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ARTHUR D. LITTLE, INC.

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ABSORPTION OF CO_2 FROM NORMAL AIR BY SODA LIME

In September, 1943 considerable interest was expressed in the use of Soda Lime to remove the CO_2 content of normal air before it was compressed for use in the NDRC liquid-air oxygen units. Very little data was available at the time on the performance of Soda Lime under these conditions. Arthur D. Little, Inc. was requested to initiate as rapidly as possible an experimental program to evaluate Soda Lime and particularly Dewey & Almy's High Moisture Low Caustic Soda Lime for this purpose.

A review of the literature showed available data to be very meager.

Two articles by R. E. Wilson are of interest. (J.I.E.C. Vol. 11, p. 420; 1919 and J.I.E.C. vol. 12, p. 1000-7; 1920). The latter reference offers some interesting data on various compositions of Soda Lime plus some equilibrium moisture data for the CO_2 absorbing type. This data is tabulated below.

Sample Designation	Moisture Content %	% NaOH Dry Basis	Time to 99% Efficiency	Gm. CO_2/Gm. of absorbent at 50% efficiency
A	14.8	41.5	17	.029
B	1.2	21.0	14	.024
C	14.4	43.4	34	.063
D	2.1	40.8	12	.020
E	11.75	39.9	26	.041
Army Industrial Soda Lime	12.0	5.0	70	.240
Special CO_2 Soda Lime	17.6	4.0	110	.320

15 cm. deep bed--85% RH--2% CO_2
flow rate 500 $cm^3/cm^2/min$.

Equilibrium Moisture Content of 4.5% NaOH (Dry Basis) Soda Lime.

% Water	% R.H. of Equilibrium Air at 25°C.
2	17
4	43
5	50
10	73
15	82

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Since the efficiency of Soda Lime as a CO_2 absorbent is markedly affected by its moisture content, the importance of the above data is quickly seen. Data at other temperature levels is unavailable as far as is known.

The Navy has set up specifications for Soda Lime. Considerable work has been done recently by the Naval Research Laboratory on various CO_2 absorbents submitted to them for testing according to the above specifications. This test is run with a flow rate of 500 $cm^3/cm^2/min.$ using a gas containing 2.0% CO_2 and 80% R.H. Absorbents to meet specifications must pick up 0.25 gm. CO_2 per gm. of absorbent before the stripping efficiency on the gas gets below 50%. Given below is a digest of the data included in their reports bearing NDRC identification numbers A1173, A1174, A1175, and A1115.

Absorbent	Mesh Size	Time of Complete Stripping-min.	Grams CO_2 per gram of reagent when stripping efficiency reaches 50% Room Temp.	0°C.
Ascarite	8-20	180	.361	.191
Baralyme	3/16 pills	0	.139	.183
Cardoxide	8-14	80	.241	.064
Dioxorb	"	140	.249	.063
MgO	"	0	.020	.017
Mikohbite	"	20	.154	.135
Shell Natron	2-8	140		
Soda Lime Mallinckrodt	8-14	10	.046	.046
Navy Spec. Soda Lime	"	100	.238	.086
LiOH new	8 fines	210	.761	.795
LiOH stored	"	200	.693	.694
Indicator Soda Lime	----	20	.200	----
Indicator Soda Lime	----	110	.242	----
D. & A. Soda Lime	8-14	100	.309	----
" " "	8-14	140	.310	----
Soda Lime from Medical Supply Depot	4-8	20	.159	----

The Shell Natron could not be run to 50% efficiency as it plugged to such a point, due to water absorption, that the gas could not be forced through the bed.

The flow rate used here of 500 $cm^3/cm^2/min.$ is equivalent to .114 CFM/sq. in.

The above data is with gas streams high in CO_2. It is questionable of just how much value the data is in indicating an answer to the problem at hand. If one assumes 0 vapor pressure of CO_2 above the absorbent and 100% diffusion of CO_2 through the gas film at the surface of the absorbent, one might calculate the above data over into performance on gas streams containing .03-.04% CO_2. However, these assumptions particularly as regards diffusion do not appear warranted.

Some data has also been obtained on absorption of the CO_2 by Soda Lime from the Dewey & Almy Co. and from a British Admiralty Report having an NDRC number C-2564. In both cases they are working with gas streams high in CO_2 compared to air. The British report does show that upon exposure to 5% CO_2 gas streams Soda Lime can pick up .44 grams/gram of absorbent or 200 volumes of CO_2 per volume of absorbent. However, no data is given as to the stripping efficiency on the gas stream when using Soda Lime under these conditions.

From this literature no specific data directly applicable to the problem at hand was available.

An experimental program was set up which consisted of passing air of known humidity, temperature, and pressure through a bed of Dewey and Almy High Moisture Low Caustic Soda Lime at known mass air flow rates. In order to determine the performance of the bed an analytical method was needed to determine the CO_2 contents of the inlet air to the bed and the CO_2 stripped air from the bed.

Several methods were considered but only two seemed to offer promise. Norman Spector's method described in NDRC report #1426 appeared attractive. However, the necessary equipment was not at hand. A second method, the Van Slyke Manometric method, was chosen.

Considerable work has been done in attempting to use this procedure. A technique was worked out whereby when using 300 cc. samples of gas, fair checks could be obtained on air with .003-.005% CO_2 and good checks obtained on air with .03-.04% CO_2. However, one man and one apparatus could only make about 3 or 4 determinations per day. Further, the technique required considerable skill and concentration. (See Appendix for notes on this method).

A faster less tedious method was sought. Reconsideration of Mr. Spector's work suggested that rather than determining the change in pH of an alkali solution by change in color of an indicator it might be done on a glass electrode pH meter. $Ba(OH)_2$ was chosen rather than NaOH since the change in pH would be greater with thesame CO_2 input, due to the insolubility of the carbonate formed.

A technique has been worked out which appears satisfactory. A .001N $Ba(OH)_2$ solution is used. 20 cc. is placed in a medium porosity fritted glass buchner funnel of 30 cc. total capacity. A flow of about .009 CFM is passed through the filter atomizing the gas into tiny bubbles which pass through the alkali. (See Appendix for details of method).

Inlet air to the filter is run for 1 to 2 minutes and the pH change noted. Stripped air is run with fresh $Ba(OH)_2$ until the same pH change is obtained. The ratio of the CO_2 concentrations in the two gas streams can then be easily calculated from the times required to get the same pH change.

The studies on the effect of mass flow were initiated before the work was stopped. A bed of Soda Lime 12 inches deep with a cross sectional area of 12.72 sq. in. was used. Atmospheric pressure operation data was obtained first.

Fresh D. & A. High Moisture Soda Lime was used for the tests. 100% stripping of CO_2 was obtained at mass flows of 36.2-158 CFM per cubic foot of fresh absorbent.

After 18 hours of operation at a mass flow of 39 CFM per cubic foot of absorbent and with 67°F. air at a relative humidity of 38%, complete stripping was obtained at flows of 36.2-106.3 CFM per cubic foot of absorbent. Higher flow rates were not checked at this point. After 10 hours more operation with air at 65.8°F. and a relative humidity of 25%, the stripping efficiency was as follows.

Performance After 28 Hrs.

Mass Flow CFM/CF of Soda Lime	% of CO_2 Fed Removed
20.4	50
39.0	40
58.8	28
80.8	16
103.6	5

The Soda Lime was removed and its moisture and CO_2 determined.

	Location in Tower	% H_2O
Moisture Content	Top	2.65
	Middle	2.46
	Bottom	2.73
		% CO_2
CO_2 Pickup	Top	7.31
	Middle	7.33
	Bottom	9.00

Air inlet to the tower is at the bottom.

It should be noted that the above moisture content checks very well the equilibrium value of 2.6% obtainable from equilibrium moisture data from R. E. Wilson given earlier in this report.

The CO_2 content of the spent material is very low compared to data of other workers. However, it is almost certain this is due to the dehydration of the Soda Lime under the condition it was used.

A second test in which the humidity of the air was maintained at 80-90% relative humidity was started before the work was discontinued. This test was on stream for eleven hours and at the end of this time showed better than 95% stripping at mass air flow rates up to the maximum tested namely 114 CFM per cu. ft. of absorbent.

At this point in the work the N.D.R.C. contractors using the Soda Lime found they obtained superior results when they operated in a different manner from that originally proposed. Freeing the air of CO_2 after compression to 2000 to 3000 p.s.i. ga. rather than before compression has given better results in practice.

Arthur D. Little, Inc. does not have facilities at hand to study the absorption at these preferred operating conditions. It was therefore decided not to pursue the work here further.

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APPENDIX

Use of Van Slyke Manometric Apparatus

The general procedure followed in the use of the Van Slyke Manometric Apparatus to determine the CO_2 content of gas streams containing 0.003 to 0.04% CO_2 was that described in Peters and Van Slyke's book "Quantitative Clinical Chemistry", volume II Methods page 119.

Approximately 286 cc. samples of air were used for the determinations in a procedure as outlined on page 125 in the above mentioned book. All measurements of gas volumes subsequent to the initial air sample were at the 0.5 cc. volume mark.

Results on air using 286 cc. air samples gave these results.

% CO_2	Deviation from average
0.0459	+ 0.0009
0.0513	+ 0.0063
0.0405	- 0.0045
0.0454	+ 0.0004
0.0513	+ 0.0063
0.0414	- 0.0036
0.0393	- 0.0057

0.0450 average

Results on stripped air are given below.

% CO_2	Deviation
0.00204	+ 0.00038
0.00177	+ 0.00011
0.00117	- 0.00049

0.00166 average

The method was very slow (3 or 4 determinations could be made by one man in 8 hours) and required extreme attention to detail. Because of this and the not too good agreement of the results, the method was abandoned as a means of checking the stripping efficiency of the Soda Lime bed.

Glass Electrode CO_2 determination

Instead of using the Van Slyke method to determine CO_2 at concentrations of 0.003-0.03%, a procedure was worked out based on determining the change in pH of a $Ba(OH)_2$ solution due to exposure to CO_2. The pH change was measured on a Beckman glass electrode pH meter.

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The method assumes that under the conditions of the test that all the CO_2 present in the gas stream is removed by the $Ba(OH)_2$ solution. Thus if one takes two portions of standard $Ba(OH)_2$ and determines the times necessary to get the same pH change with gas streams of different CO_2 content, the CO_2 contents of the gas streams may be determined easily from the times determined.

Inlet air	Outlet Air
Δ pH of 0.10 in 2 min.	Δ pH of 0.10 in 2.35 min.

$$\% \ CO_2 \text{ stripped} = \left(100 - 100\left(\frac{2}{2.35}\right)\right) = \underline{15\%}$$

The reproducibility of the method seemed satisfactory for the purpose at hand.

The following pH's were taken on the standard $Ba(OH)_2$ solution used over the period of about one week.

Date	pH
10/23	11.36
10/25	11.34
10/26	11.36
10/27	11.36
10/29	11.37

In one period of operation the changes in pH of the standard solution on several duplicate tests of the inlet air to the Soda Lime bed were as follows: 0.10; 0.09; 0.10; 0.13; 0.10.

The procedure briefly may be described as follows.

Before each test, the fritted glass plate filtering funnel serving as a test chamber was washed with dilute nitric acid, distilled water, acetone, and ether to free the cup of solutions and residues from previous determinations and to thoroughly dry it.

20 cc. of 0.001 N $Ba(OH)_2$ was placed in the funnel whose total capacity above the fritted plate was 30 cc. The glass electrodes of the Beckman pH meter were mounted in a rubber stopper along with a suction tube serving as a gas outlet for the test chamber. The rubber stopper assembly was inserted in the funnel test chamber and air to be tested was drawn through the test chamber with a water aspirator. The air flow was measured on a #0 Rotameter and maintained at .009 CFM.

Time for the test was measured from the time the first cloud of bubbles appeared above the fritted plate after the air was turned on, until the air was turned off.

The reading of the pH of the exposed solution was made after precautions had been taken to free the glass electrodes of adhering air bubbles. Tapping the electrodes served to remove these air bubbles.

In early runs there was some tendency during the insertion of the rubber stopper into the test chamber for the slight build up in pressure within the chamber to force the $Ba(OH)_2$ solution through the fritted plate. This was eliminated by incorporating a vent in the exhaust air line which was open during the inserting of the stopper but closed off by a stopcock during the test.

Respectfully submitted,

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