-1-

ARGONNE NATIONAL LABORATORY
P. O. Box 299
Lemont, Illinois

REMOVAL OF HALOGENS, CARBON DIOXIDE, AND
AEROSOLS FROM AIR IN A SPRAY TOWER

by

R. C. Liimatainen and W. J. Mecham

Chemical Engineering Division

February 28, 1955

This document is
PUBLICLY RELEASABLE

NK.
Authorizing Official
Date: 3/27/05

Operated by The University of Chicago
under
Contract W-31-109-eng-38

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency Thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

2

TABLE OF CONTENTS

	<u>Page</u>
ABSTRACT	5
I. INTRODUCTION.	5
II. DESCRIPTION OF EQUIPMENT	8
III. CARBON DIOXIDE ABSORPTION	11
IV. HALOGEN VAPOR ABSORPTION	25
V. AEROSOL TESTS	31
VI. CONCLUSIONS.	36
VII. REFERENCES	37

3

LIST OF FIGURES

<u>No.</u>	<u>Title</u>	<u>Page</u>
1.	Diagram of Gas Scrubber System	9
<u>Absorption of Carbon Dioxide</u>		
2.	Variation of K_{Ga} with Carbonate Concentration	13
3.	Variation of K_{Ga} with Carbon Dioxide Concentration.	16
4.	Variation of K_{Ga} with Gas Rate.	18
5.	Variation of K_{Ga} with Liquid Rate	19
6.	Variation of K_{Ga} with Potassium Hydroxide Concentration. .	20
<u>Absorption of Bromine Fluorides and Iodine</u>		
7.	Variation of K_{Ga} with Inlet Concentration	28
<u>Removal of Aerosols</u>		
8.	Ammonium Chloride Particle Size Distribution	33
9.	Sodium Oxide Particle Size Distribution	34

4

LIST OF TABLES

<u>No.</u>	<u>Title</u>	<u>Page</u>
1	Absorption in a Single Nozzle Spray Tower	7
2	Flow Characteristics of Horizontal Scrubber.	10
3	Two-Stage Carbon Dioxide Absorption	12
4	Three-Stage Carbon Dioxide Absorption.	15
5	Single-Stage Carbon Dioxide Absorption.	17
6	Comparison of Absorption of Atmospheric Carbon Dioxide in a Packed Tower and in a Spray Tower	23
7	Absorption of Interhalogens in a Horizontal Spray Tower. . .	26
8	Comparison of Large and Small Spray Tower	29
9	Removal of Aerosols in a Spray Tower.	32

S

REMOVAL OF HALOGENS, CARBON DIOXIDE, AND
AEROSOLS FROM AIR IN A SPRAY TOWER

by

R. C. Liimatainen and W. J. Mechem

ABSTRACT

Tests were made of the removal from air of bromine fluoride and iodine vapors, of atmospheric carbon dioxide, and of two aerosols (of 0.5 and 0.10 micron mean diameter) from a multiple nozzle caustic spray tower with gas flow rates up to 6000 cu ft/min. The halogen absorption efficiencies ranged from 60 to 100 per cent, with an average K_Ga of 13 lb-mol/(hr)(cu ft)(atm). The corresponding average gas rate was 1442 lb/(hr)(sq ft) and the average liquid rate was 112 lb/(hr)(cu ft). The average concentration of potassium hydroxide used was 6 weight per cent. Carbon dioxide runs over a range of gas rates, liquid rates, carbon dioxide concentrations, and potassium hydroxide concentrations showed values of K_Ga as high as 3.74 lb-mol/(hr)(cu ft)(atm), which is comparable to those obtained in packed towers. The K_Ga was independent of the gas rate, but increased with liquid rate, carbon dioxide concentration, and potassium hydroxide concentration. Aerosol absorption efficiencies were between 35 and 57 per cent in the tests made. Analysis of the spray contacting mechanism was developed for the purpose of aiding in the design of highly efficient spray scrubbers.

I. INTRODUCTION

This report describes tests made on a multiple-nozzle spray tower designed to remove highly reactive and toxic halogen compounds, such as bromine pentafluoride, bromine trifluoride, etc., that might be carried in the exhaust air from a laboratory area using these materials. A previous report⁽¹⁾ from this Laboratory reviewed the biological tolerances and some earlier absorption work reported in the literature. This report described experiments on the absorption of these materials in a limestone bed and in a single-nozzle spray tower using caustic solutions. The present work is an extension of the spray tower studies to larger scale operation and to some additional airborne materials, namely, iodine, carbon dioxide, and aerosols.

6

In the work cited above, the limestone bed was relatively poor in both efficiency and capacity for halogen compounds other than hydrogen fluoride, and larger scale bed designs involved high weight and pressure drop for the ventilation installation proposed. The spray tower, however, proved quite generally attractive. Some typical results are shown in Table 1 for later comparison with results of the larger unit. A spray tower rather than a packed tower was chosen primarily because of the former's lower pressure drop, a very attractive feature in a ventilation system with a 6000 cu ft/min throughput, light gauge ductwork, and low pressure blowers. Also, the general simplicity and safety of an open tower with a minimum of aqueous material present were factors deemed favorable to the spray tower.

It was found also in these tests of the small scrubber, that the caustic solution was quickly carbonated by the normal concentration of carbon dioxide in the air. This indicated that the spray contactor was a competitor of the packed tower for efficient absorption of carbon dioxide, and probably for other substances, such as acid vapors. This comparison of the two scrubbers is considered herein.

To gain more information as to the general applicability of the spray tower as a contacting device, a few tests on the removal of aerosols were made also.

The tests described herein were performed in the period between January, 1954 and May, 1954.

7

Table I

ABSORPTION IN SINGLE-NOZZLE SPRAY TOWER (5-INCH DIAMETER)

(Data from ANL-5015)

Run No.	Absorbed Gas	Air Rate, lb/(hr)(sq ft)	Liquid Rate, lb/(hr) (sq ft of spray cone)	Liquid Rate, lb/(hr)(cu ft)	Contact Time, Seconds	Inlet Conc., ppm		Over-all $K_G a$, lb-mol/(hr)(cu ft)(atm)	
						Fluoride	Other Halide	Fluoride	Other Halide
A3	F ₂	344	1820	865	3.1	4510	0	12.2	--
A8	Br ₂	218	3110	1450	4.9	0	6500	--	10.7
B1	HF	214	3110	1450	5.0	32,000	0	19.2*	--
B6	HBr	213	3110	1450	5.0	0	6700	--	12.4
Interhalogen									
2	ClF ₃	217	1750	830	4.9	11,800	7370	5.7	9.1*
3	BrF ₅	357	1820	865	3.0	7360	6170	15.4	13.9
4	BrF ₅	345	1820	865	3.0	6300	5300	16.1	12.8
5	BrF ₃	342	3110	1450	3.1	1010	1410	12.0	10.0
6	BrF ₃	221	3110	1450	4.8	5820	818	10.6	6.2
7	BrF ₃	331	1820	865	3.2	360	502	7.0	6.6
Average of Fluoride Runs			2295	1030	3.8	8642		12.4	

*Assuming 1 ppm rather than 0 as the exit concentration

8

II. DESCRIPTION OF EQUIPMENT

The scrubber was a box of welded, one-eighth-inch steel plate, four feet square and seventeen feet long, with connections at each end for ductwork. It consisted of three successive sections or stages, each having a bank of four hollow cone spray nozzles (Schutte-Koerting 622 C) impinging on cast iron throat pieces mounted on the three stage dividers. The tower rested on its side, and the flows of gas and liquid were co-current and horizontal. Following the last stage was a simple array of staggered baffle plates and a four-inch bed of 250-micron Monel fibers to provide de-entrainment. Finned tube steam heaters were used at the gas exit to raise the temperature of the gas and thus to lower its relative humidity. Potassium hydroxide solution was circulated through the system by an iron centrifugal pump operated by a seven and one-half horsepower electric motor. Three-inch black iron pipe conducted the solution to the spray header, and a four-inch drain line returned the solution to a large stainless steel recycle tank, which also fed the pump. The layout is shown in Figure 1.

Flow Characteristics of Spray Tower

Flow characteristics measured at two different run conditions are presented in Table 2. The increase of pressure drop with flow rate for both the liquid and the gas streams is shown, as well as the effect of the heaters on the relative humidity of the exit gas.

The over-all pressure drop of the tower was zero at 5400 cu ft/min gas flow and 101 gal/min water flow. This was due to the fact that the high velocity co-current water spray imparted velocity to the air. This test was made with the tower open to the air at both ends. In another test, with an air throughput 4000 cu ft/min, the pressure drop across the stage (with the spray off) was 0.11 inch of water. On the basis of these tests, the over-all pressure drop in the vicinity of 6000 cu ft/min of air was zero with the spray on, and about one inch of water with the spray off.

Evaporation loss of water from the circulating liquid was 0.1 gal/min as calculated from the humidity data of Table 2. This loss was confirmed by measurement of the loss of water from the circulating system and was compensated for by discharging condensate from the steam heaters into the system.

Although observations through the Lucite windows of the tower spray section revealed considerable splashing of high speed droplets, no liquid entrainment was observed under any of the runs reported here. The highest humidity observed in the exit air was 89 per cent, and heating of the air to 104°F reduced this to 33 per cent. Low relative humidity increases the life-time of the "Chemical Warfare Service" type asbestos filters which were part of the ventilation system.

9

FIGURE 1.

GAS SCRUBBER SYSTEM.

Because of oxidative corrosion of the steel, several different chemical resistant paints were applied. However, no such protective coating has been entirely satisfactory in maintaining a permanent bond under operating conditions. For long term use, it is believed that the use of stainless steel as a construction material may be the most satisfactory way of handling this problem.

Table 2

FLOW CHARACTERISTICS OF HORIZONTAL SCRUBBER

	<u>Test 1</u>	<u>Test 2</u>
<u>Water</u>		
Total flow, gal/min	54.6	101
Pressure drop across nozzles, lb/sq in.	20	72
<u>Inlet Air</u>		
Rate, cu ft/min	2500	5400
Temperature, F	77	72
Relative Humidity, per cent	40	36
<u>Exit Air (No Heating)</u>		
Temperature, F	71	66
Relative Humidity, per cent	89	75
<u>Exit Air (Heating with 70 psi Steam in Tubes)</u>		
Temperature, F	104	92
Relative Humidity, per cent	33	34
<u>Pressure Drop Across De-entrainment Section</u>		
Inches of water	0.2	0.7

III. CARBON DIOXIDE ABSORPTION

a. Objectives

Absorption tests of carbon dioxide from its normal atmospheric concentration were made to obtain spray tower efficiencies on this commonly encountered system to provide comparison with other absorbers, and also to serve as "shake down" on the equipment. Absorption efficiency was obtained as a function of the process variables, namely: gas rate, liquid rate, and carbon dioxide, potassium hydroxide, and potassium carbonate concentrations.

b. Procedure

The scrubber was equipped with tubes to withdraw metered gas samples from the inlet, exit, and two interstage points. Determinations of the carbon dioxide concentrations were made by passing the streams through absorption trains. The tower sample gas was first dried and then passed through two combination Ascarite-Anhydrone stages in which the Ascarite (solid sodium hydroxide and asbestos) reacted with the carbon dioxide to produce water which the Anhydrone (magnesium perchlorate) absorbed. The gain in weight of the latter two stages gave a direct quantitative determination of the total carbon dioxide in the sample stream. A Pressovac pump was used to draw the air sample from the tower through the analysis train; the flow rate was measured with orifices which were calibrated with a wet test meter.

c. Results of Carbon Dioxide Absorption in Spray Tower

Run 1 - In Run 1, only the first two spray sections of the scrubber were used, with a total of eight nozzles. The air rate was 1760 lb/(hr)(sq ft), based on the nominal 16 sq ft cross sectional area of the tower. The liquid rate was 164 lb/(hr)(cu ft), based on the 160 cubic feet total volume of the two five-foot sections of tower used. The air was at normal atmospheric pressure and at room temperature. The entering carbon dioxide concentration was normal, about 500 parts per million. The run conditions and data are summarized in Table 3, which indicates the absorption behavior with respect to time and degree of carbonation. Data from this table are plotted in Figure 2.

The circulated spray solution was 2.1 M potassium hydroxide. The first sample of the caustic solution, taken after one hour of running, showed 2.1 weight per cent of carbonate as potassium carbonate; thus the caustic was about 15 per cent carbonated at this point. The first exit sample of the gas showed 275 ppm of carbon dioxide, thus corresponding to an absorption efficiency of 44 per cent. The exit concentration of carbon dioxide rose with increasing carbonate concentration in the liquid as the run

12

Table 3

RUN SERIES NO. 1. TWO-STAGE CARBON DIOXIDE ABSORPTIONRun Conditions:

Air Rate 1760 lb/(hr)(sq ft)
 Vapor Residence Time 1.5 sec
 Total Liquid Rate 164.0 lb/(hr)(cu ft)
 Initial KOH Concentration 11 Wt per cent (2.1 M)
 Total Solution Volume 225 gallons
 Spray: Two spray banks, total 8 nozzles
 Length - 10 feet

Running Time, Hours	CO ₂ Inlet Concentration, ppm	CO ₂ Exit Concentration, ppm	K ₂ CO ₃ Conc'n in Tank, Per Cent (wt)	Per Cent Absorbed of CO ₂ Entering	K _{Ga} , lb-mol (hr)(cu ft)(atm)
1	---	---	2.1	---	
2	490.	275.	2.9	43.8	3.48
3	---	---	3.4	---	
4	---	---	3.6	---	
5	---	---	4.5	---	
5.5	505.	340.	---	32.7	2.41
6	---	---	5.1	---	
7	---	---	6.0	---	
8	---	---	6.0	---	
8.5	490.	375.	---	23.5	1.63
9.0	---	---	6.4	---	
11.25	530.	430.	---	18.9	1.26
12.5	---	---	8.5	---	

13

FIGURE 2.

ABSORPTION OF CARBON DIOXIDE IN A
 SPRAY TOWER: VARIATION OF $K_G a$
 WITH CARBONATE CONCENTRATION.

14

proceeded. At the termination of the run, the exit concentration was 430 ppm carbon dioxide, indicating an absorption efficiency of 19 per cent for a solution about 57 per cent carbonated. The degree of carbonation is expressed as the percentage of total potassium associated with the potassium carbonate concentrations listed in Table 3.

Run 2 - In Run 2, all twelve nozzles were used, employing the entire 240 cubic feet of the tower (15 feet of useful contacting length) at a gas rate of 790 lb/(hr)(sq ft) and a total liquid rate of 103 lb/(hr)(cu ft). Conditions were otherwise the same as in Run 1, but the duration of this run was only one hour in order to approach steady state absorption values for essentially uncarbonated solution. The data are summarized in Table 4 for the three individual sections of the tower. A decrease in absorption is shown with lower carbon dioxide concentration, in which the $K_G a$ varied as the 0.4 power of the concentration. A plot of data from this table is given in Figure 3.

Runs 3 through 11 - A series of runs at several liquid and gas rates were made, using only a single bank of four nozzles. The general conditions were the same as Run 2, except that only one-third of the tower was used, and in two runs lower potassium hydroxide concentrations were used. These data are summarized in Table 5. Plots of $K_G a$ versus gas rate, liquid rate, and potassium hydroxide concentration are shown, respectively, in Figures 4, 5, and 6. No effect of the gas rate is evident, but $K_G a$ increases with the 1.6-power of liquid rate. The $K_G a$ apparently drops off at an increasing rate below 5 per cent potassium hydroxide.

d. Calculations

In all of the tables referred to above, calculated values of absorption efficiency and over-all mass transfer coefficient, $K_G a$, are shown corresponding to the measured inlet and exit carbon dioxide concentrations. The absorption efficiency, E , was calculated as the per cent absorbed of carbon dioxide entering the scrubber section. In terms of inlet concentration, C_1 , and exit concentration, C_2 ,

$$E = \frac{C_1 - C_2}{C_1}$$

The equation defining $K_G a$ is:

$$-\frac{G}{M_{ave}} dy = K_G a (y - y^*) PdH$$

where G = mass rate of flow of gas, lbs/(hr)(sq ft)

M_{ave} = average molecular weight of the gas

Table 4

RUN 2. THREE-STAGE CARBON DIOXIDE ABSORPTIONRun Conditions:

Air Rate 790 lb/(hr)(sq ft)
 Total Liquid Rate 103 lb/(hr)(cu ft)
 KOH Concentration 11.2 per cent (wt)
 Spray: Three banks, total 12 nozzles
 Time of Run: One hour (steady state)
 Length: 15 feet

Location in Tower	CO ₂ Conc., ppm	Per Cent Absorbed of CO ₂ Entering Stage	K _{Ga} , lb-mol/(hr)(cu ft)(atm)	Residence Time, Seconds
Inlet	480	---	---	---
Leaving 1st Stage	330	31.3	2.06	1.70
Leaving 2nd Stage	240	27.3	1.76	1.70
Leaving 3rd Stage (Exit)	190	20.8	1.27	1.70
Over-all	---	60.4	1.68	5.1

16

FIGURE 3.

ABSORPTION OF CARBON DIOXIDE IN A
CAUSTIC SPRAY TOWER: VARIATION
OF $K_G a$ WITH CO_2 CONCENTRATION.

Table 5

SINGLE-STAGE CARBON DIOXIDE ABSORPTIONRun Conditions:

Spray: One spray bank, total 4 nozzles

Time of Run: One hour (steady state)

Stage Length: 5 Feet

Run	Air Rate, lbs/(hr)(sq ft)	Liquid Rate, lbs/(hr)(cu ft)	KOH Conc., per cent (wt)	CO ₂ Conc., ppm		Per Cent Absorbed of CO ₂ Entering	K _G ^a , lb-mol (hr)(cu ft)(atm)	Residence Time, Seconds
				Inlet	Exit			
3	1150	55.5	10.0	526	485	8.0	0.667	1.16
4	1150	110	10.0	526	412	21.6	1.95	1.16
5	1150	164	10.0	526	328	37.6	3.74	1.16
6	1120	110	10.0	518	402	22.5	1.98	1.20
7	790	110	10.0	520	348	33.0	2.21	1.69
8	545	110	10.0	520	328	37.0	1.76	2.46
9	1640	110	10.0	520	424	18.5	2.35	0.87
10	1120	110	1.9	518	495	4.5	0.36	1.20
11	1120	110	5.0	518	443	14.5	1.23	1.20

FIGURE 4.

ABSORPTION OF CARBON DIOXIDE IN A
CAUSTIC SPRAY TOWER: VARIATION
OF $K_G a$ WITH GAS RATE.

19

FIGURE 5.

ABSORPTION OF CARBON DIOXIDE IN A
CAUSTIC SPRAY TOWER: VARIATION
OF $K_G a$ WITH LIQUID RATE.

20

FIGURE 6.

ABSORPTION OF CARBON DIOXIDE IN A
CAUSTIC SPRAY TOWER: VARIATION
OF $K_G a$ WITH KOH CONCENTRATION.

21

y = mol fraction of absorbed gas in the differential element of height, dH , of the tower

y^* = mol fraction of absorbed gas at equilibrium with the liquid phase at that point in the tower

P = total pressure, atmospheres

H = Total height of tower, ft

K_{Ga} = over-all mass transfer coefficient, lb-mol/(hr)(cu ft)(atm).

The number of transfer units, N_T , is defined as:

$$N_T = \int_{y_2}^{y_1} \frac{dy}{y - y^*} = \frac{K_{Ga} P H M_{ave}}{G}$$

In the present case of absorption with chemical reaction, y^* may be taken as zero, and, for the dilute concentrations of absorbable component used,

$$M_{ave} = M_{air} = 29, \text{ and } \frac{y_1}{y_2} = \frac{C_1}{C_2}$$

Also, for atmospheric pressure $P = 1$.

Thus,

$$\frac{29 K_{Ga} H}{G} = 2.3 \log \frac{C_1}{C_2} = N_T$$

By definition, $(HTU) = \frac{H}{N_T}$.

$$\text{Hence, } (HTU) = \frac{H}{2.3 \log \frac{C_1}{C_2}} = \frac{H}{2.3 \log \frac{1}{1 - E}}$$

$$\text{and } K_{Ga} = \frac{G}{29 (HTU)} = \frac{2.3 G}{29 H} \log \frac{1}{1 - E}$$

The residence time (or contact time) of the gas in the tower, T_c , is given, in seconds, by the expression

$$T_c = \frac{3600 H \rho}{G}$$

where ρ is the density of the gas in lb/cu ft.

22

The absorption performance is measured by N_T , E , (HTU), and $K_G a$. However, only $K_G a$ is independent of contact time in principle, and it does show more constancy with respect to the gas rate and contact time than the HTU. In packed columns, the HTU, which is the ratio of G to $K_G a$, is often more nearly constant than $K_G a$ over a range of gas rates. This is due mainly to the fact that $K_G a$ increases with the gas rate in these cases. Such is sometimes the case for the individual gas and liquid films, too. In spray towers, this situation does not hold. The $K_G a$ is used here throughout as the measure of absorption performance.

e. Analysis of Spray Contacting

A spray tower is essentially a volume in which gas flows through a dispersion of liquid droplets. Usually these droplets are moving at high speeds relative to the gas stream. Thus the relative speed of the two phases in contact is a characteristic of the liquid flow and spray nozzle rather than the gas flow and cross sectional area of the tower. On the other hand, the gas flow and tower volume determine the contact time and hence the fraction absorbed at any given liquid rate.

The actual droplet velocities in the nozzle used in these tests were measured to be 48 ft/sec at 2.4 gal/min flow and 66 ft/sec at 3.5 gal/min. The observations were made with high speed motion pictures at 800 frames/sec. The Schutte-Koerting nozzle (type 622-C) imparts a rotary movement to the liquid by means of a helix in the entrance section of the body of the nozzle. When the liquid leaves the nozzle it forms a 30-degree hollow cone. This stream is in high turbulence, breaking up into irregular sheets and droplets within about an inch of the nozzle, but holding the over-all conical configuration to a length of about two feet, depending on liquid rate. The motions were not completely stopped at 800 frames/sec, but a large number of droplets of 0.004 to 0.028 inch diameter were seen. The length of the cone, the density of droplets, and their speed, all increased with liquid flow through the nozzle. This, of course, amounted to a large increase in interfacial area. The practical range of flows through a single nozzle was between 1.0 and 7.0 gal/min. Above this range the pressure drop increased rapidly, making the pumping requirements uneconomical. Below this range the cone size and the interfacial area were only a small fraction of the nozzle capabilities. In the single-nozzle, five-inch diameter spray tower tests summarized in Table 1, the liquid rates per nozzle were between 1 and 2 gal/min. In the present scrubber tests, the range was between 2 and 7 gal/min per nozzle.

Practically all the interfacial area in the tower is concentrated in the high density droplet region which makes up the spray cone. (With a different nozzle, one that produces a "fog," this might not be so, but such a nozzle was not used because it tends to make entrainment a difficult problem.) The liquid rate per unit volume was taken here as an approximate measure of the interfacial area produced in the tower.

From the above considerations, it is evident that, in general, the gas rate does not influence the relative phase velocity in spray towers, and hence neither the film resistance nor the K_Ga . The liquid rate strongly influences the K_Ga , but this comes about by affecting the interfacial area rather than the film resistance, since within the droplet the liquid is static, whatever the flow rate may be.

f. Comparison of Spray Tower Results With Absorption of Carbon Dioxide in Packed Towers

Absorption of atmospheric carbon dioxide in a 12-inch diameter tower, 7.8 feet long, packed with 3/4-inch Raschig rings, has been reported by Spector and Dodge.⁽²⁾ Both sodium and potassium hydroxide at about 12.7 per cent (wt) were used; the potassium hydroxide was found to be slightly superior in absorption performance. The absorption studies were carried on with solutions less than 15 per cent carbonated, since up to this point carbonation had negligible effect on absorption. The results of two packed tower runs from the work cited above are compared with two of the spray tower runs in Table 6. The percentage of entering carbon dioxide absorbed was, of course, higher in the case of the packed tower, corresponding to the longer contact time. On the other hand, more gas was put through the spray tower, with a lower pressure drop. The fact that the K_Ga values were comparable is rather interesting considering the different means of producing interfacial area.

Table 6

COMPARISON OF ABSORPTION OF ATMOSPHERIC CARBON DIOXIDE
IN A PACKED TOWER AND IN A SPRAY TOWER

	<u>Spray Tower**</u>		<u>Packed Tower*</u>	
Concentration of KOH, per cent (wt)	10.0	10	12.7	12.7
Air mass velocity, lb/(hr)(sq ft)	790	1150	316	314
Vapor contact time, sec.	1.7	1.2	6.7	6.7
Liquid Rate, lb/(hr)(cu ft)	110	164	178	805
K_Ga , lb-mol/(hr)(cu ft)(atm)	2.21	3.74	3.89	4.45
Pressure Drop, in. H ₂ O	0	0	1.4	7.4
Tower Length, feet	5	5	7.8	7.8

* Data of Spector and Dodge, op. cit.

** Data from Table 5.

24

In this report of Spector and Dodge, certain conclusions were drawn about absorption processes:

- (1) A rather low order of dependence on the gas rate is shown by $K_G a$, although the gas film is shown to be at least partially controlling because $K_G a$ decreases with increasing partial pressure of the inert gas.
- (2) The liquid film is not expected to be controlling, since the chemical reaction involved is fast and complete. Nor does the data show the liquid rate to have much influence, the small effect shown probably being due to increased interfacial area produced by a higher degree of wetting of the packing. On the other hand, the hydroxide concentration and the liquid temperature show a strong effect on the $K_G a$. The possibility was mentioned that this liquid film rate factor might be chemical rather than physical in nature.

In the present spray tower tests, the carbon dioxide concentration effect and the hydroxide effect were confirmed. No effect of gas rate on $K_G a$ was found, but this is a characteristic of spray contacting more than of the carbon dioxide-caustic system. A strong effect of liquid rate was shown, quite definitely due to interfacial area variation. The temperature effect was not investigated.

IV. HALOGEN VAPOR ABSORPTION

a. Objectives

The primary purpose of the tests of absorption of halogen vapors from air in this scrubber was to measure its effectiveness in removing toxic halogen vapors that might be released into the ventilation system in which the scrubber is installed. In addition, the data obtained, together with the previous halogen absorption data from the smaller spray scrubber,⁽¹⁾ were to provide information on scale-up factors in spray tower design.

b. Procedure

Introduction of halogen vapors into the scrubber was accomplished by passing a preheated air stream of about two cubic feet per minute through a small tank containing the halogen. The vapor mixture was then introduced into the entrance air duct to the scrubber. In the case of bromine pentafluoride, the air was bubbled through the liquid at room temperature. In the case of bromine trifluoride, which has a low vapor pressure at room temperature, the air was bubbled through the liquid heated to about 100C. In the case of iodine, the air was passed over the surface of iodine heated to about 110C, at which temperature its vapor pressure is about 75 mm Hg absolute.

Sampling of the air stream at the exit and entrance to the tower was performed by withdrawing metered gas streams through a three-stage bubbler containing 10 per cent by weight of potassium hydroxide. Halogen concentrations were then determined on the basis of chemical analysis of halides in the bubbler solution. Fluoride analysis was performed spectrophotometrically using Thoron reagent in the method described by Horton, et al.⁽³⁾ Bromide analysis was done by a standard Volhard titration. Iodine analysis was done spectrophotometrically after extraction into carbon tetrachloride.

c. Results

Two runs were made with bromine trifluoride, three with bromine pentafluoride, and one with iodine. All runs were made with the full twelve spray nozzles. Two different liquid rates and two gas rates were used, all at one atmosphere total pressure and room temperature. The range of inlet concentration was from 91 to 680 ppm. Fluoride absorption efficiencies ranged between 92 and 100 per cent and bromine efficiencies from 69 to 100 per cent. The data are summarized in Table 7.

26

Table 7

ABSORPTION OF INTERHALOGENS IN A HORIZONTAL SPRAY TOWER

Run No.	Absorbed Gas	Air Flow, lb/(hr)(sq ft)		Liquid Flow, lb/(hr) (cu ft)	Contact Time, Sec**	Absorbing Liquid		Halogen Conc. (ppm)				Over-all Eff. of Absorption		K _G ^a , lb-mol/(hr)(cu ft)(atm)		
		Based on Tower Area	Based on Cone Area			(Conc Wt %)	KOH	K ₂ CO ₃	Inlet Total		Exit		(per cent)		Fluoride	Other Halide
									Fluoride	Other Halide	Fluoride	Other Halide	Fluoride	Other Halide		
1	BrF ₃	1195	728	109	3.36	7.5	4.3	38	53.2	3.4	15.5	92.0	69.0	6.6	3.4	
2	BrF ₃	1195	728	109	3.36	7.5	4.3	832	116.8	0.0	3.6	100.0	97.0	12.1*	10.5	
3	I ₂	1690	728	109	2.38	6.1	2.1	--	114	--	4.8 (total I ₂)	--	95.8 (I ₂)	--	12.3 (I ₂)	
4	BrF ₃	1690	728	109	2.38	5.1	1.4	249	209	3.5	0	98.6	100.0	16.5	20.7*	
5	BrF ₃	1690	828	124	2.38	3.3	2.2	318	267	0	29.4	100.0	89.0	22.3*	8.5	
6	BrF ₃	1195	728	109	3.36	2.9	3.0	369	311	25.7	14.1	93.0	95.5	7.3	8.5	
Average of Fluoride Runs		1442	749	112	2.9			211						12.9		

*Calculated assuming 1.0 ppm rather than 0 as the exit concentration.

**Based on total tower volume.

d. Discussion of Results

Calculations of $K_G a$ were made in the manner described previously. However, because some samples showed zero concentration in the exit stream and the $K_G a$ could only be calculated by assuming a finite exit concentration a value of 1 ppm was chosen. Because of this situation and a general scattering of the data, no clear quantitative variation of $K_G a$ with gas or liquid rates can be shown, although there is a rough upward trend with both stream rates. On the other hand, a definite increase of $K_G a$ with inlet concentration is shown by a plot in Figure 7. $K_G a$ appears to be approximately proportional to the 0.7 power of concentration. In the range of 5 to 10 per cent KOH, neither the KOH concentration nor the fraction carbonated has an appreciable influence on $K_G a$.

The average of the $K_G a$ values for fluoride absorption from the bromine fluorides was 13 lb-mol/(hr)(cu ft)(atm); for bromide, 11. The single value for iodine absorption was 12.

As a guide to general scrubber design, it is significant to compare the present large scrubber with the small scrubber described in ANL-5015. From absorption data for halogen compounds given in Tables 1 and 7 it is seen that the over-all $K_G a$ values are in the vicinity of 13 lb-mol/(hr)(cu ft)(atm). It is likely that most of the liquid spray is concentrated in the hollow cone produced by the nozzles and that the liquid flow rate itself contributes to interfacial area. These factors, together with other relevant information on the two towers, are shown in Table 8. Perhaps the ratio of cone area to tower volume values is the best measure of relative interfacial area, but the observed $K_G a$ for the two towers are more nearly alike than predicted on this basis. Possibly also vapor phase reactions tend to equalize results. As shown in Figure 7, increase of inlet concentration tends to increase $K_G a$, so that the concentration effect would tend to raise rather than lower the $K_G a$ of the small tower relative to the large one. The nozzle used in the small tower has a 'finer' spray, which might be supposed to increase $K_G a$ also. However, from the data presented, it is concluded that $K_G a$ is approximately 12 lb-mol/(hr)(cu ft)(atm) for all the halogen compounds tested, the flow conditions, and the design parameters of Tables 1, 7, and 8.

e. Work at Very High Interhalogen Concentrations

The small scrubber referred to above has been equipped with two nozzles for use in hydrolyzing laboratory waste BrF_3 . Concentrations of BrF_3 in air up to 80 per cent (wt), with BrF_3 rates up to 6 lb/hr, have been run without difficulty and with quantitative absorption (by odor test) right up to the point where the solution goes acid. A heat exchanger was used to cool the circulating caustic. This performance indicates a $K_G a$ greater than 1.0 lb-mol/(hr)(cu ft)(atm). Also, it shows that absorption is not strongly affected by buildup of KF.

28

FIGURE 7.
ABSORPTION OF BROMINE FLUORIDES AND
IODINE IN A CAUSTIC SPRAY TOWER:
VARIATION OF $K_G a$ WITH INLET CONCENTRATION.

29
Table 8

COMPARISON OF SPRAY CONES IN LARGE AND SMALL TOWER

<u>Tower Dimensions</u>	<u>Small Scrubber*</u>	<u>Present Large Scrubber</u>
1. Over-all length of spray section	4.0 ft	10.0 ft
2. Over-all cross-sectional area of spray section	0.139 sq ft	16.0 sq ft
3. Over-all volume of spray section	0.556 cu ft	160 cu ft
<u>Estimated Interfacial Area</u>		
4. Superficial area of spray cone as installed	0.26 sq ft	2.00 sq ft
5. Total superficial area of spray cones	0.26 sq ft	24.0 sq ft
6. Cone area per unit tower volume	0.465 sq ft/cu ft	0.150 sq ft/cu ft
<u>Water Rate</u>		
7. Average water flow per sq ft cone area	$2295 \frac{(\text{lb})}{(\text{hr})(\text{sq ft})}$	$749 \frac{(\text{lb})}{(\text{hr})(\text{sq ft})}$
8. Average water flow per cu ft of tower	$1030 \frac{(\text{lb})}{(\text{hr})(\text{cu ft})}$	$112 \frac{(\text{lb})}{(\text{hr})(\text{cu ft})}$
<u>Average K_G^{**}</u>	$12 \frac{\text{lb-mol}}{(\text{hr})(\text{cu ft})(\text{atm})}$	$13 \frac{\text{lb-mol}}{(\text{hr})(\text{cu ft})(\text{atm})}$
Average inlet concentration**	8642 parts per million	211 parts per million
Average residence time	3.8 sec	2.9 sec

* The body of this scrubber was a vertically mounted piece of standard 5-inch steel pipe containing a single Schuette-Koerting, 60° hollow cone, 3.5 mm-orifice spray nozzle. Operation is described in ANL-5015.

** For fluoride absorption.

30

f. Comparison with Carbon Dioxide Absorption

In carbon dioxide absorption the K_G is more highly dependent on hydroxide concentration, liquid rate, and vapor concentration than the case with halogen absorption. Also, for comparative runs in the large scrubber the (CO_2) K_G was lower by a factor of 3 to 6.

In the course of the absorption process the halogen compounds (F_2 , BrF_3 , etc.) react with water upon contact, forming hydrogen halides. The hydrogen halides themselves are readily absorbed (Table 1). Carbon dioxide goes through an analogous step in forming carbonic acid. In both systems the acid-base reactions go to completion in the liquid phase. The rate of the process as a whole may be viewed as the following steps: (1) the vapor contacting the liquid phase by film diffusion, (2) chemical reaction and formation of ions in solution, (3) acid-base reactions. It is expected that because of its lower molecular weight, HF might be expected to be absorbed more rapidly than CO_2 in step (1). Also, because of its higher chemical reactivity and more strongly ionic products, HF may be faster in step (2). The ionic reactions in step (3) are probably so fast that they are not controlling in either case. In summary, it seems quite reasonable that the absorption processes for both carbon dioxide and these halogen compounds proceed by similar mechanisms, but that the halogen absorption is somewhat faster.

31

V. AEROSOL TESTS

a. Objectives

In order to observe the performance of the spray tower as a contacting device to remove aerosols, tests were made with fumes of a range of sizes commonly encountered in air cleaning practice.

b. Procedure

Metered gas samples were taken from the inlet and exit streams bearing the aerosols and drawn through a Millipore membrane filter. This filter removes particles greater than 0.1 micron with nearly 100 per cent efficiency.⁽⁴⁾ Counting and sizing the particles on the filter was done with a microscope of 900-diameters magnification by the oil immersion method with transmitted light. An electron microscope was also used in the case of sodium oxide.

Ammonium chloride aerosol was formed by passing a heated air stream first through concentrated hydrochloric acid and then over a concentrated ammonia solution. A second air stream was used to dilute the smoke formed and carry it to the gas inlet to the scrubber. All twelve spray nozzles were used in the two ammonium chloride runs.

Sodium oxide aerosol was produced by igniting some of the metal in the inlet section of the tower. The aerosol then passed through the last two sections of the tower with eight nozzles operating.

c. Results

The run data and conditions for all three runs are shown in Table 9 and the size distributions in the form of log-probability plots are given in Figures 8 and 9. The ammonium chloride aerosol had a mean diameter of 0.5 micron; the efficiencies of removal were 57 per cent for a residence time of 4.5 seconds and 44 per cent for a residence time of 3.2 seconds. The sodium oxide had a mean particle diameter of 0.04 micron as determined with an electron microscope; the mean diameter determined at 900X was approximately 0.2 micron. A figure of 0.1 micron might be used as the mean sodium oxide particle diameter thus giving less weight to the 900X microscope determination since with that device the particle size was very nearly at the limit of detectability. The efficiency of sodium oxide removal was found to be 35% for a residence time of 5.8 seconds. For both aerosols, no preferential size removal was shown.

The visibility of aerosols was related to concentration approximately as follows: (1) a dense white, opaque cloud of ammonium chloride was produced at the generator; the concentration was about 10^{10} particles

32

per cubic foot. (2) The fume produced in the sodium oxide test was plainly visible in the tower; the concentration was 3×10^8 particles per cubic foot. (3) No definite fumes of ammonium chloride were observed in the tower; the concentration was 3×10^7 particles per cubic foot.

Table 9

REMOVAL OF AEROSOLS IN A SPRAY TOWER

Run	1	2	3
Length of Tower, ft	15	15	10
Aerosol	NH ₄ Cl	NH ₄ Cl	Na ₂ O
Mean Particle Diam., Microns	0.5	0.5	0.1
Gas Flow, lb/(hr)(sq ft)	900	1250	460
Liquid Flow, lb/(hr)(cu ft)	109	109	150
Residence Time, sec.	4.48	3.21	5.83
Inlet Conc., particles/cu ft	79×10^6	107×10^6	511×10^6
Inlet Mass Conc.,* grams/cu ft	805×10^{-7}	1135×10^{-7}	4×10^{-7}
Exit Conc., particles/cu ft	34×10^6	60×10^6	333×10^6
Efficiency of Removal, Per Cent	57	44	35
K _c a, (hr) ⁻¹	680	648	265

* Assuming spherical particles.

d. Discussion of Aerosol Results

The aerosol collection efficiencies for the spray tower are substantial; spray towers usually have efficiencies less than 20 per cent for particles one to five microns, according to First.⁽⁵⁾

Just as in vapor absorption, it is important to have a material transfer coefficient independent of contact time to serve as a measure of absorption capabilities of the equipment. Such a coefficient is defined by

$$vGdC = -K_c a C dH \quad ,$$

33

FIGURE 8.

AMMONIUM CHLORIDE PARTICLE
SIZE DISTRIBUTION.

34

FIGURE 9.

SODIUM OXIDE PARTICLE SIZE
DISTRIBUTION AS DETERMINED
WITH AN ELECTRON MICROSCOPE.

where

35

C is the number of particles per cubic foot of the air stream in the differential element of length dH

H is the length of the tower, ft

G is the mass velocity of the air stream, lb/(hr)(sq ft)

v is the specific volume of the air stream, cu ft/lb

$K_C a$ is the material transfer coefficient, (hr)⁻¹

In this expression, the transfer rate is expressed as particles per hour per cubic foot of tower volume and the driving force is in particles per cubic foot of air; this leaves the net dimensions of $K_C a$ as merely reciprocal hours. The integrated form for air at 70°F and 1 atmosphere is

$$K_C a = \frac{30.8G}{H} \log \left(\frac{C_1}{C_2} \right)$$

The $K_C a$ values were shown to be roughly independent of gas rate and contact time. However, the effects of $K_C a$ of concentration, liquid rate, and particle size were not separated in this study. It would be expected that $K_C a$ show a slight increase with concentration and a strong increase with liquid rate and particle size. The concentration can also be expressed as mass (of particles) per cubic foot. Calculated values of this concentration C_m are also shown in Table 8. C_m is, of course, related to C_n by the particle volume and density. The same numerical values of E (efficiency) and $K_C a$ apply to concentrations based on either particle- or mass-density.

As an illustration of the use of this coefficient in design, the calculation of the length of tower required for 90% removal for an aerosol having a $K_C a$ of 300 is as follows: Assume $G = 135$ lb/(hr)(sq ft) and tower area = 16 sq ft. Then for 90% removal $K_C a = 300 = \frac{30.8 \times 135 \times 1}{H}$

$$H = 13.9 \text{ feet}$$

36

VI. CONCLUSIONS

For a range of inlet concentrations of bromine fluorides and iodine up to 690 ppm, efficiencies of absorption in the large scrubber ranged from 69 to 100 per cent, the lower figures being those for the bromide component. Although there was some scattering of the data, most of the runs showed absorption efficiencies above 95 per cent, which is considered adequate for safety in the 6000 cu ft/min ventilation system in which the scrubber is installed. The average K_{Ga} for absorption of the above halogen is 13 lb-mols/(hr)(cu ft)(atm). The corresponding average gas rate was 1442 lb/(hr)(sq ft); the liquid rate, 112 lb/(hr)(cu ft). The K_{Ga} , and hence the absorption efficiency, increases with inlet concentration to about the 0.7 power, a fact which provides a safety factor.

The above K_{Ga} values are consistent with those of earlier halogen absorption work in a single nozzle spray tower,⁽¹⁾ and subsequent runs in the small tower have verified that absorption efficiency increases with concentration.

Absorption of atmospheric carbon dioxide was performed over a range of gas rates, liquid rates, potassium hydroxide concentrations, and carbon dioxide concentrations. One run, at a liquid rate of 164 lb/(hr)(cu ft), a gas rate of 1150 lb/(hr)(sq ft), and 10 per cent (wt) potassium hydroxide provided K_{Ga} of 3.74 lb-mol/(hr)(cu ft)(atm). In general the values of K_{Ga} for carbon dioxide absorption were of the same magnitude as those obtained under absorption under approximately similar conditions in a packed tower of 1 ft diameter and 7.8 ft height (see Table 6).

The carbon dioxide runs indicated the effect of process variables on K_{Ga} . K_{Ga} increased with the 0.4 power of carbon dioxide concentration and with the 1.6 power of the liquid rate. The K_{Ga} increased rapidly with potassium hydroxide concentrations up to 10 per cent (wt); the rate of increase above 10 per cent was slower. There was no appreciable effect of gas rate on K_{Ga} .

Aerosol removal runs were made for two ranges of particle size; the mean diameters were 0.5 and about 0.10 micron. The removal efficiencies were between 35 and 57 per cent. A material transfer coefficient analogous to K_{Ga} was calculated for aerosol removal, and this coefficient appeared to be independent of the gas rate. Hence higher removal efficiencies could be achieved by lengthening the residence time of gas in the scrubber.

The spray tower showed absorption performance that is comparable to packed towers, and has a wide range of possible applications, especially where simplicity, low weight, and low gas pressure drop are important.

REFERENCES CITED

1. Liimatainen, R. C., and Levenson, M., "Absorption of Some Halogen Gases from Air by a Limestone Bed and a Spray Tower" - ANL-5015.
2. Spector, N. A., and Dodge, B. F., Trans. Am. Inst. Chem. Engrs., 42, 827 (1946).
3. Horton, A. D., Thomason, P. F. and Miller, F. J., Anal. Chem., 24, 548 (1952).
4. First, M. W. and Silverman, L., A.M.A. Arch. Ind. Hyg. and Occup. Med., 7, 1 (1953).
5. First, M. W. et al, "Air Cleaning Studies Progress Report," NYO-1581, (1951), p. 43.

ACKNOWLEDGMENTS

The aerosol measurements were greatly facilitated by the cooperation of Donald P. O'Niel of the Industrial Hygiene and Safety Division. Lester F. Dorsey of the Chemical Engineering Division assisted in all phases of the experimental work. Analysis of aqueous halide solutions was done by the analytical section of the Chemical Engineering Division. The design of the scrubber was done under the guidance of M. Levenson.