.90
2.	64			16,910	588	589	93.6	92.4	1.90	2.53
3.	63			14,770	992	5570	87.8	17.5	2.53	2.58
4.	63			18,800	513	8350	95.0	3.0	2.58	3.66
G.										
1.	64	chlorine trifluoride	36	9,980	267	2250	95.7	41.2	0	0.193
2.	65			10,760	365	2990	94.5	27.6	0.193	0.394
3.	66			10,280	405	3280	93.6	17.0	0.394	0.527

\*1/8 to 1/4-inch particles used for all runs with interhalogens.

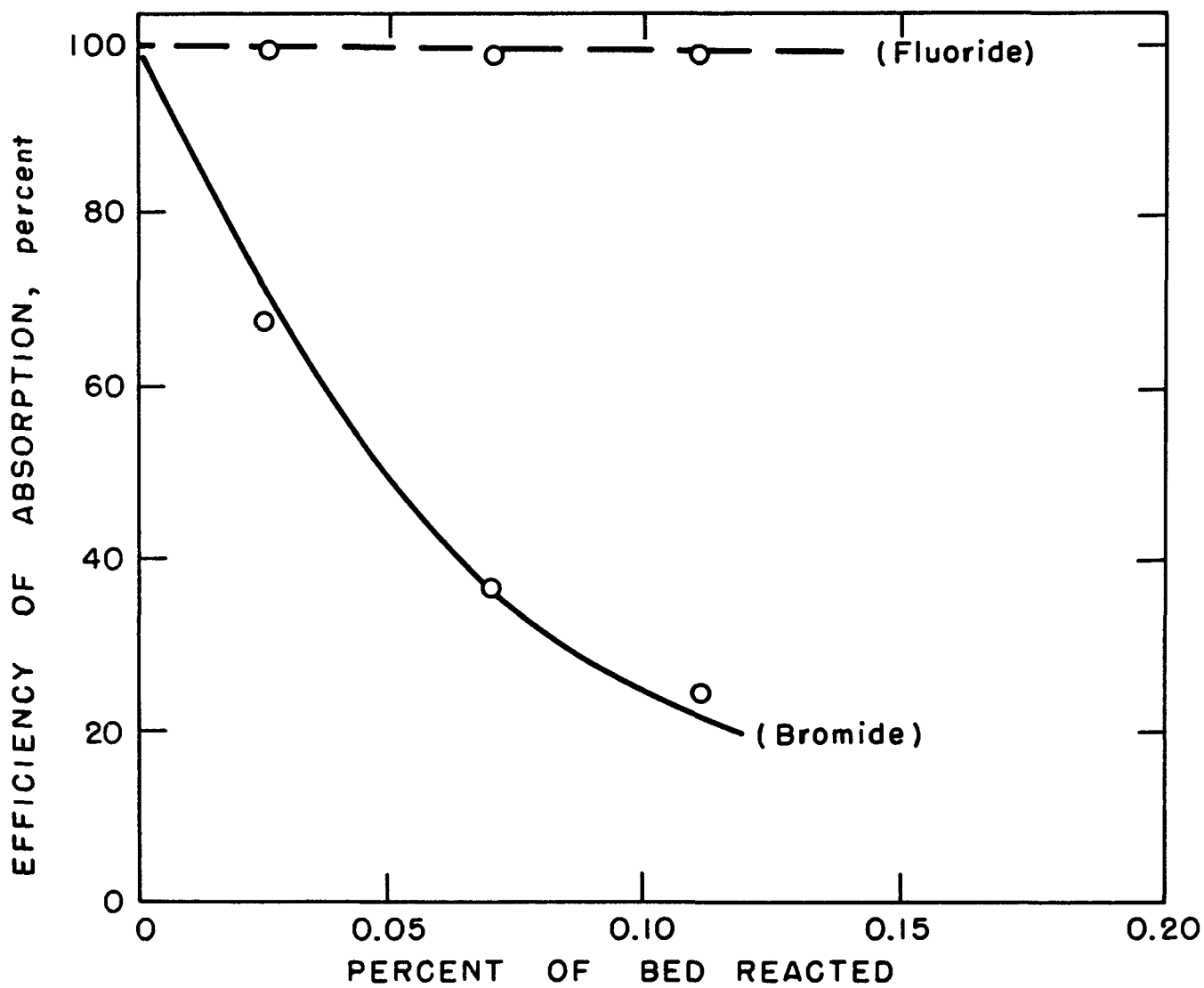
\*\*For run D, the bromine trifluoride was absorbed with 100 per cent efficiency until 0.001 per cent of the bed was reacted.

\*\*\*Air at average of 40 per cent relative humidity for Run E.

FIGURE 5.

ABSORPTION OF BROMINE TRIFLUORIDE FROM AN  
AIR STREAM WITH A LIMESTONE BED.

66 in. Bed Depth,  $\frac{1}{8}$  -  $\frac{1}{4}$  in. Particles - Oölitic



place throughout the equipment.) This information, in addition to the rapid decrease in efficiency at a low capacity for anhydrous hydrogen bromide, indicates that hydrolysis of the interhalogens to the hydrogen halides before entering the calcium carbonate bed would not be a satisfactory solution to the bromine absorption problem.

The absorption of bromine pentafluoride and chlorine trifluoride from an air stream is shown in Runs F and G, respectively, of Table 3. Despite the slight scatter in the efficiencies, it can be seen that the bromide from bromine pentafluoride is absorbed somewhat better than the bromide from bromine trifluoride and at slightly higher capacities. The absorption of chlorine trifluoride is shown in Figure 6. As with the other interhalogens, the fluoride is absorbed at a relatively high efficiency whereas the chloride absorption declines steadily from an initial value of only 41 per cent.

At the conclusion of any given series of runs it was noted that when air alone was passed through the packed tower or when a partially exhausted bed was discharged from the tower, a slight halogen odor could be detected regardless of the solute gas used. These observations suggest that physical absorption (as distinct from a chemical reaction which converts the solute gas to a calcium halide) accounted for a portion of the total absorption.

Besides efficiency and capacity, another important characteristic to be determined is the pressure drop that a bed will offer at a given gas velocity. The results of numerous measurements (for five different beds of various depths and two different particle sizes) are shown in Figure 7. The data were correlated by plotting the pressure drop per unit of length versus the ratio of the air mass velocity to the porosity of the bed. The porosities ranged from 34 to 42 per cent. The ratio  $\Delta P / \rho L$  varied as the 1.3 power of  $G/F$ . The pressure drop for the 1/4 to 1/2-inch particles, at any given  $G/F$  ratio, is 1/4 that for the 1/8 to 1/4-inch particles, thus indicating that the pressure drop varies inversely as the square of the particle diameter in this range. It is emphasized that the purpose here was to measure the pressure drop of the limestone just as received and used with no screening to restrict the particle size to a more limited range or to eliminate the fines. Where particles with little size variation are employed (with no fines), this plot will give high results. For this application, the pressure drop can be predicted by use of the data of Fujita and Uchida,<sup>8</sup> who used particles of limestone of a highly restricted size range.

### B. Spray Tower

At a gas rate of 200 lb./hr. (sq.ft.) and a liquid rate of 5800 lb./hr. (sq.ft.) the cocurrent spray tower operated under conditions of no pressure drop (the gas emerged at a pressure of 0.10 inch of water greater than that at which it entered the tower as determined by an inclined manometer).

FIGURE 6.

ABSORPTION OF CHLORINE TRIFLUORIDE FROM AN  
AIR STREAM WITH A LIMESTONE BED.

36 in. Bed Depth,  $\frac{1}{8}$  -  $\frac{1}{4}$  in. Particles - Oölitic

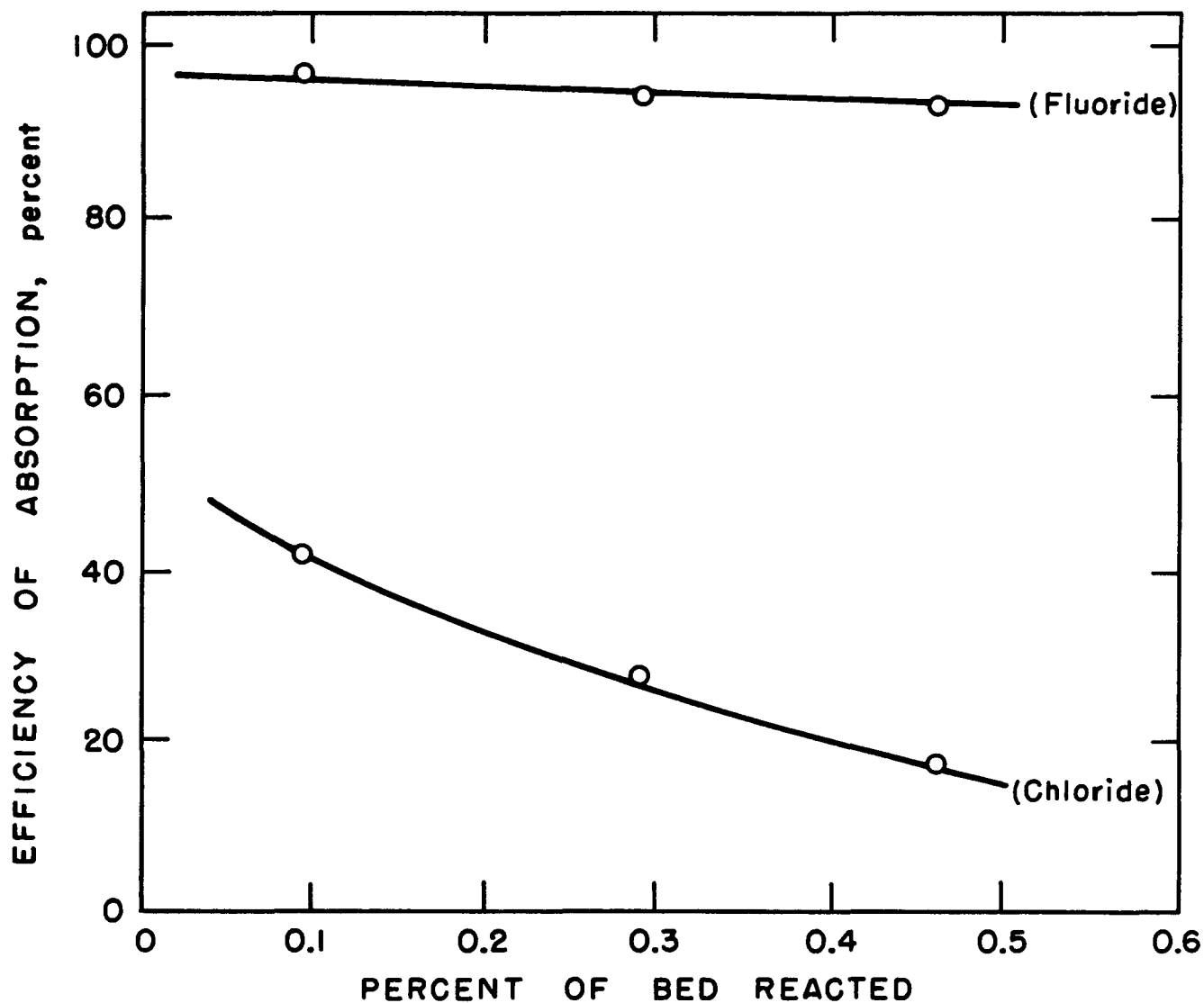
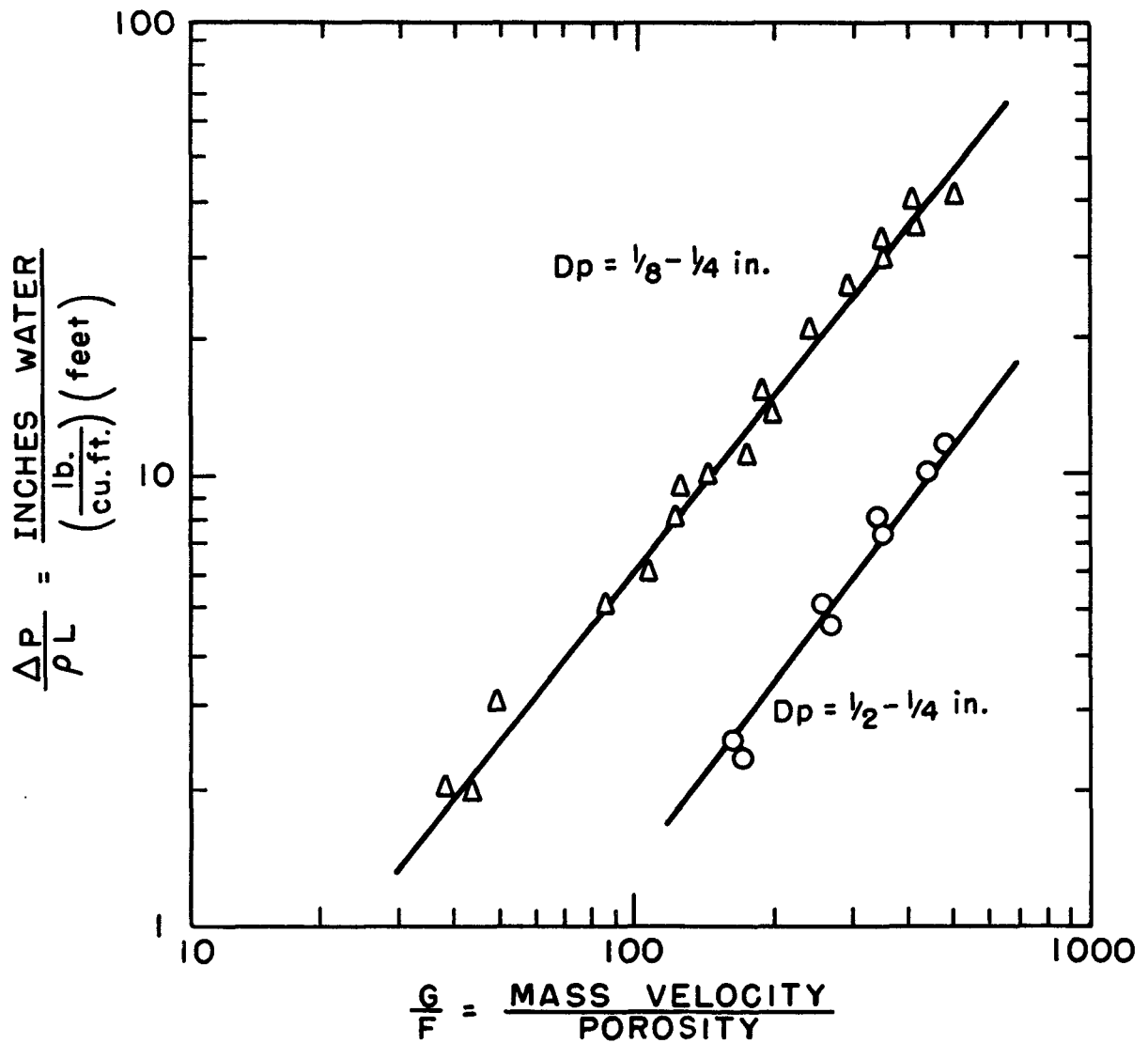


FIGURE 7.  
 PRESSURE DROP IN A 5.047 in.-I. D. TOWER  
 PACKED WITH PARTICLES OF OÖLITIC LIMESTONE.



A Monel fiber de-entraining section 4 inches in depth was used in the exit gas line; this removed the liquid droplets entrained in the gas stream up to velocities of 8 ft./sec. Air velocities higher than this were not employed. Two preliminary runs with fluorine and bromine trifluoride in air were made to test the operation of the equipment. These runs were rejected because entrainment of the liquid containing some potassium fluoride gave spuriously low efficiencies. Modification of the gas sampling probe, improvement of the impingement de-entraining device, and employing lower flow rates through the gas analysis train eliminated this problem in subsequent runs.

The results obtained for the absorption of elemental halogens and hydrogen halides are shown in Table 4. A comparison of Runs A1 and A2 for the absorption of fluorine shows that reducing the tower height from 3.5 to 2.0 feet (and hence lowering the time of contact since the gas velocity is constant) does not decrease the efficiency. This lack of variation of efficiency with length of the spray stage indicates that the bulk of the absorption occurs in the first few inches of contacting section following the spray nozzle. For Runs A3 and A4 all variables were held constant except the concentration of potassium hydroxide in the absorbing liquid, which is 10 per cent by weight for Run 3 and 5 per cent for Run 4. This decrease in concentration of potassium hydroxide causes a slight drop in the efficiency of absorption from 98.4 to 97.8 per cent. In both Runs A3 and A4 very high efficiencies were achieved at the lowest attainable liquid rate at which the spray nozzle could be run to give a full spray (0.9 g./min.). The contact time of the gas stream in these runs was only 1.8 seconds.

The influence of a reducing agent on the efficiency of absorption of bromine is negligible as shown in Runs A5 and A6. Making the absorbing potassium hydroxide solution 0.3 M in sulfite ion concentration gave substantially the same efficiency (99.6 per cent as compared to 99.8 per cent) as a 10 per cent potassium hydroxide solution with no reducing agent. Doubling the gas rate, all other variables being constant, gave essentially the same efficiency, as shown in Runs A7 and A8.

Part B of Table 4 shows the absorption of hydrogen halides in the spray tower. In Run B1, hydrogen fluoride is absorbed quantitatively (no fluoride ion in the analysis train and no detectable odor in the exit gas stream). Runs B3 and B4 show that over a threefold range of inlet bromide concentrations, all else being constant, the efficiency of absorption changes from 99.7 per cent at the higher inlet concentration (and hence the higher driving force) to 99.4 per cent at the lower concentration. These two results are practically equal. Decreasing the length of the spray stage, at a constant gas and liquid rate, yielded no change in efficiency as shown in Runs B5 and B6.

Table 4

ABSORPTION OF ELEMENTAL HALOGENS AND HYDROGEN HALIDES IN A 5.047-INCH DIAMETER SPRAY TOWER

Run No.	Absorbed Gas	Tower Ht., feet	Air Rate $G^1$ , lb./(hr.) (sq.ft.)	Liquid Rate L,* lb./(hr.) (sq.ft.)	Inlet Conc., $C_1$ - ppm	Exit Conc., $C_2$ - ppm	Efficiency of Absorption, per cent	HTU, feet
A. 1	F <sub>2</sub>	3.5	215	6750	1,850	30	98.4	0.85
2	F <sub>2</sub>	2.0	208	5800	952	7	99.3	0.41
3	F <sub>2</sub>	2.0	344	3460	4,510	74	98.4	0.49
4	F <sub>2</sub>	2.0	353	3460	2,510	56	97.8	0.53
5	Br <sub>2</sub>	3.5	110	5800	64,500	115	99.8	0.55
6	Br <sub>2</sub>	3.5	110	5800**	38,000	140	99.6	0.63
7	Br <sub>2</sub>	3.5	109	5800	6,300	37	99.4	0.68
8	Br <sub>2</sub>	3.5	218	5800	6,500	23	99.7	0.62
B. 1	HF	3.5	214	5800	32,400	0	100.0	-
2	HBr	3.5	216	3460	69,000	367	99.5	0.67
3	HBr	3.5	219	4620	14,500	50	99.7	0.62
4	HBr	3.5	209	4620	3,930	22	99.4	0.67
5	HBr	3.5	214	5800	8,900	9	99.9	0.51
6	HBr	2.0	213	5800	6,700	8	99.9	0.30

\*A 10 per cent aqueous KOH solution for all runs except A4; A4 = 5 per cent KOH.

\*\*Liquid made 0.3 M in SO<sub>3</sub>

The results obtained for the absorption of interhalogens are given in Table 5. Runs 1 and 2 indicate 100 per cent efficiency for chloride absorption from chlorine trifluoride. The fluoride and chloride efficiencies remained essentially constant over a twofold gas rate change (109 to 217 lb./hr.)(sq.ft.). The same pattern is shown for Runs 5 and 6 for the absorption of bromine trifluoride where the gas rate was changed from 221 to 342 lb./hr.)(sq.ft.). Runs 3 and 4, for the absorption of bromine pentafluoride from an air stream, were made to evaluate the reproducibility of the data. The mass velocity of the air stream (corresponding contact time for  $G = 357$  lb./hr.)(sq.ft.) is 1.7 seconds), the liquid rate (5 per cent potassium hydroxide), and the inlet concentration were held as constant as possible for both runs. The variation in the efficiency of fluoride absorption is 99.3 and 99.5 or  $\pm 0.1$  from the mean; the bromide absorption efficiency varies from 98.9 to 98.6, representing a deviation of  $\pm 0.15$  from the mean. Material balances varied quite widely. The main cause of this variation is that the combining of aqueous and halogen materials is a corrosive operation giving rise to the alternate formation and removal of fluoride and bromide films. Considering this limitation, the values obtained are satisfactory (the material balances ranged from 73 to 141 per cent for the hydrogen halides, 59 to 116 per cent for the interhalogens, and 67 to 144 per cent for the elemental halogens).

The relationship between  $L$ , the mass velocity of the liquid stream, and the height of a transfer unit (and hence efficiency) is shown in Runs 6 and 7 for the absorption of bromine trifluoride. (It has been shown that the gas rate has little influence on the efficiency over the range employed in this investigation.) Lowering  $L$  from 5800 to 3460 lb./hr.)(sq.ft.) increases the HTU from 0.62 to 0.85 (average value). The greater number of transfer units at the higher flow is due to the increase in the number of droplets and hence the interfacial area. Runs A2 and A3 for fluorine show the same variation. Here, lowering  $L$  by the same amount increases the HTU from 0.41 to 0.49. Runs B2 through B5 for the absorption of hydrogen bromide (at constant gas velocity) again show this relationship. The values of  $L$  of 3460 and 5800 (nozzle pressures are 10 and 38 psig, respectively) represent the minimum and maximum flows that could be achieved with the particular nozzle and pump employed. The variation between  $L$  and HTU is plotted in Figure 8 for purposes of comparison.

The values for the HTU were calculated by means of the equation  $HTU = \frac{H}{N_T}$ ; where  $H$  = tower height in feet, and  $N_T$  is the number of transfer units. Under conditions of absorption accompanied by a rapid, irreversible chemical reaction, the equilibrium partial pressure ( $Y_e$ ) is zero; hence for dilute gases, the equation  $N_T = \int_{Y_1}^{Y_2} \frac{dY}{Y - Y_e}$  simplifies to  $N_T = 2.3 \log Y_2/Y_1$ .



Table 5

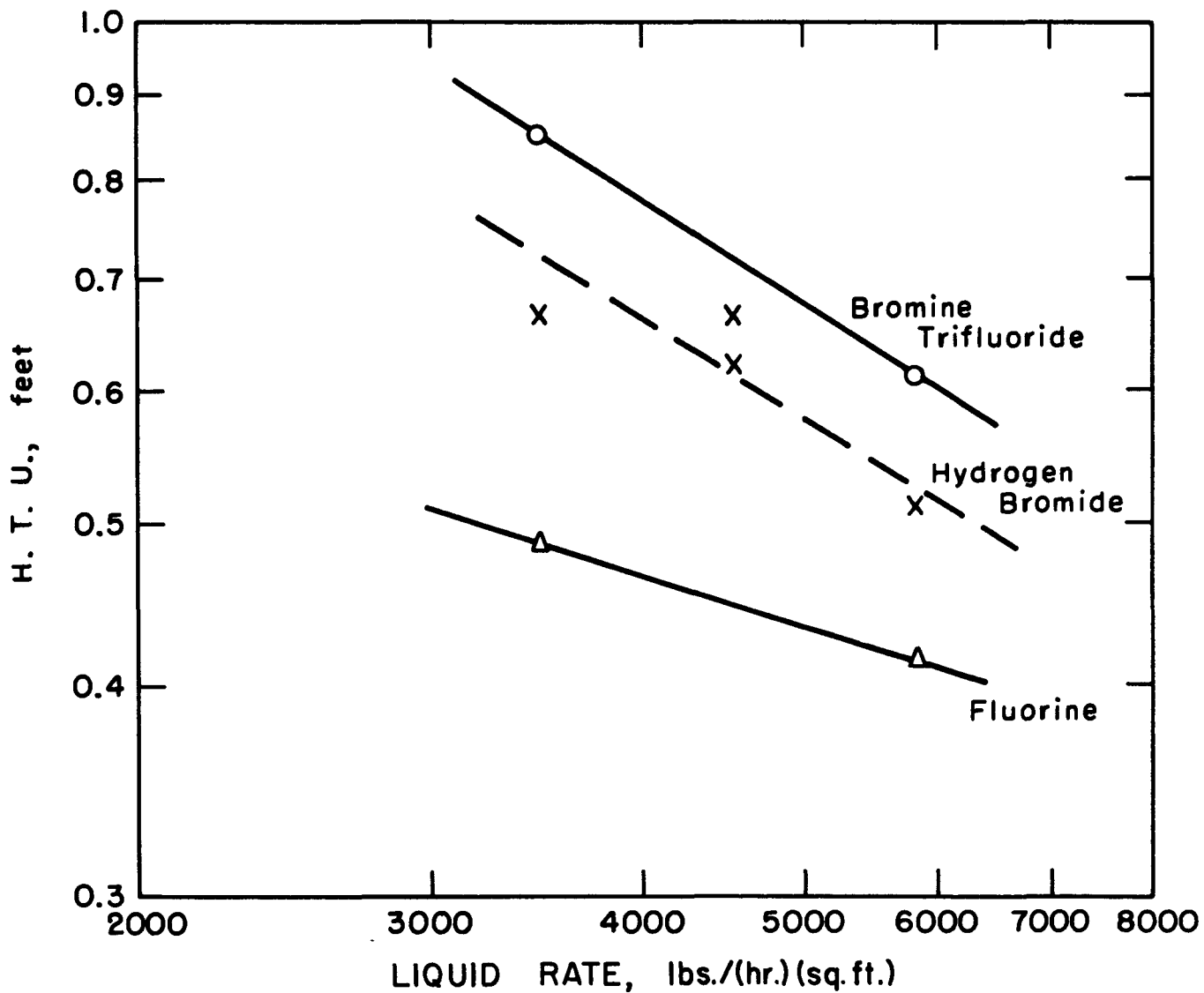
ABSORPTION OF INTERHALOGENS IN A 5.047-INCH DIAM. SPRAY TOWER

Run No.	Absorbed Gas	Tower Height, feet	Stream Rate, lb./ (hr.) (sq. ft)		Total Inlet Concentration, ppm	Exit Concentration, ppm		Efficiency of Absorption, per cent		Ave. HTU, feet
			Air	Liquid*		Fluoride	Chloride	Fluoride	Chloride	
1	ClF <sub>3</sub>	3.5	109	5800	13,750	93	0	98.9	100.0	0.78**
2	ClF <sub>3</sub>	3.5	217	5800	19,230	46	0	99.6	100.0	0.63**
							(bromide)		(bromide)	
3	BrF <sub>5</sub>	2.0	357	3460	13,520	50	70	99.3	98.9	0.42
4	BrF <sub>5</sub>	2.0	345	3460	11,600	29	74	99.5	98.6	0.42
5	BrF <sub>3</sub>	2.0	342	5800	2,415	18	46	98.2	96.7	0.55
6	BrF <sub>3</sub>	2.0	221	5800	1,400	23	32	96.1	96.1	0.62
7	BrF <sub>3</sub>	2.0	331	3460	864	32	50	91.1	90.1	0.85

\*A 10 per cent aqueous potassium hydroxide solution for all runs except 3 and 4; for these a 5 per cent solution was used.

\*\*Values for fluoride absorption.

FIGURE 8.  
ABSORPTION OF HALOGENS IN A  
5.047 IN.-DIA. SPRAY TOWER.  
2 ft. Tower Height, Cocurrent Operation



For the values of Y in mol fraction, the corresponding values of C in parts per million can be substituted with an error of less than 2 per cent (since the values of Y are small and appear as a ratio). The equations

$$\text{HTU} = \frac{H}{2.3 \log C_2/C_1} = \frac{G}{K_g a P}$$

show the relationship between the height of tower, the number of transfer units, and the mass transfer coefficient for the type of absorption and the range of concentrations involved in this study. It was chosen to express the tower performance in terms of the HTU since it afforded a ready means of comparison to other data published in literature on countercurrent spray towers.

At the conclusion of the halogen absorption studies, two runs were made to determine the rate of conversion of potassium hydroxide to potassium carbonate in the recycle tank by absorption of carbon dioxide from the air. The results obtained are shown in Figure 9. From the data it was estimated that during the first 18 hours of operation the degree of absorption was of the same order as the results obtained for the absorption of halogens by the spray tower. During the next 22 hours of operation the extent of carbon dioxide absorption decreased to 35 per cent as the carbonate content of the caustic increased. These estimates were based on an inlet concentration of 530 grams of carbon dioxide/10<sup>6</sup> grams of air.<sup>9</sup> The results are comparable to those obtained by Spector and Dodge<sup>9</sup> in a packed tower with similar gas and liquid rates. With continued absorption of carbon dioxide, the potassium carbonate is converted to potassium bicarbonate. The pH of a potassium carbonate solution, whose initial value is 11.2, is lowered to 9.0 with 80 per cent conversion to the bicarbonate.<sup>10</sup> Because of the depletion in hydroxide ion concentration with carbon dioxide absorption, batch experiments were performed to compare the rates of bromine absorption with potassium hydroxide and potassium carbonate solutions of equal concentrations. The results showed qualitatively that the rate of bromine absorption was slower with the potassium carbonate.

#### IV. DISCUSSION OF RESULTS

It is of interest to note the relatively poor absorption of elemental fluorine as compared to hydrogen fluoride, which is absorbed both with high efficiencies and capacities. In analogy to the reaction between fluorine and a caustic solution where OF<sub>2</sub> is formed as a product of the first reaction, one might expect that with calcium carbonate the following would take place:

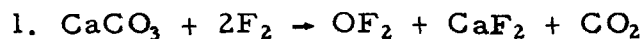
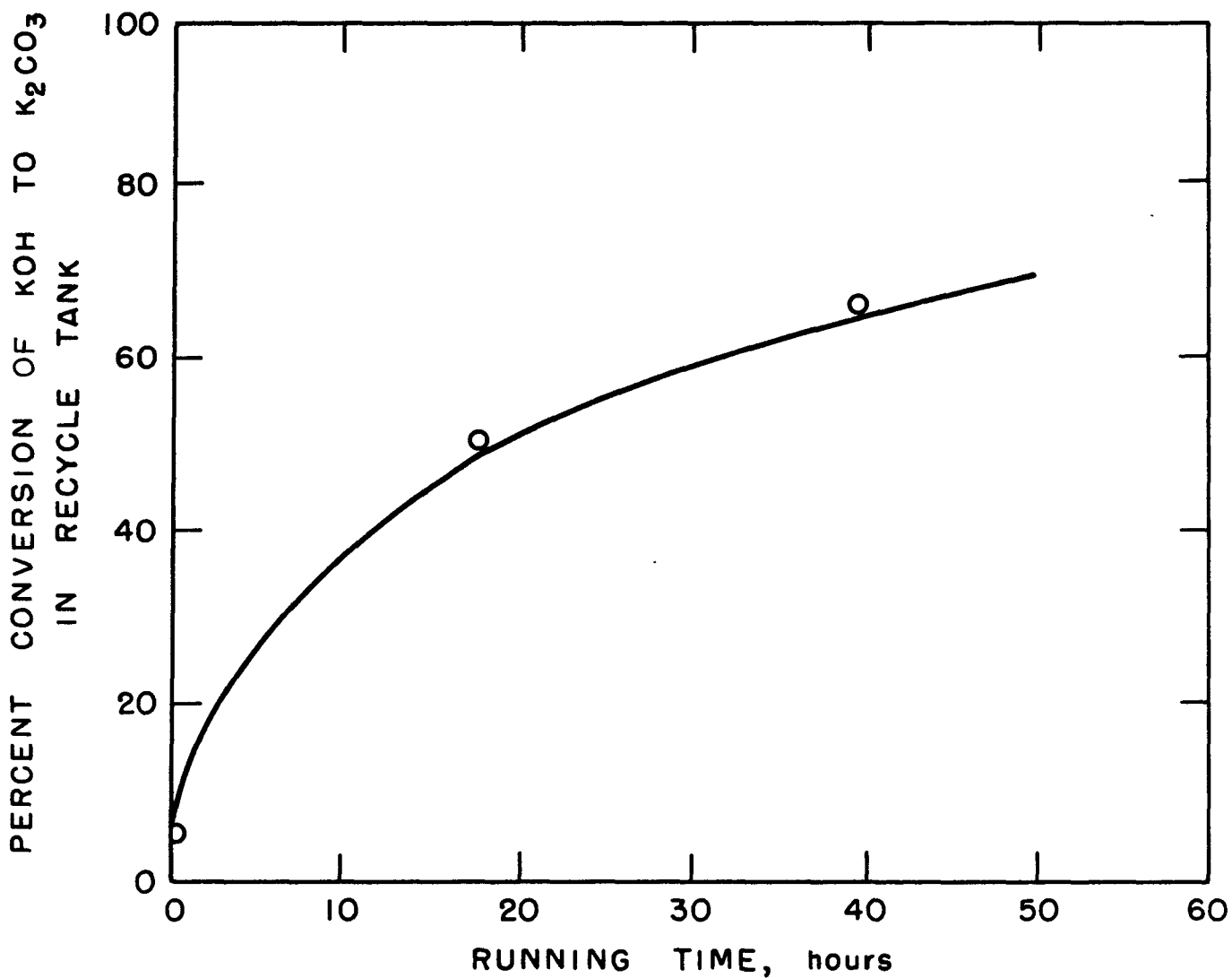


FIGURE 9.

## RATE OF ABSORPTION OF CARBON DIOXIDE.

Test Conditions: Air Rate: 100 lb./hr.(sq. ft.)  
Liquid Rate: 3460 lb./hr.(sq. ft.)  
4.6 percent KOH initially



The rate of the second reaction would be slower than the first because of the high energy of activation of  $\text{OF}_2$  as compared to that for fluorine,<sup>11</sup> thus permitting much  $\text{OF}_2$  to pass through the tower. Should  $\text{OF}_2$  be formed, it would be unsatisfactory to have large quantities of fluorine come in contact with a limestone bed since  $\text{OF}_2$  is even more undesirable than fluorine itself as regards toxicity.<sup>11</sup> However, with hydrogen fluoride a simple displacement reaction occurs, giving calcium fluoride and no  $\text{OF}_2$  ( $\text{CaCO}_3 + 2\text{HF} \rightarrow \text{CaF}_2 + \text{CO}_2 + \text{H}_2\text{O}$ ).

It is also interesting to note that for the absorption of hydrogen fluoride in both a 6-inch and a 12-inch bed, with the same particle size, over the initial range where steady-state conditions prevail (as shown in Figure 3 on the plot of the exit fluoride concentration versus the per cent of bed reacted), a slight improvement in efficiency results but with a marked increase in capacity. The data show that one 6-inch bed gives an initial efficiency of 99.9 per cent, thereby reducing the inlet concentration from 54,600 to 48 ppm; one might then expect that the next 6-inch depth would remove 99.9 per cent of what enters it, thus giving a final exit concentration of less than 1 ppm. However, the data show that the exit concentration for the 12-inch bed initially is an average of 20 ppm, thus giving an efficiency of about 60 per cent for the second 6-inch thickness. Thus the assumption of "equal percentage absorption per stage" does not hold as the fluoride concentration in the air stream becomes very dilute, probably because of the increased difficulty in diffusing both across the gas film and the calcium fluoride film as the driving force is decreased. (The average film thickness of the calcium fluoride coating at which the efficiency began to decrease sharply was 1/16 inch calculated on the basis of average particle size.)

The influence of variables upon the efficiency of absorption (and hence the number of transfer units) for the spray tower is summarized qualitatively for purposes of discussion:

1. Gas Rate (contact time)

There is no detectable effect over the range 100 to 360 lb./hr.(sq. ft).

2. Inlet Halide Concentration

With inlet concentrations up to 69,000 ppm, no improvement in efficiency results.

3. Type of Halogen

All elemental halogens, hydrogen halides, and interhalogens are absorbed with efficiencies greater than 90 per cent in one spray stage.

#### 4. Liquid Rate

The efficiency of absorption varies approximately as the liquid rate to the one-half power. (A nozzle pressure of 10 psig is required to give a full spray.)

#### 5. Spray Contacting Length

Most of the absorption occurs in the first few inches of spray from the nozzle; hence, a greater number of transfer units per unit of tower length are obtained with a short spray section.

#### 6. Potassium Hydroxide

Both 5 and 10 per cent potassium hydroxide solutions gave equal rates of absorption.

Over a somewhat limited range of gas rates the efficiency appeared to be independent of the contact time of the gas phase; however, as indicated by Burford and Hamilton,<sup>3</sup> with contact times of about 1 minute the fluorine concentration could be reduced to a value less than 5 ppm as compared to the values of 56 and 74 ppm which were attained in this study at contact times of 1.8 seconds.

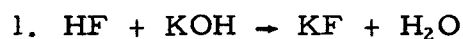
The lack of variation of efficiency with inlet concentration indicates that even at very low inlet concentrations (in the order of 100 ppm) one can still expect good absorption.

The fact that all halides investigated, covering a wide range of reactivity and physical properties such as density, viscosity, and diffusivity, are absorbed with high efficiencies is the best measure of the performance of the spray tower as contrasted to the limestone bed. The data relating the number of transfer units and the liquid rate show that, in general,  $N_T$  varies as  $L^{0.5}$ . Pigford and Pyle,<sup>12</sup> for the absorption of ammonia in a countercurrent spray tower, found that the number of transfer units varied directly as the liquid rate. Their data also showed that the surface area of the liquid stream was approximately proportional to the liquid rate. Their work substantiates the observation made herein that more transfer units per unit of tower length are obtained with a shorter spray section.

It is probable that the use of potassium hydroxide rather than sodium hydroxide is one of the two factors which contributed to high efficiency of fluorine absorption at contact times of as low as 1.8 seconds. This is supported by the work of Damiens,<sup>13</sup> who reported the following two reactions for a dilute potassium hydroxide solution:



Both reactions proceeded rapidly; as fast as the  $\text{OF}_2$  was formed it reacted according to equation No. 2, giving potassium fluoride. However, with a 2 per cent sodium hydroxide solution and fluorine,  $\text{OF}_2$  can be prepared and isolated.<sup>11</sup> These facts indicate that, particularly with dilute alkaline solutions, potassium hydroxide favors the rapid formation of potassium fluoride, whereas the sodium hydroxide gives a rapid reaction yielding  $\text{OF}_2$  followed by a slower reaction giving sodium fluoride. Since no direct comparison is available to the present work with 5 to 10 per cent solutions, it is possible that the second factor which could account for the whole effect of rapid absorption is the use of a spray nozzle. This gives a high liquid velocity (and hence a thin film through which the solute gas must diffuse) and a large surface area for reaction. Using the values for drop sizes from spray nozzles obtained by Pigford and Pyle, it is calculated that 400 sq. ft. of surface area is formed per gallon of liquid. (This allows for a 50 per cent reduction in area to coalescence of drops or possible wall effects.) Other reactions occurring in the spray tower during contact of the gas stream and the liquid spray may be written as follows:



There is evidence that  $\text{KBrO}_3$  is also formed as one of the reaction products of hydrolysis.

A comparison of the values of the HTU obtained in this study to those obtained for Saran fiber cells for the absorption of hydrogen fluoride<sup>6</sup> shows that a spray tower is not quite as effective per unit of height. At comparable gas and liquid rates, the HTU for Saran fiber is 0.18 foot as compared to approximately 1.0 foot for the spray tower. This slight disadvantage is offset, however, by the fact that increasing the number of fiber cells increases the pressure drop, whereas increasing the number of cocurrent spray stages will give no increase in pressure drop.

The scale-up of a cocurrent spray tower can be accomplished for dimensionally similar equipment by determining the number of transfer units from the equation  $N_T = 2.3 \log \frac{Y_2}{Y_1}$ ; then knowing the value of the HTU as reported herein, for the same liquid rate and gas rate and type of halogen, the total height =  $(N_T)(\text{HTU})$ . The number of spray stages can then be calculated by dividing the required height by the height between spray stages.

## V. CONCLUSIONS

A bed of oolitic limestone can be employed at room temperature to remove hydrogen fluoride from an air stream at high efficiencies until 50 per cent of the bed is exhausted if 1/8 to 1/4-inch particles are used. Increasing the

bed depth (which gives an increase in the efficiency) and decreasing the particle size will give a proportionate increase in capacity. A limestone bed is not a satisfactory absorption unit for other halogens (particularly bromides) in applications where high efficiency and capacity are required.

A cocurrent spray tower with one spray stage will effectively remove interhalogens, hydrogen halides, and elemental halogens from an air stream with efficiencies greater than 90 per cent when a 5 per cent potassium hydroxide solution is used as the absorbing liquid. This cocurrent spray tower offers the advantage of operating under conditions of negligible pressure drop. A conservative figure of 1 foot for the HTU can be used for design purposes within the range of liquid rates of 3000 to 6000 lb./hr.(sq.ft.) and with contact times for the gas phase as low as 1.7 seconds. Under these operating conditions, three spray stages in series will reduce the halogen concentrations in an air stream from 2000 to less than 10 ppm. Because of the fine droplets produced by the spray it is necessary to provide this type of absorption tower with a de-entraining device; for this purpose it was found that a 4-inch section of 250-micron Monel fibers gave satisfactory performance.



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