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THE EFFECT OF WATER VAPOR ON THE LiOH-CO2 REACTION. PART I. DYNAMIC ISOTHERMAL SYSTEM,

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CONTENTS

ABSTRACT

The role of water vapor (H_2O) in the reaction of carbon dioxide (CO_2) with lithium hydroxide (LiOH) in a dynamic system was isolated by maintaining an essentially isothermal system through the use of low concentrations of CO_2. The LiOH was found to be hygroscopic, with the rate of water pickup directly related to the relative humidity of the feed system. Hydration to the monohydrate ($LiOH{\cdot}H_2O$) proved to be a necessary precursor to the CO_2 reaction but the rate of hydration must not exceed the rate of carbonation if high efficiencies are to be realized. The controlled rate of hydration is necessary in order to maintain the high surface area and porosity of pelletized LiOH.

The previously accepted equation,

$$2\ LiOH + CO_2 \longrightarrow Li_2CO_3 + H_2O,$$

thus becomes the summation of the two-step reaction,

$$2\ LiOH + 2\ H_2O \leftrightarrows 2\ LiOH{\cdot}H_2O$$

$$2\ LiOH{\cdot}H_2O + CO_2 \longrightarrow Li_2CO_3 + 3\ H_2O.$$

PROBLEM STATUS

An interim report on a continuing problem.

AUTHORIZATION

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THE EFFECT OF WATER VAPOR ON THE LiOH-CO_2 REACTION

PART 1 – DYNAMIC ISOTHERMAL SYSTEM

INTRODUCTION

Over the years, research on carbon dioxide (CO_2) removal by solid absorbents such as lithium hydroxide (LiOH) and soda lime has been more or less limited to solving problems of the moment. This has resulted in the accumulation of considerable empirical data which prove that this or that absorbent is the equal or better than others for a particular set of operating conditions, not all of which, it now appears, were well defined or even considered. This situation was a quasi-natural result of the various restrictions and/or operating parameters laid on by the end use desired. For example, the Navy's original interest in CO_2 removal by nonregenerative systems was for emergency use in sealed spaces such as a stricken submarine, or individually used equipment such as escape or diving gear. In all cases a common parameter was the reduction to safe levels of a high concentration of CO_2. Other factors, including low alkalinity potential in self-contained systems, were often overriding considerations in final material selection, as was economics when two or more chemicals were shown to be equally effective for a given application.

In any event, the users of these materials became such reservoirs of empirical knowledge concerning the ability to provide breathable air, that complacency deterred work on the actual mechanisms of the absorption processes. Occasional anomalies in conventional applications, as well as new requirements laid on by the current desire of men to go deeper into the sea, exposed the inadequacy of our knowledge in the area of absorbent performance prediction.

The historically accepted reaction for CO_2 removal by LiOH is

$$2\ \mathrm{LiOH} + \mathrm{CO_2} \longrightarrow \mathrm{Li_2CO_3} + \mathrm{H_2O}. \qquad (1)$$

It has been known for some time, however, that the extent to which Eq. (1) progressed in a dynamic system was affected by the presence of water vapor. An incomplete qualitative study at NRL (1) showed that a direct correlation existed between the relative humidity of the inlet feed stream and the efficiency of the absorbent bed in a nonisothermal 2% CO_2-air-LiOH system. A summary plot of these data is shown in Fig. 1.

Similarly, the Naval Civil Engineering Laboratory, while testing LiOH canisters for use in personnel shelters (2), reported cyclic CO_2 removal efficiencies, wherein they experienced earlier-than-expected CO_2 breakthrough (appearance of CO_2 in effluent), followed by periods of increased efficiency. The cycles corresponded to humidity and temperature excursions in the effluent air. They also reported that the canisters recovered some CO_2 removal capacity if allowed to rest for a short period. The input air in their system contained 3% CO_2 and 20% to 30% relative humidity at 25°C.

Meager data from Sealabs I and II indicate that LiOH did not perform as well as predicted (3). Some of the reported lack of efficiency could have been due to premature changing of the canisters, but the data also emphasize the need for a critical evaluation of the problem of CO_2 removal, particularly in hostile or novel environments.

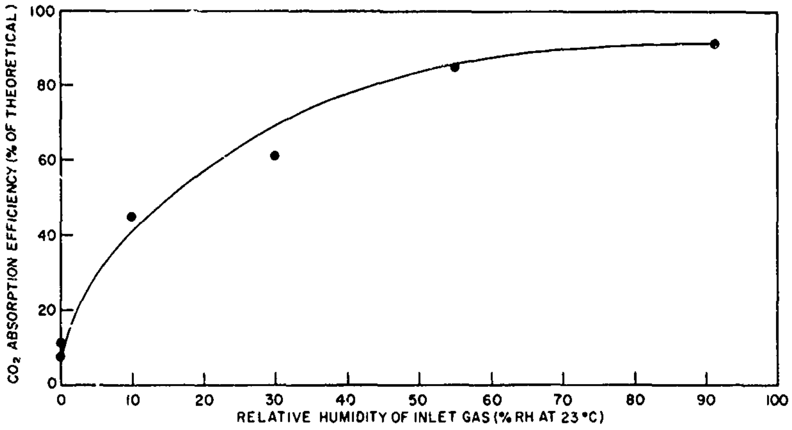

Fig. 1 - Effect of inlet humidity on the CO_2 absorption efficiency of LiOH (as taken from Ref. 1)

The physiological action of CO_2 in the respiration process is a function of its partial pressure, and the desired upper limit for man's prolonged exposure has been set at 3.8 torr, which is 0.5 vol-% atmospheric or surface equivalent. Maintaining this partial pressure as one increases total pressure (i.e., depth) means the removal of lower and lower percent concentrations; at 20 atmospheres, or about 600-ft deep, 0.5 vol-% surface equivalent becomes 0.025 vol-% ambient. The same weight of CO_2 per man must be removed in a given time since his production rate remains essentially the same as at surface conditions. The problem of air revitalization at depth, with respect to CO_2, becomes one of removing and monitoring a trace gas. The high heat transfer characteristics of helium, the major diluent in this application, further complicates the problem

All of the preceding emphasize the lack of ability to explain or predict the performance of LiOH under all conditions of use. There are indications that both heat and moisture affect the system. Moisture, particularly, is not amenable with Eq. (1), which may, therefore, require modification. The work to be reported is aimed at defining mechanisms which may limit or enhance the reaction, in order to explain past anomalies and to establish more orderly ground rules for efficiency prediction.

GENERAL EXPERIMENTAL BACKGROUND

This study was not concerned with demonstrating the effectiveness of LiOH as a CO_2-removal agent, per se. For that reason a single system geometry, not necessarily ideal, was employed for both the water absorption and CO_2 reaction runs. The principal variable, water vapor content or relative humidity (RH) of the feed gas, was isolated by the use of a low CO_2 level, thus eliminating gross heat of reaction temperature effects on the system. Similarly, the amount of water produced by the CO_2-LiOH reaction did not significantly alter the RH of the gas stream.

The chemical used for most of the runs, standard Navy LiOH (4), is pelletized to minimize dusting and to insure low pressure drop in packed beds. These pellets are made by pressing, cracking, sizing, and dehydrating crystalline lithium hydroxide monohydrate ($LiOH{\cdot}H_2O$). The anhydrous pellets resulting from this process have high porosity and surface area. Table 1 (5) lists porosity values for the various pelletized lithium compounds that are pertinent to this report.

Table 1
Porosity of Pelleted Lithium Compounds by the Mercury Intrusion Method: Aminco-Winslow Porosimeter

Compound	Pore Size Distribution (% of total volume)			
	$>100\ \mu$	$100\text{-}0.012\ \mu$	$<0.012\ \mu$	Total
$LiOH \cdot H_2O$	–	15-20	–	25.2
LiOH	0.8	43.6	24.5	68.9
LiOH-28% Li_2CO_3	2.5	40.2	19.4	62.1
LiOH-51% Li_2CO_3	2.4	38.0	15.6	56.0
LiOH-75% Li_2CO_3	2.2	36.6	10.8	49.6
Li_2CO_3	2.3	38.7	1.8	42.8

The $LiOH \cdot H_2O$ data in Table 1 were taken on a cake pressed to 75% of crystal density. No significant increase in density was observed for a pressing range of 25,000 through 135,000 psi. From this it is assumed that the indicated porosity represents the "base" conditions for the pressed cakes from which anhydrous pellets are made, and also to which those pellets would return if completely rehydrated. It is of interest to note, for later reference, the large increase in porosity resulting from dehydration and that fully carbonated pellets have more porosity than the monohydrate pellets.

DATA

The data are not presented here in chronological order. Early runs revealed such a clear relationship between CO_2 absorption efficiency and humidity that a study of the $LiOH\text{-}H_2O$ system was required in order to interpret the $LiOH\text{-}H_2O\text{-}CO_2$ system data.

Vapor Pressure of Water over $LiOH \cdot H_2O$

The determination of the vapor pressure of water over $LiOH \cdot H_2O$ was required because of the possibility that the single literature value found (6) might not hold for pelletized material or for a wide range of composition. Separate determinations were made on three source materials: virgin $LiOH \cdot H_2O$ crystals, $LiOH \cdot H_2O$ pellets made by the complete rehydration of Navy LiOH pellets, and a 1/1 mixture of $LiOH \cdot H_2O$ and LiOH pellets prepared by the controlled partial rehydration of LiOH pellets.

Approximately 5 grams of material were placed in an apparatus consisting of a 50 ml flask, a mercury manometer, and a vacuum connection, all contained in a thermostated constant temperature box. After a fast evacuation of the system, the flask and manometer were isolated, and pressure data, corrected for variations in atmospheric pressure during equilibration, collected at four temperatures between 25°C and 90°C.

The vapor pressure results for the three starting materials were identical, indicating that the rehydrated pellets were indeed $LiOH \cdot H_2O$. These data (Fig. 2) are in good agreement with Ref. 6, and in excellent agreement with Ref. 7 which appeared just as we were concluding our determination.

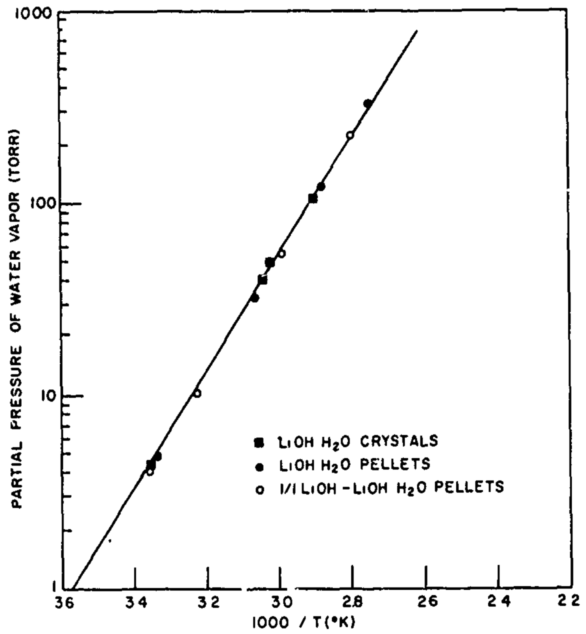

Fig. 2 - Vapor pressure of water over $LiOH \cdot H_2O$

Dynamic Effect of Humidity on LiOH and $LiOH \cdot H_2O$

From the vapor pressure data for $LiOH \cdot H_2O$, it is seen that LiOH is hygroscopic and will absorb water from a cover gas having a partial pressure of water vapor in excess of the vapor pressure of water over $LiOH \cdot H_2O$, at any given temperature, and give up water to a system having a lower partial pressure of water.

The rate at which water exchange would occur in the dynamic system used for the CO_2 absorption studies was determined gravimetrically in a number of runs involving various relative humidities of helium over LiOH and $LiOH \cdot H_2O$. The tube geometry and loadings were identical to what will be described later for the CO_2 runs. For this single geometry, the dynamic rates of water gain or loss by mixtures of LiOH and $LiOH \cdot H_2O$ versus humidity in helium is shown in Fig. 3. These rates are essentially constant until the affected component of the system nears extinction, at which time the rates taper off asymptotically.

These water gain and loss data confirm that LiOH is hygroscopic and that the $LiOH \cdot H_2O$ system will reversibly equilibrate according to the vapor pressure of water over $LiOH \cdot H_2O$. The data also revealed, although not shown, that while $LiOH \cdot H_2O$ is not hygroscopic, it will absorb a slight excess of water beyond stoichiometry. A comparison of Figs. 2 and 3 indicates that the point of zero water loss or gain in the $LiOH\text{-}LiOH \cdot H_2O$ system occurs when the partial pressure of water vapor in the gas stream equals the vapor pressure of water over $LiOH \cdot H_2O$. At 25°C this corresponds to a vapor pressure of about 4 torr or a relative humidity of about 17%.

CO_2 Absorption

The feed gas source for all runs was laboratory compressed air (100 psi). Periodic analysis for CO_2 content over the several months of experimentation showed values

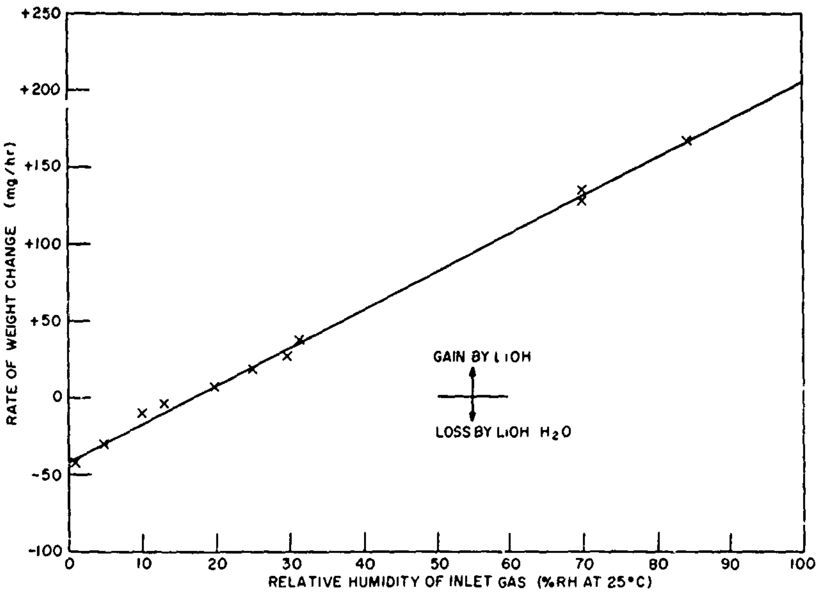

Fig. 3 - Rate of water exchange over LiOH and $LiOH \cdot H_2O$ (3.2 g LiOH equivalent - 300 cc/min helium - 25°C)

ranging from 0.025% to 0.032% CO_2, with the norm being approximately 0.03%. The relative humidity of this air was less than 1% at room temperature, which was not strictly controlled and varied between 20° and 26°C during the various experiments. The humidity of the feed gas for a given experiment was controlled originally by shunting an appropriate portion of the feed stream through a water-filled Milligan bottle, and later by feeding the entire stream through various constant-RH salt solutions in either the Milligan bottle or a spinning-disk saturator based on an NRL-developed gas stripper (8). RH between 35% and 95% was measured on an electric hygrometer (9). Calibration of the hygrometer and RH determination below 35% was made with chemical detector tubes (10).

The LiOH used for all tests was from a single lot of Navy stock material (4) which analyzed 98.2% LiOH and 1.8% Li_2CO_3 at the beginning, middle, and end of the overall time of all the runs. All absorption and reaction runs were made in cylindrical polyethylene tubes. The geometry of the reaction bed, a constant for all runs, was 1.6 cm in diameter by 3.5 cm long. The charge tared into the bed, 3.2 ± 0.28 grams calculated as anhydrous LiOH, was held firmly in place by glass-wool plugs and molded end caps which contained tubulations for connecting into the gas system. For the runs involving pelletized $LiOH \cdot H_2O$, the anhydrous material was charged into the tubes and hydrated in situ by a stream of wet helium. The stoichiometry of hydration was checked gravimetrically and chemically.

CO_2 content analysis of the feed gas was made by sparging large volumes of the line air through a barium hydroxide solution and titrating the resulting barium carbonate with 1N HCl. Inlet and outlet CO_2 concentrations were monitored on a relative basis by gas chromatography, using 5cc samples, a 30-inch silica gel column, a thermal conductivity detector (11), and a 1mV recorder equipped with an integrator (12). Variations in ambient conditions had sufficient effect upon the latter instrumentation to obviate using the data for quantitative CO_2 analysis in the parts-per-million range without frequent calibration. However, immediately consecutive inlet and outlet samples had good relative significance and were correlated on a "percent of inlet CO_2 in the outlet" basis, as calculated directly from the integrator count data. The inlet CO_2 peak averaged about 4000 counts and the minimum detectable peak at breakthrough was 50 counts, or about 4 ppm. With a few exceptions, all runs were terminated when the CO_2 content of the effluent stream was 50% of the inlet stream, or 150 ppm.

The flow rate for all comparative runs was nominally 300 cc/min, giving a bed residence time of about 1.4 seconds. This rate varied some during periods of unattended operation, with maximum known short time excursions of ±50 cc/min, but these excursions did not materially affect the data.

Following the termination of a run, the reaction bed was analyzed for LiOH, Li_2CO_3, and water content. For most runs this analysis was done as a split sample representing the inlet and outlet half of the bed. These data, which gave overall bed content values, were used to calculate $LiOH/H_2O$ mole ratios and percent of theoretical CO_2 capacity.

While it is reported (13) that lithium bicarbonate ($LiHCO_3$) is stable only in solution, a run was made to insure that the undetected presence of this compound did not complicate data interpretation. Completely carbonated pellets of LiOH were exposed to $>95\%$ RH line air in the same geometry and dynamics as for all other runs. CO_2 equal to the inlet concentration immediately appeared in the outlet air, and gravimetric data showed no significant water pickup. Hence the carbonated species in all reported runs was assumed to be the normal carbonate, Li_2CO_3.

Figure 4 is a plot of the dynamic instantaneous CO_2 absorption efficiency in percent (effluent $CO_2 \times 100$/inlet CO_2) versus time at the indicated relative humidities for both LiOH and $LiOH \cdot H_2O$ as starting materials. To prevent additional crowding of the data, duplicate runs, runs which demonstrated that the only effect of flow rate was to alter the time to breakthrough, and the slope of the postbreakthrough curve are not included in this figure. Table 2 gives, for all runs, the post-run analytical data, the percent of theoretical CO_2 capacity attained, and the extent of residual LiOH hydration.

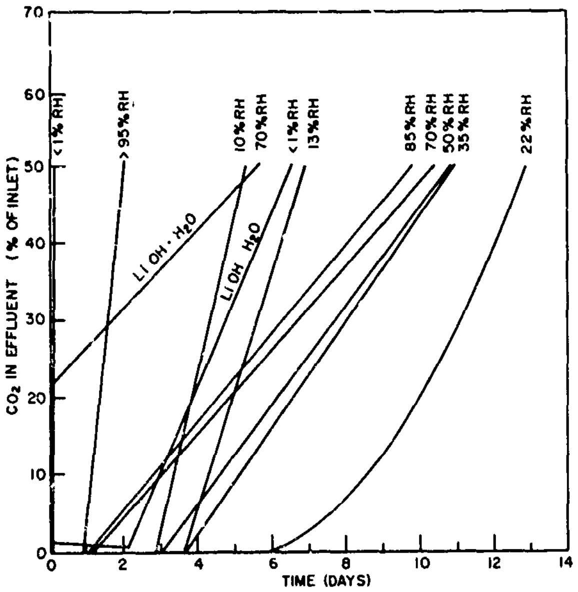

Fig. 4 - Effect of humidity on the CO_2 removal efficiency of LiOH and $LiOH \cdot H_2O$ (0.03% CO_2 feed)

Table 2
Post-Run Analyses

Run Parameters			Analysis					LiOH/ H_2O (mole ratio)	CO_2 Absorption Efficiency (% of theoretical capacity)*	Remarks
Material	Weight (g)	RH (% at 25°C)	Weight (g)		Components (wt-%)					
					LiOH	Li_2CO_3	H_2O			
LiOH	3.1248	<1	Total	3.1270	98.0	2.0	0.0	∞	<1	
LiOH	2.9801	10	Inlet	1.5628	41.5	58.5	0.0	∞		
			Outlet	2.1525	45.6	54.3	0.1	342		
			Total	3.7153	43.9	56.05	0.05	657	45.4	
LiOH	3.4876	13	Inlet	2.2067	27.6	70.9	1.5	13.8		
			Outlet	2.2920	44.0	54.9	1.1	30.0		
			Total	4.4987	36.0	62.8	1.2	22.5	52.5	
LiOH	3.3065	22	Inlet	2.6871	8.1	85.5	6.4	0.923		
			Outlet	2.4767	17.4	71.0	11.6	1.12		
			Total	5.1638	12.5	78.5	9.0	1.045	79.5	
LiOH	3.1470	35	Total	4.9989	22.0	61.8	16.2	1.02	68.2	
LiOH	3.1400	50	Total	5.0543	21.0	63.6	15.4	1.02	66.4	
LiOH	3.1250	70	Total	5.1310	21.9	61.6	16.5	0.996	65.6	
LiOH	3.1035	70	Inlet	2.4202	9.8	83.1	7.1	1.03		270 cc/min
			Outlet	2.5155	20.1	65.4	14.5	1.04		
			Total	4.9357	15.0	74.1	10.9	1.03	76.4	
LiOH	3.1589	70	Inlet	2.3391	4.8	91.2	4.0	0.9		200-400 cc/min
			Outlet	2.6770	20.9	62.9	16.2	0.97		
			Total	5.0161	13.3	76.1	10.6	0.94	78.4	
LiOH	3.0134	85	Inlet	2.4000	31.35	45.1	23.55	0.996		
			Outlet	2.5470	25.8	54.6	19.6	0.996		
			Total	4.9470	28.55	50.0	21.45	0.997	53	More CO_2 in outlet
LiOH	3.1700	>95	Total	~6.9	37.7	11.3	51.0	0.557	16	Soaking wet, pellets destroyed
$LiOH \cdot H_2O$ (Pellets)	5.2330	<1	Inlet	1.8324	35.0	63.6	1.4	18.7		
			Outlet	2.1266	32.0	66.7	1.3	18.5		
			Total	3.9590	33.4	65.3	1.3	19.3	56	
$LiOH \cdot H_2O$ (Pellets)	5.4711	70	Total	5.2764	39.4	31.4	29.2	1.01	34	

*0.917 grams of CO_2 per gram of LiOH or equivalent.

The data (Fig. 4) for LiOH as the starting material, show the following points. At < 1% RH, little or no CO_2 is removed, and no water is picked up by the bed. For all other humidities, the system exhibits an "induction" period during which all CO_2 is removed. Following breakthrough, all curves except the 22% RH run exhibit a linear slope to the 50% efficiency point. The similarity between the slopes of the postbreakthrough curves for all humidities above 35% and the 70% RH-$LiOH \cdot H_2O$ curve implies that the absorption species at this time in the runs was the monohydrate.

Table 2 shows that the residues from all runs above 22% RH, except the > 95% run, contain water in an amount which is in close agreement with the stoichiometry required for the monohydration of the residual LiOH (mole ratio $LiOH/H_2O = 1$). The > 95% RH run contains water in excess of this amount by reason of physical condensation in the bed due to temperature variations during the run and the lack of a "humidity reservoir" in the feed stream to remove the water produced by the CO_2 reaction. The 10% and 13% RH runs have nearly dry residues, and the postbreakthrough slopes of the curves are intermediate between the no-reaction < 1% RH run and the others. The 22% RH run residue indicates hydration, and the slope of the postbreakthrough curve is exponential.

Figure 4 and Table 2 show that $LiOH \cdot H_2O$ is not efficient in removing CO_2 from a feed stream which contains sufficient moisture to inhibit dehydration. It is also shown that operation at a humidity which allows simultaneous reaction and dehydration is somewhat more efficient, but still much below the theoretical capacity.

DISCUSSION

Three general conclusions can be made from the data presented.

1. The partial pressure of water vapor over LiOH in a dynamic system will determine the equilibrium compounds in that system and their rate of formation. If the partial pressure exceeds that of the vapor pressure of water over the monohydrate, then the final product will be $LiOH \cdot H_2O$. If the partial pressure is below that critical vapor pressure, a quasi-equilibrium in which a small amount of $LiOH \cdot H_2O$ is constantly being formed and dehydrated will be established. The final product in any system containing $LiOH \cdot H_2O$ exposed to completely dry gas will be LiOH.

2. The reaction of CO_2 with LiOH requires the presence of water in an amount sufficient to produce $LiOH \cdot H_2O$ prior to or simultaneously with the CO_2 reaction.

3. The rate at which water is absorbed by pelletized LiOH to form the monohydrate determines the reaction efficiency of a given bed for CO_2 removal. The efficiency of pelletized LiOH as a CO_2 absorbent is a function of the porosity and surface area resulting from the method of preparation of the material (Table 1). If the pores are refilled with water at a rate in excess of the rate at which CO_2 is being presented, the sites available for reaction will be greatly reduced. In this same vein, isothermal operation of a system at approximately 100% RH provides no means of removing the additional water produced by any CO_2 reaction. This water, condensed in situ, is a further barrier to reaction and destroys the $LiOH \cdot H_2O$ particle integrity by dissolution. Such a system can function effectively only if the CO_2 content is sufficiently high to produce a significant temperature rise in the downstream air to provide a means for water removal.

It is apparent, therefore, that for a given CO_2 content and temperature of operation there is a corresponding humidity of the feed stream which will result in maximum reaction efficiency. This ideal water content is directly related to the rate of formation of $LiOH \cdot H_2O$, which in turn is a function of the vapor pressure of water over the monohydrate at the temperature of operation.

The humidity required for the nonisothermal conditions, resulting from the reaction of somewhat higher CO_2 concentrations, will depend on the temperature profile in the bed. The CO_2 reaction releases all of the potential water in the system, that which has been absorbed plus an additional molecule of water for each molecule of CO_2 reacted. This water is repetitively available for reabsorption and reaction downstream of the reaction front. Maximum utilization will be realized only if the temperature profile in the bed maintains the RH of the downstream air in the proper relationship to the vapor pressure of water over $LiOH \cdot H_2O$ so that hydration does not greatly precede CO_2 reaction. To maintain both chemical and physical efficiency at a high level, the hydration of LiOH and the reaction of CO_2 with the $LiOH \cdot H_2O$ produced must occur essentially in the same reaction zone and proceed down the bed at the same rate.

Evidence for most of the above is provided by the post-run chemical analysis of the reaction products. For all runs involving water uptake rates that exceed the potential CO_2 reaction rate the residual water and LiOH contents agree with the stoichiometry of $LiOH \cdot H_2O$, and the overall CO_2 absorption efficiency (capacity to the 50% effluent point) is considerably lower than theoretical. These facts indicate that CO_2 reaction was efficient until the hydration of the bed was completed, at which time the reaction zone exceeded the bed length. Operation of the system at humidities below 17%, where there is no sustained water pickup, is even less efficient. The bed residues are essentially dry, although the 13% RH run demonstrates the retention of a small amount of water as a result of the quasi-equilibrium that is established in these systems. The CO_2 absorption efficiency increases as the critical hydration humidity is approached from either side for these low-CO_2 (i.e., low water-demand) runs.

The high reaction efficiency shown by the 22% RH run demonstrates the effectiveness of maintaining a chemical and physical balance between the rate of hydration and the CO_2 content. The bed was hydrated at approximately the same rate as CO_2 was being reacted, thus maintaining the reaction potential provided by water and the high porosity of the pellets.

One of the more significant effects shown in Fig. 4 is the breakthrough point. Calculations based on the rate of water pickup for the various humidities (Fig. 3), correcting for the rate of carbonation during the "induction" period, show that the breakthrough point for all runs above 22% RH coincides very closely with the time required to convert all uncarbonated LiOH in the bed to the monohydrate. Correlated with these calculations is the similarity in slope between the postbreakthrough curves and the slope of the absorption curve for $LiOH \cdot H_2O$ (70% RH). This agreement substantiates that the absorbent species after breakthrough for all of these runs is $LiOH \cdot H_2O$. The linearity of the curves indicates a reaction zone whose length exceeds the length of the bed. For the 22% RH run, breakthrough also coincided with the calculated hydration point, but the exponential shape of the 22% RH curve is indicative of a shorter reaction zone and more efficient absorption yielding a rate of hydration very close to the rate of carbonation. The breakthrough point for the runs below the critical RH do not correlate with water retention because there is none. The induction periods shown for the 10% and 13% RH runs is indicative of the utilization of what little water is retained and reused after CO_2 reaction. The steep slopes of the curves and the residue analysis both indicate inefficient CO_2 removal.

The "reverse" effect of humidity is demonstrated by the $LiOH \cdot H_2O$, $< 1\%$ RH run. Here CO_2 absorption is enhanced by the dehydration process. A calculation based on rate of water loss shows that CO_2 breakthrough occurred nearly simultaneously with the complete dehydration of the bed, at which time the system reverted to the LiOH, $< 1\%$ RH condition.

PERTINENCE TO PAST ANOMALIES

This investigation has shown that the historical expression for the LiOH-and-CO_2 reaction (Eq. (1)) is not valid, insofar as it does not define the role of water vapor. It has been demonstrated that more than a trace amount of water is required and that too much water is detrimental to the reaction. The latter effect indicates that the reactant species is not a gaseous form of H_2CO_3, since such a compound should become more stable as the moisture content increases.

The data indicate that the true CO_2 reactant is $LiOH \cdot H_2O$. Such being the case, the overall reaction must proceed in two steps:

$$2\ LiOH + 2\ H_2O \rightleftarrows 2\ LiOH \cdot H_2O \qquad (2)$$

$$2\ LiOH \cdot H_2O + CO_2 \longrightarrow Li_2CO_3 + 3\ H_2O . \qquad (3)$$

The summation of Eqs. (2) and (3), of course, give Eq. (1) as the apparent reaction. Equations (2) and (3), however, define a finite quantity of water, directly related to the CO_2 content of the gas stream, which must be supplied to maintain effective reaction. This study has shown that, for physical reasons, the water must be furnished at a rate which will produce the hydrate molecules only as fast as they are needed for reaction.

Applying Eqs. (2) and (3) to the data from Ref. 1, it is seen that the preabsorption of 2 moles of H_2O is required for each mole of CO_2 to be reacted (33 mg of H_2O per liter of 2% CO_2 feed). If the feed stream were saturated at 23°C, it would contain only 20 mg H_2O per liter, and not all of this would be absorbed in the dynamic system. Enough would be absorbed, however, to initiate the CO_2 reaction of Eq. (3), which produces 3 moles of H_2O for each mole of CO_2 absorbed (49 mg H_2O per liter of 2% CO_2 feed gas), and this produced water, repetitively condensed and absorbed downstream, sustains the overall reaction for this CO_2 level, with the heat of reaction removing any excess water. As shown in Fig. 1, the most efficient CO_2 absorption, in that study, occurred when the feed gas was nearly saturated with water for the inlet temperature, which effect our research explains. Figure 1 also shows a significant increase in absorption efficiencies between 10% and 30% inlet humidity, a figure in good agreement with the critical hydration humidity indicated by the current work.

In a similar manner, the early breakthrough and cyclic operation (2) for 3% CO_2 and 20% to 30% RH in 25°C air streams is explicable. The feed stream was humid enough to initiate reaction but too dry to sustain 3% CO_2 removal. Additionally the thermal effect of the heat of reaction did not permit the reutilization of the product water downstream of the reaction front. As the CO_2 removal became less efficient and the bed temperature fell, the product water became available for LiOH hydration, and CO_2 removal efficiency again increased. Similarly, a short rest period allowed the bed to cool and additional CO_2 removal was realized.

The work reported here also demonstrates that the lower-than-predicted CO_2 absorption efficiencies experienced by the Sealabs probably resulted from the physical loss of porosity by prehydration of the LiOH at the high RH and low CO_2 levels prevailing in those habitats.

CONCLUSION

While the data presented apply specifically to the dynamic system studied, they indicate and imply more general application. This work has clarified the role of water vapor in the reaction of CO_2 with LiOH. It is evident that the partial pressure of water vapor in the inlet stream must equal or exceed the partial pressure of water vapor over $LiOH \cdot H_2O$ in order to perpetuate reaction. The data demonstrate that ideal chemical and physical conditions for CO_2 reaction exist when the rate of $LiOH \cdot H_2O$ formation balances the rate of its consumption. Neglecting gross temperature effects, the system is self-sustaining because the CO_2 reaction repetitively releases water for further use in hydrating the bed. The inlet humidity must be maintained, however, to prevent dehydration of unreacted portions of the bed at the training edge of the reaction zone. The requirement that the rate of hydration cannot exceed the rate of CO_2 reaction is physical, relating to the porosity reduction and loss of available reaction surface when the LiOH pellets become fully hydrated before the CO_2 reaction can proceed to the interior of the pellets.

An exact formula for performance prediction cannot be made at this time because the effect of the heat of reaction cannot be neglected at other than very low CO_2 levels. An arbitrary empirical approximation would require the feed stream to provide that amount of water vapor (RH) which would result in the absorption, on the bed, of two moles of water for each mole of CO_2 present. The RH required to satisfy this condition at the proper rate must be empirically determined for the geometry and flow dynamics of each system being considered.

FUTURE WORK

The natural extension of this work is to examine the effect of temperature on both the LiOH-and-CO_2 and the $LiOH \cdot H_2O$-and-CO_2 systems. The initial study should incorporate low levels of CO_2 and externally provided heat. The effects of self-generated heat produced by higher concentrations of CO_2 could then be interpreted.

Similar studies are needed on other solid CO_2 absorbents such as soda-lime and Baralyme. The fact that both of these materials contain considerable moisture in their virgin state implies an entirely different set of reaction-controlling parameters.

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13 ABSTRACT

The role of water vapor (H_2O) in the reaction of carbon dioxide (CO_2) with lithium hydroxide (LiOH) in a dynamic system was isolated by maintaining an essentially isothermal system through the use of low concentrations of CO_2. The LiOH was found to be hygroscopic, with the rate of water pickup directly related to the relative humidity of the feed system. Hydration to the monohydrate ($LiOH{\cdot}H_2O$) proved to be a necessary precursor to the CO_2 reaction but the rate of hydration must not exceed the rate of carbonation if high efficiencies are to be realized. The controlled rate of hydration is necessary in order to maintain the high surface area and porosity of pelletized LiOH.

The previously accepted equation,

$$2\ LiOH + CO_2 \longrightarrow Li_2CO_3 + H_2O,$$

thus becomes the summation of the two-step reaction,

$$2\ LiOH + 2\ H_2O \leftrightarrows 2\ LiOH{\cdot}H_2O$$

$$2\ LiOH{\cdot}H_2O + CO_2 \longrightarrow Li_2CO_3 + 3\ H_2O.$$

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