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Carbon-14 Immobilization Via the CO_2—$Ba(OH)_2$ Hydrate Gas-Solid Reaction

G. L. Haag

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CARBON-14 IMMOBILIZATION VIA THE CO_2—$Ba(OH)_2$ HYDRATE GAS-SOLID REACTION

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NOTICE This document contains information of a preliminary nature. It is subject to revision or correction and therefore does not represent a final report.

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CARBON-14 IMMOBILIZATION VIA THE CO_2–$Ba(OH)_2$ HYDRATE GAS-SOLID REACTION

G. L. Haag

ABSTRACT

Although no special* restrictions have been placed on the release of ^{14}C, it has been identified as a potential health hazard due to the ease in which it may be assimilated into the biosphere. The intent of the Carbon-14 Immobilization Program, funded through the Airborne Waste Program Management Office, is to develop and demonstrate a novel process for restricting off-gas releases of ^{14}C from various nuclear facilities. The process utilizes the CO_2–$Ba(OH)_2$ hydrate gas-solid reaction to directly remove and immobilize ^{14}C. The reaction product, $BaCO_3$, possesses both the thermal and chemical stability desired for long-term waste disposal. The process is capable of providing decontamination factors in excess of 1000 and reactant utilization of >99% in the treatment of high-volumetric, airlike (330 ppm CO_2) gas streams.

Experimental studies have been conducted on fixed and fluidized beds of $Ba(OH)_2$ hydrates. For these studies, commercial-grade $Ba(OH)_2 \cdot H_2O$, $Ba(OH)_2 \cdot 5H_2O$, and $Ba(OH)_2 \cdot 8H_2O$ and analytical-grade $Ba(OH)_2 \cdot 8H_2O$ have been examined. Studies at ambient conditions have indicated $Ba(OH)_2 \cdot 8H_2O$ to be the active species. Therefore, process operating conditions will likely be required which favor the formation of $Ba(OH)_2 \cdot 8H_2O$. The dissociation water vapor pressure for $Ba(OH)_2 \cdot 8H_2O$ at 25°C is 1.10 kPa (8.26 mm Hg). Although both commercial- and analytical-grade $Ba(OH)_2 \cdot 8H_2O$ have been found to be reactive toward CO_2, they are considerably less reactive than either $Ba(OH)_2 \cdot H_2O$ or $Ba(OH)_2 \cdot 5H_2O$ which have been hydrated to $Ba(OH)_2 \cdot 8H_2O$. We have observed that during the fixed-bed treatments of humidifed-air gas streams, the two reactants undergo a conditioning period during which the CO_2 removal efficiency of the bed dramatically improves. However, this activation step is accompanied by a twofold increase in bed volume and degradation of the reactant particles. The resultant bed is extremely active for CO_2 removal, but gas throughput is restricted because of increased pressure-drop problems. For the operation of a fluidized bed, this would likely not present a problem. However, because of the many merits of the simpler fixed-bed concept, considerable effort has been directed toward reducing the magnitude of the pressure drop problem. Recent experimental results have indicated that for the treatment of an air-based off-gas stream, packed beds of commercially available $Ba(OH)_2 \cdot 8H_2O$ flakes possess acceptable CO_2 removal, bed utilization, and pressure drop properties. Under appropriate conditions, we have observed a pressure drop of 3.64 kPa/m (0.14 psi/ft) at a superficial gas velocity of 13 cm/s.

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*General release limits for ^{14}C and other radionuclides are tested in 10 CFR 20.

1. INTRODUCTION

In the radiation field which exists within a nuclear reactor, radioisotope ^{14}C is produced by neutron interactions with ^{14}N, ^{15}N, ^{16}O, ^{17}O, and ^{13}C which is present in the fuel, the cladding, and the primary cooling system.[1-9] Although it is a weak beta emitter, ^{14}C poses a long-term health hazard due to its long half-life of 5730 yr and the ease with which it may be assimilated into living matter.[10-14]

An appreciable fraction of the ^{14}C produced would be expected to be converted to gaseous effluent during normal operation of a light-water reactor, extensive fuel element failure, storage of spent fuel, and upon fuel reprocessing. The ^{14}C would exist as either CO_2 or low-molecular-weight hydrocarbons with the most probable method of treatment being the oxidation of the hydrocarbons to CO_2 and subsequent fixation of the CO_2. Likely CO_2 gas concentrations containing traces of ^{14}C would range from 10 to 330 ppm with gas flow rates of up to 20 m^3/min (700 ft^3/min) anticipated. Expected release rates from various nuclear facilities are presented in Table 1.

Table 1. Approximate Production and Release Rates of Carbon-14 in the Nuclear Fuel Cycle[2]

Nuclear reactors	Ci/Gw(e)yr
LWR	8-10
CANDU	500
Reprocessing plant	
LMFBR	6
LWR	18
HTGR	200

For the removal and fixation of ^{14}C in selected off-gas streams at nuclear facilities, we have established the following criteria with respect to process development. First, the process removal efficiency must be consistent with or greater than anticipated NRC release criteria. Second, the final product must be an acceptable form for final waste disposal. Third, the process must possess excellent on-line reliability characteristics. Fourth, it is desirable that the process operate at ambient conditions. Fifth, maximum process costs should not exceed $1000/man-rem.

2. SUGGESTED TECHNOLOGIES FOR $^{14}CO_2$ CONTROL

Suggested technologies for ^{14}C control have generally followed commercially available technology for inert CO_2 control. The processes range from CO_2 absorption in amine-bearing solutions to physical adsorption on molecular sieves to chemical reaction with a NaOH solution and carbonate interchange with $Ca(OH)_2$, the double alkali process.[15] However physical absorption, adsorption, and reaction with NaOH solution share a common trait in that they are CO_2 removal processes, but they do not chemically fix the CO_2 for final disposal, a requisite for the disposal of nuclear waste. Therefore, suggested technologies for the treatment of dilute CO_2-bearing gases have generally employed a removal or an enrichment step, to increase the CO_2 gas concentration, followed by a final fixation step whereby the CO_2 is reacted with $Ca(OH)_2$ slurry.[15-20] The product, $CaCO_3$, possesses excellent thermal and chemical stability making it suited for long-term waste disposal (thermal decomposition at 825°C and water solubility of 0.0153 g/L at 25°C).[21,22] However for the treatment of high-volumetric, low-CO_2-content gas streams, this process suffers severely as an enrichment step is required to restrict the overall size of the $Ca(OH)_2$ slurry reactor. Other areas of concern with this technology are the generation and recycle of aqueous wastes and the need for solid-liquid separation equipment.

For the treatment of a high-volumetric, dilute CO_2-bearing off-gas stream, many potential advantages could be realized if a suitable technology utilizing a gas-solid reaction for ^{14}C removal and fixation existed. However, widely acceptable CO_2 sorbents such as ascarite (NaOH on asbestos) and $LiOH \cdot H_2O$, which has been used extensively for CO_2 control in life support systems, lack sufficient carbonate stability for final waste disposal. Studies in CO_2 removal have been conducted on soda lime [$NaOH$-$Ca(OH)_2$ mixture] and baralyme [$Ca(OH)_2$-$Ba(OH)_2$ mixture] with reasonable success.[23-28] However, the solubility of Na_2CO_3 in the former and poor reactant utilization in the latter make the use of these reactants doubtful. An examination of the carbonate products of potential Group 1 (alkali metals) hydroxides (Table 2) indicates that they may be categorically classified as possessing excessive solubility in water for long-term waste disposal.

Table 2. Solubility and decomposition properties of Group 1 (alkali metal) and Group 2 (alkaline earth) carbonates at low CO_2 partial pressures[21,22]

	Molal solubility		Decomposition temperature (°C)
	25°C	100°C	
Group 1 carbonates			
Li_2CO_3	0.18	0.10	1310
Na_2CO_3	2.80	4.26	--
K_2CO_3	8.10	4.41	--
Rb_2CO_3	19.48	--	740
Cs_2CO_3	8.00	--	610
Group 2 carbonates			
$MgCO_3$	0.00126[a]	--	350
$CaCO_3$	0.00013	0.000375	825
$SrCO_3$	0.000075	0.00044	1340
$BaCO_3$	0.000124	0.000332	1450

[a] Cold water.

However, the higher-molecular-weight carbonates of the Group II (alkaline earths) are considerably more stable. As shown in Table 2, the carbonates of calcium, strontium, and barium possess excellent solubility characteristics and furthermore, decompose at considerably greater temperatures.

It has been suggested in the literature, and confirmed experimentally at ambient conditions in our lab, that a $CaCO_3$ coating forms about the $Ca(OH)_2$ reactant thereby resulting in severe diffusional limitations.[29] Some success has been reported at higher temperatures. A German patent was issued in which thermal ramping was used to enhance the reactivity and conversion of the $Ca(OH)_2$ reactant.[30] Process temperatures were 100 to 200°C. Work performed by Ontario Hydro has indicated that the reaction proceeds more readily at 400°C, but reactant conversions in excess of 60% have been uncommon.[5]

The alkaline earth hydroxides of strontium and barium differ from the other alkaline earth hydroxides in that they may exist in a hydrated form. The most commonly reported coordination numbers are 1 and 8, although 2 and

3 waters of hydration have been reported for $Ba(OH)_2$. Our studies have concentrated on the use of $Ba(OH)_2$ hydrates since the hydrates of $Sr(OH)_2$ are not as available in commercial quantities.

To determine the likelihood of a reactant being coated by a nonporous product which would result in severe diffusional limitations of the gaseous reactant, a comparison of the molar crystal volume ratios of the product and reactant, referred to as the Pilling-Bedworth ratio, is often beneficial. The Pilling-Bedworth ratios for several alkali and alkaline earth hydroxides and their carbonate products are presented in Table 3. With the exception of the $Ba(OH)_2$ and $Sr(OH)_2$ data, the table was taken from a paper by Markowitz.[31] A Pilling-Bedworth ratio >1 indicates a high probability of diffusional limitations, and a value of <1 indicates that product porosity may exist. Apparent exceptions to this relationship may result for various mixtures where synergistic effects or physical changes of the solid such as sintering or melting may occur. From Table 3, one would anticipate that $LiOH_2 \cdot H_2O$, $Sr(OH)_2 \cdot 8H_2O$, $Ba(OH)_2 \cdot H_2O$, and $Ba(OH)_2 \cdot 8H_2O$ would be efficient CO_2 absorbents if the chemical reactions were kinetically favored. One might also predict $Ba(OH)_2 \cdot 8H_2O$ to be more efficient than $Ba(OH)_2 \cdot H_2O$ for CO_2 removal. The Pilling-Bedworth ratio of 1.18 for $Ca(OH)_2$ is consistent with the reported formation of an impervious shell about the $Ca(OH)_2$ particle, thus resulting in diffusional limitations. Similarly, work performed by Boryta and Maas[32] and the Naval Research Laboratory[33] have indicated $LiOH \cdot H_2O$, Pilling Bedworth ratio of 0.64, to be the reactive species in CO_2 removal studies and LiOH, Pilling Bedworth ratio of 1.07, to be unreactive.

3. LITERATURE REVIEW

Although hydrates of $Ba(OH)_2$ have been cited in the literature[29] as being reactive toward CO_2 in ambient air, the extent of this reactivity had not been examined until this study. The stoichiometry of the overall reaction may be represented by

$$Ba(OH)_2 \cdot xH_2O(s) + CO_2(g) \rightarrow BaCO_3(s) + (x+1)H_2O(g), \tag{1}$$

where x is the initial degree of hydration.

Table 3. Molar volume relationships among some possible carbon dioxide absorbents

Substance	Formula weight	Density $g \cdot cm^{-3}$	Molar volume ($cm^3/g \cdot mol$)	Pilling-Bedworth ratio
LiOH	23.95	1.43	16.75	1.07
$LiOH \cdot H_2O$	41.96	1.51	27.79	0.64
Li_2CO_3	73.89	2.07	35.70	
NaOH	40.01	2.13	18.78	1.47-$Na_2CO_3 \cdot H_2O$ 1.13-Na_2CO_3
Na_2CO_3	106.00	2.51	42.25	
$Na_2CO_3 \cdot H_2O$	124.02	2.25	55.12	
$Mg(OH)2$	58.34	2.39	24.41	1.14
$MgCO_3$	84.33	3.04	27.77	
$Ca(OH)_2$	74.10	2.34	31.63	1.18
$CaCO_3$	100.09	2.71	36.92	
$Sr(OH)_2 \cdot 8H_2O$	265.76	1.90	139.87	0.29
$SrCO_3$	147.63	3.70	39.90	
$Ba(OH)_2 \cdot 8H_2O$	315.48	2.10	150.23	0.30
$Ba(OH)_2 \cdot 1H_2O$	189.48	3.65	51.8	0.86
$BaCO_3$	197.35	4.43	44.47	

In the opinion of this author, the most credible study conducted to date on the dissociation vapor pressures of $Ba(OH)_2$ hydrates was that of Kondakov, Kovtunenko, and Bundel.[34] The results were published in 1964. In this study, the water vapor pressure of $Ba(OH)_2 \cdot xH_2O$ samples with x values of 0.3896, 1.342, 2.260, 3.282, 4.196, 5.042, 5.882, and 6.763 were determined. When the results were plotted (log p vs 1/T), three distinct lines were obtained as shown in Fig. 1. The lines correspond to $Ba(OH)_2$ hydrate samples in which $Ba(OH)_2 \cdot H_2O$, $Ba(OH)_2 \cdot 3H_2O$, and $Ba(OH)_2 \cdot 8H_2O$ were the contributing species to the water vapor pressure within the system. The controlling decomposition reactions and their respective dissociation vapor pressure equations were found to be the following:

$$Ba(OH)_2 \cdot 1H_2O(s) \rightarrow Ba(OH)_2(s) + H_2O(g) \tag{2}$$

$$\log P = -\frac{61353}{19.155T} + 12.421 ,$$

$$Ba(OH)_2 \cdot 3H_2O(s) \rightarrow Ba(OH)_2 \cdot 1H_2O(s) + 2H_2O(g) \tag{3}$$

$$\log P = -\frac{62618}{19.155T} + 13.823 ,$$

$$Ba(OH)_2 \cdot 8H_2O(s) \rightarrow Ba(OH)_2 \cdot 3H_2O(s) + 5H_2O(g) \tag{4}$$

$$\log P = -\frac{58230}{19.155T} + 13.238 ,$$

where

P = vapor pressure, Pa or $nt \cdot m^{-2}$,

T = temperature, K.

Using the Van't Hoff equation, the data were analyzed for thermodynamic consistency. Based upon the entropy change for the formation of the trihydrate, they concluded that the trihydrate may be less stable than the other crystalline hydrates. However, other investigators under highly controlled conditions have reported $Ba(OH)_2 \cdot 2H_2O$ and amorphous compounds to exist.

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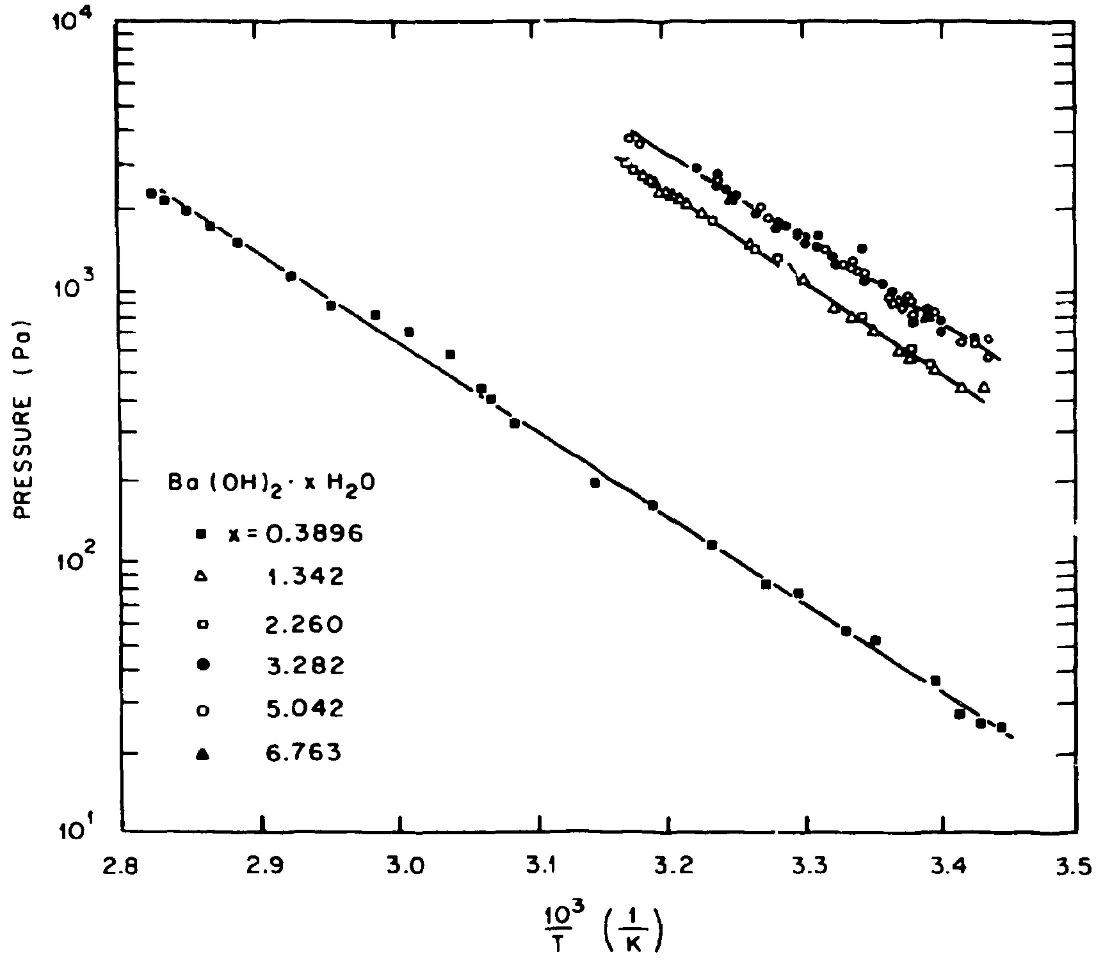

Fig. 1. Dissociation vapor pressures for $Ba(OH)_2$ hydrates.

With the exception of $Ba(OH)_2 \cdot 2H_2O$, the thermodynamics of the CO_2-barium hydroxide hydrate gas-solid reaction may be calculated from published values.[34-40] Presented in Table 4 are the thermodynamic calculations for the following reactions:

$$Ba(OH)_2(s) + CO_2(g) \rightarrow BaCO_3(s) + H_2O(g) \qquad \Delta H = -115 \text{ kJ/mol} \; ; \qquad (5)$$

$$Ba(OH)_2 \cdot H_2O(s) + CO_2(g) \rightarrow BaCO_3(s) + 2H_2O(g) \qquad \Delta H = -53 \text{ kJ/mol} \; ; \qquad (6)$$

$$Ba(OH)_2 \cdot 3H_2O(s) + CO_2(g) \rightarrow BaCO_3(s) + 4H_2O(g) \qquad \Delta H = -73 \text{ kJ/mol} \; ; \qquad (7)$$

$$Ba(OH)_2 \cdot 8H_2O(s) + CO_2(g) \rightarrow BaCO_3(s) + 9H_2O(g) \qquad \Delta H = 364 \text{ kJ/mol} \; . \qquad (8)$$

Table 4. Thermodynamic properties of the CO_2–$Ba(OH)_2$ hydrate gas-solid reaction at 298.15 K[32-37]

Reaction	ΔG kJ/mol	ΔH kJ/mol	ΔS $J \cdot mol^{-1} \cdot K^{-1}$	K_{eq}
5	-85.7	-114.6	-37.2	$1.05 \cdot 10^{15}$
6	-66.5	-53.0	104.6	$4.52 \cdot 10^{11}$
7	-41.6	-72.6	442.3	$1.94 \cdot 10^{7}$
8	15.9	364.4	1230.0	0.00187
9	-61.9	-31.8	161.3	$6.84 \cdot 10^{10}$

At 298 K and 1 atm, the fugacities of the gas species may be approximated by their partial pressures (atm), and the fugacities of the crystalline species, with respect to their reference states, is equal to ~1. If the water product is present as vapor, the equilibrium constant, K_{eq}, is equal to $[P(H_2O)]^{x+1}/[P(CO_2)]$, where x is the hydration number of the reacting species and $P(H_2O)$ and $P(CO_2)$ are the partial pressures of water and carbon dioxide that exist within the system. The maximum partial pressure water vapor that can exist within the system at a fixed temperature is that at complete saturation. At 25°C, this value is 3.165 kPa or 23.75 mm Hg. Therefore, based upon the previously calculated equilibrium constants for the speculated reactions, the corresponding CO_2 partial pressure at equilibrium may be calculated for the possible carbonation

reactions. These values are presented in Table 5. With respect to the preceding analysis, if any of the speculated reaction mechanisms were equilibrium controlled, the effluent CO_2 concentration would be less than 15 part per trillion.

Table 5. Equilibrium values for the CO_2–$Ba(OH)_2$ hydrate gas-solid reaction

Reaction	K_{eq}	Reactant hydration	P_{CO_2} Pa	P_{CO_2} mm Hg
5	$1.0 \cdot 10^{15}$	0	$3.1 \cdot 10^{-12}$	$2.4 \cdot 10^{-14}$
6	$4.52 \cdot 10^{11}$	1	$2.2 \cdot 10^{-10}$	$1.7 \cdot 10^{-12}$
7	$1.94 \cdot 10^{7}$	3	$5.0 \cdot 10^{-9}$	$3.7 \cdot 10^{-11}$
8	$1.37 \cdot 10^{-3}$	8	$1.5 \cdot 10^{-6}$	$1.1 \cdot 10^{-8}$
9	$6.84 \cdot 10^{10}$	8	$1.5 \cdot 10^{-6}$	$1.1 \cdot 10^{-8}$

Based upon a dissociation pressure for $Ba(OH)_2 \cdot 8H_2O$ of 1.1 kPa (8.26 mm Hg) at 298 K, any water vapor pressure greater than this value would override the thermodynamic constraints for formation of $Ba(OH)_2 \cdot 8H_2O$. However, the kinetics of this exothermic transformation are unknown. If the gas surrounding the particle is water saturated, the excess water of reaction (nine molecules of water per molecule of CO_2 reacted) must remain as a liquid in the pore structure and may have a deleterious effect on the overall reaction. Thermodynamic and equilibrium values for this reaction sequence are also presented in Tables 4 and 5 for the following reaction:

$$Ba(OH) \cdot 8H_2O(s) + CO_2(g) \rightarrow BaCO_3(s) + 9H_2O(l) \quad \Delta H = -32 \text{ kJ/mol.} \qquad (9)$$

Again, the reactions will be equilibrium controlled only for very low CO_2 partial pressures.

When no work is being performed on or by the system, the enthalpy change is a measure of the endo- or exothermicity of the reaction at 298 K.

Although hydroxide-carbonate reactions are generally regarded as exothermic, as reflected by the stability of the carbonate product, the waters of reaction (when released as a vapor) tend to make the reaction less exothermic. If the surrounding gas is water saturated and heat is not removed from the system by vaporization of the released waters of hydration, the reaction becomes more exothermic. Therefore, for situations in which the feed gas is rich in CO_2, the gas may quickly become saturated with water. In this case, part of the column may operate under endothermic conditions (Reaction 8) and another section under exothermic conditions (Reaction 9).

4. EXPERIMENTAL STUDIES

Experimental studies are being conducted to develop a better understanding of the CO_2 — $Ba(OH)_2$ hydrate gas-solid reaction and to develop a process capable of treating a high-volumetric, low-CO_2-content gas stream. Studies have been conducted on packed and fluidized beds of $Ba(OH)_2$ hydrate. Presently, the packed-bed concept is preferred due to overall operational simplicity.

4.1 Potential $Ba(OH)_2$ Hydrate Reactants

As previously mentioned, stable $Ba(OH)_2$ hydrate species with hydration of 1, 2, 3, and 8 have been reported. To date, we have examined the reactivity of reagent-grade $Ba(OH)_2 \cdot 8H_2O$ and commercially available $Ba(OH)_2 \cdot H_2O$, $Ba(OH)_2 \cdot 5H_2O$, and $Ba(OH)_2 \cdot 8H_2O$. A photograph of the materials is presented in Fig. 2. X-ray diffraction patterns were obtained for each material form, and the results presented in Table 6. Reactant analyses were conducted on two 200-lb drums of the commercial $Ba(OH)_2 \cdot 8H_2O$. These results are presented in Table 7.

From the results, one cannot statistically reject the hypothesis that the mean compositions for the drums are the same. In a similar manner, the standard deviation attributed to the experimental technique was determined to be 0.077. This value was obtained by repetitive titrations of analytical-grade $Ba(OH)_2 \cdot 8H_2O$. Therefore, the deviation about the mean which was observed for the two drums of commercial-grade $Ba(OH)_2 \cdot 8H_2O$ may

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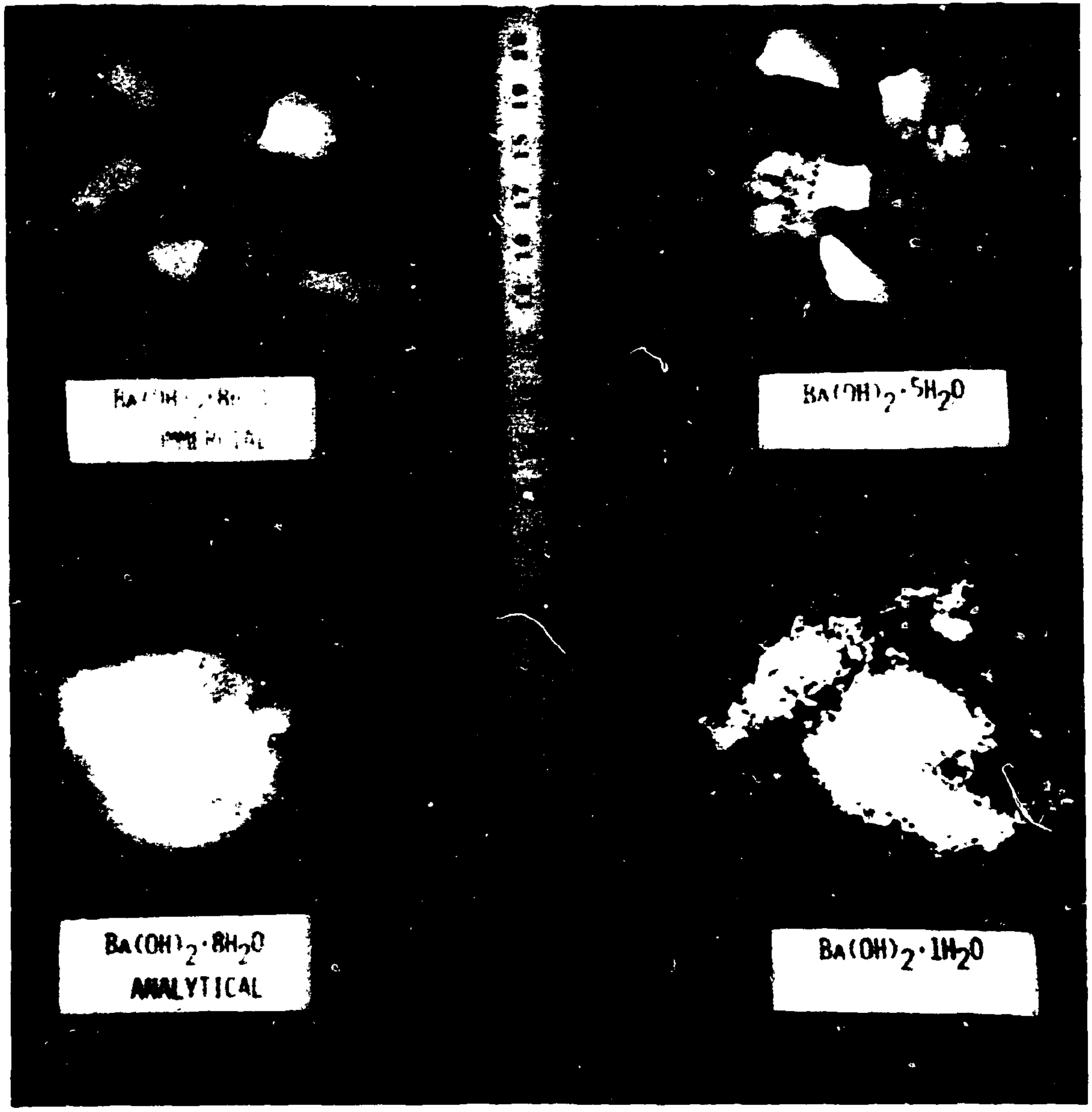

Fig. 2. Commercial and analytical $Ba(OH)_2$ hydrates.

Table 6. X-ray diffraction analyses of $Ba(OH)_2$ hydrate samples

Sample	Observed line intensities
$Ba(OH)_2\cdot H_2O$	$Ba(OH)_2\cdot H_2O$ - strongest
	$Ba(OH)_2\cdot 3H_2O$
$Ba(OH)_2\cdot 5H_2O$	$Ba(OH)_2\cdot H_2O$
	$\cdot 3H_2O$ - same intensity
	$.8H_2O$
$Ba(OH)_2\cdot 8H_2O$ - commercial	$Ba(OH)_2\cdot 8H_2O$
$Ba(OH)_2\cdot 8H_2O$ - analytical	$Ba(OH)_2\cdot 8H_2O$

Table 7. Reactant analyses on commercial $Ba(OH)_2\cdot 8H_2O$

Drum No.	Average composition	Standard deviation	Number of samples
1	$Ba(OH)_2\cdot 7.54H_2O$	0.0966	12
2	$Ba(OH)_2\cdot 7.47H_2O$	0.0830	20

be attributed to the analytical technique and not the sample position in the drum. Vendor specifications for the commercial-grade $Ba(OH)_2 \cdot 8H_2O$ indicate the reactant composition to be between $Ba(OH)_2 \cdot 7.13H_2O$ and $Ba(OH)_2 \cdot 7.86H_2O$. The mean of these values is $Ba(OH)_2 \cdot 7.50H_2O$, which agrees well with the analyses reported above. It is interesting to note that Michaud reported a $Ba(OH)_2 \cdot 3H_2O$—$Ba(OH)_2 \cdot 8H_2O$ eutectic to exist during solubility studies on the $Ba(OH)_2$ hydrate—water system.[41,42] The stoichiometric composition of the eutectic corresponds to $Ba(OH)_2 \cdot 7.12H_2O$, which agrees with the lower specification cited by the vendor. This eutectic consists of 18 mol % $Ba(OH)_2 \cdot 3H_2O$. Therefore, the samples of commercial $Ba(OH)_2 \cdot 8H_2O$ used in our studies appear to consist of 47 mol % eutectic and 53 mol % $Ba(OH)_2 \cdot 8H_2O$. The total amount of $Ba(OH)_2 \cdot 3H_2O$ in these samples would then be 10 mol %.

Discussions with the vendor have indicated that the flakes are prepared by distributing a hot magma solution of $Ba(OH)_2$ hydrate (~.3 mm thick) on a conveyer belt which is cooled on the underside by a water bath. As shown in Fig. 3, the two sides of the resultant flake are quite different — the side next to the belt is very smooth; the outer side, somewhat rough. Presented in Fig. 4 is a photo obtained by the transmission of light through the flake. Of particular interest are the star-shaped patterns appearing in the material. Based upon the observations of Flemings in *Solidification Processes* for a similar solidification process in which eutectic and pure species are present, we speculate the dendritic-like stars to be $Ba(OH)_2 \cdot 8H_2O$.[43] This material preferentially crystalizes next to the cool surface at the conveyor belt and then extends in a dendritical manner up through the flake. The eutectic then precipitates out and fills in the voids. The stoichiometric composition of the commercial $Ba(OH)_2 \cdot 8H_2O$ is 47% eutectic, 53% $Ba(OH)_2 \cdot 8H_2O$.

4.2 Experimental Equipment

A schematic of the experimental equipment is presented in Fig. 5. The equipment may be used for either differential-bed or extended-length packed-bed studies. The feed gas is metered through rotameters and fed to

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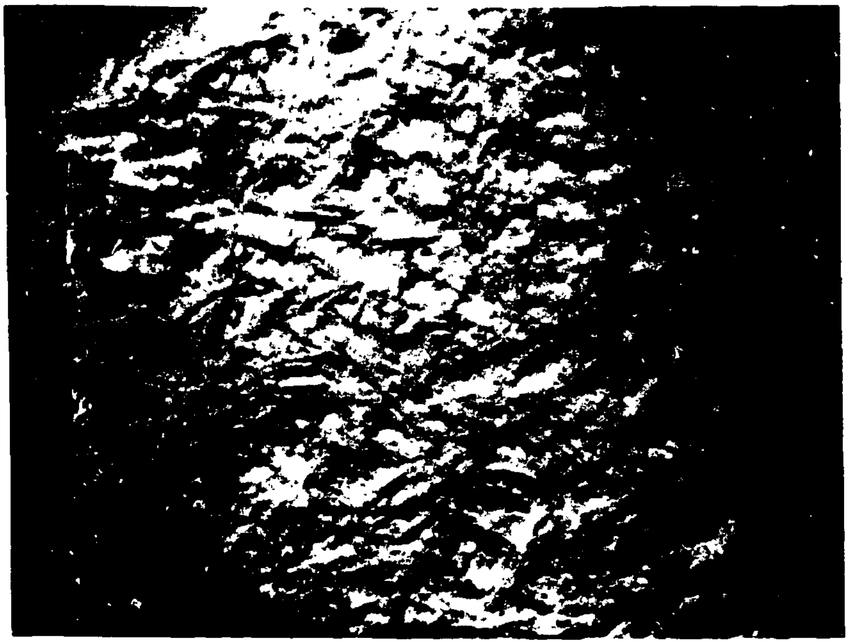

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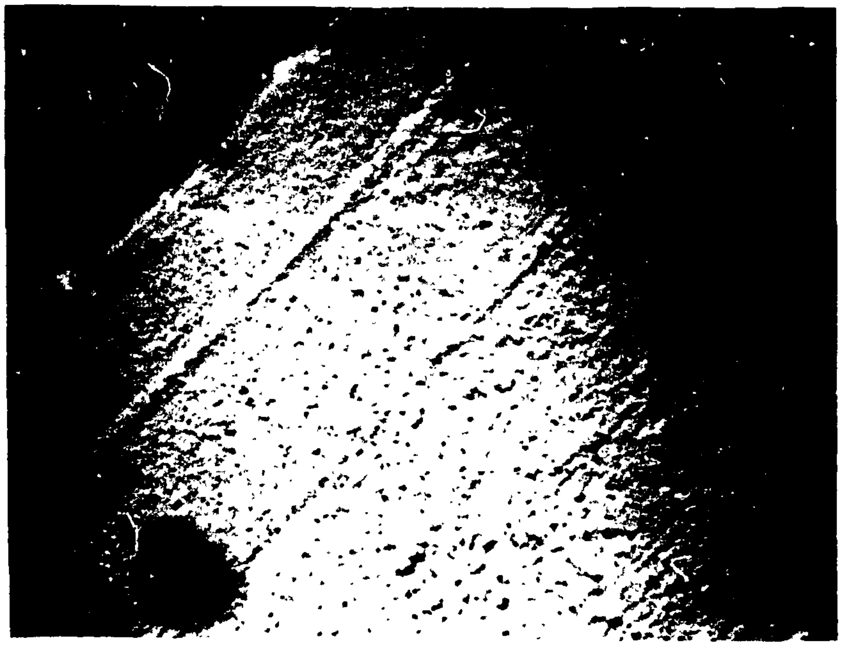

Fig. 3. Top and bottom views of commercial $Ba(OH)_2 \cdot 8H_2O$ flakes; 2.85-by 3.75-in. original photograph, magnification — 12.75X.

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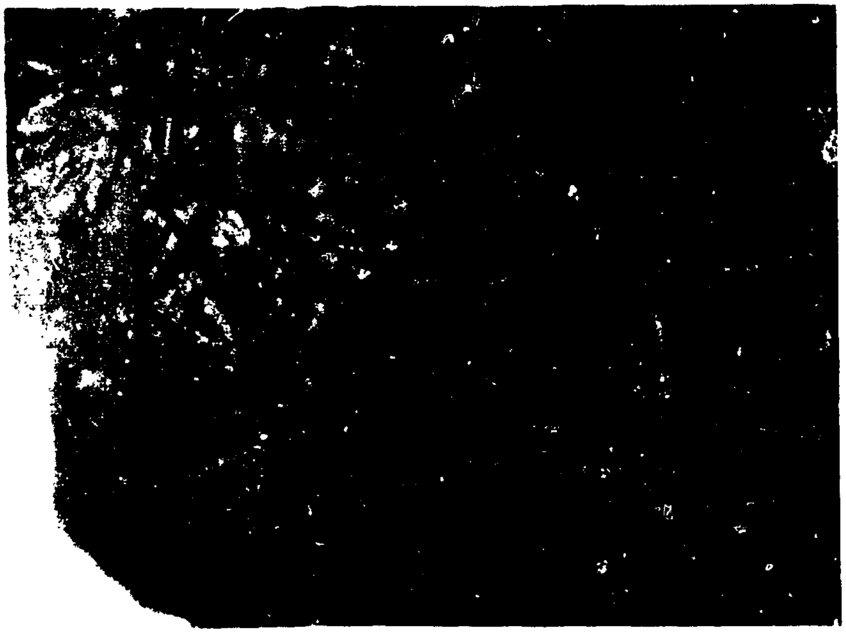

Fig. 4. $Ba(OH)_3 \cdot 8H_2O$ flake; 2.85-by 3.75-in. original photograph, magnification — 12.75X.

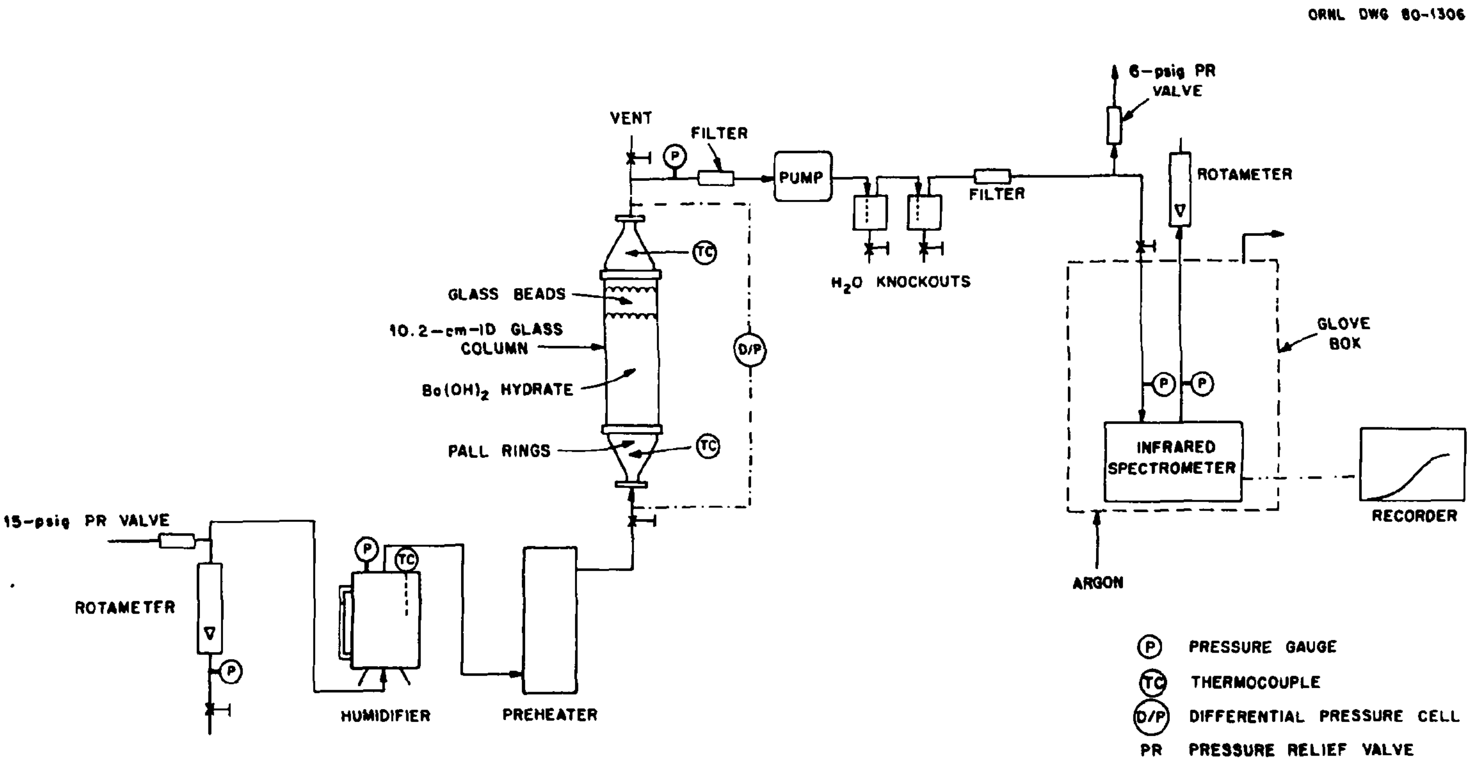

Fig. 5. Schematic of the experimental equipment for CO_2 removal studies.

a humidifier. The extent of humidification is controlled by the temperature and pressure of the humidifier. The gas is then passed through a preheater and to the reactor. At the base of the 10.2-cm (4-in.)-ID glass reactor, the gas is dispersed by Pall rings before passing through the bed. The $Ba(OH)_2$ hydrate reactant is supported in the glass column by 100-mesh wire screen. The reactor is jacketed to ensure a uniform temperature profile. The minimal bed depth for differential reactor studies is 6 mm (1/4 in.). The common length for the extended-length packed-bed studies is 51 cm (20 in.). For these studies, a differential pressure (D/P) cell was used to monitor the pressure drop increase across the bed as a function of time. To ensure a positive pressure system for gas analyses, the pressure at the top of the bed is maintained at 108 kPa (1 psig). A small portion of the effluent gas is passed through a filter and to a metal bellows pump for pressurization to 145 kPa (7 psig). Following pressurization, the gas flows through two knockout vessels for water removal and then to the off-gas analytical system.

The analytical system consists of a flowthrough Wilks-Foxboro Miran 1A infrared analyzer that is located in a glove box. Because the window to the flow cell and IR light source of the analyzer are separated by the surrounding gas, we have found it necessary to place the analyzer in a controlled environment because of fluctuations in the ambient CO_2 concentration and hence, the drifting of the baseline. The glove box is continuously purged with argon. The infrared spectrometer wavelength is set at 4.25 μm and the pathlength at 20.25 m. The cell pressure is maintained at 136 kPa (5 psig), and the cell is jacketed and maintained at 50°C to avoid water condensation within the cell. No interference from high water concentrations has been observed at extremely low CO_2 concentrations. The instrument has been calibrated over the concentration range of 100 ppb to 330 ppm CO_2, using calibration gases obtained from the Bureau of Mines Helium Operations Plant in Amarillo, Texas, and from commercial vendors. The calibration gases obtained from the Bureau of Mines are excellent sub-ppm standards as they have been analyzed by a freeze-out preconcentration technique followed by mass spectroscopy analysis.

The runs are generally continued through column loading (complete breakthrough of CO_2). The product is then analyzed by a standard acid-base titration with a Brinkmann automatic titrator. The reactant conversion is determined from the titration results, and the extent of hydration is calculated by an overall mass balance on the analyzed sample.

4.3 $Ba(OH)_2 \cdot H_2O$ Studies

Due to the lack of reactivity and poor product conversion associated with the carbonation of $Ca(OH)_2$, the prime objective in initial studies on the hydrates of $Ba(OH)_2$ was to establish the reactivity of the various hydrated species. As indicated in Fig. 6, beds of $Ba(OH)_2 \cdot H_2O$ were superior to either beds of $Ba(OH)_2 \cdot 8H_2O$ or $Ba(OH)_2 \cdot 5H_2O$ for the treatment of a humidified 4.8% CO_2 gas stream. Therefore, initial experimental emphasis was placed upon the use of $Ba(OH)_2 \cdot H_2O$ for CO_2 removal and fixation. The results of these studies indicated CO_2 removal from air (330 ppm CO_2) concentrations to <100 ppb to be possible. Reactant utilization in excess of 99% was routinely obtained, and the mass transfer zone was extremely short. As may be observed in Fig. 2, the reactant is particulate in nature. However, these runs were characterized by a twofold increase in bed volume and accompanying increases in pressure drop across the bed. As indicated in Fig. 7, when a bed of $Ba(OH)_2 \cdot H_2O$ was contacted with a dry feed gas, poor removal was noted. However, when the water vapor pressure of the feed gas exceeded the dissociation vapor pressure of $Ba(OH)_2 \cdot 8H_2O$ (Fig. 7 or Fig. 8), the reaction proceeded quite rapidly. The formation of $Ba(OH)_2 \cdot 8H_2O$ was confirmed by x-ray diffraction analysis. As shown in Run 10 (Fig. 8), a packed bed of $Ba(OH)_2 \cdot H_2O$ undergoes a conditioning period when contacted with a humid CO_2-bearing gas, during which the activity of the bed decreases and then increases. The initial reactivity is attributed to the presence of a small amount of $Ba(OH)_2 \cdot 8H_2O$ which is gradually depleted. In time, moisture from the air converts the rest of the bed to active $Ba(OH)_2 \cdot 8H_2O$. As indicated by Run 22 (Fig. 8), the bed may also be preconditioned by a humid inert gas. In both cases, a factor of 2.5 increase in bed volume, resulting from $Ba(OH)_2 \cdot 8H_2O$ formation was observed, and reactant conversions in excess of 99% were obtained. The bed expansion did

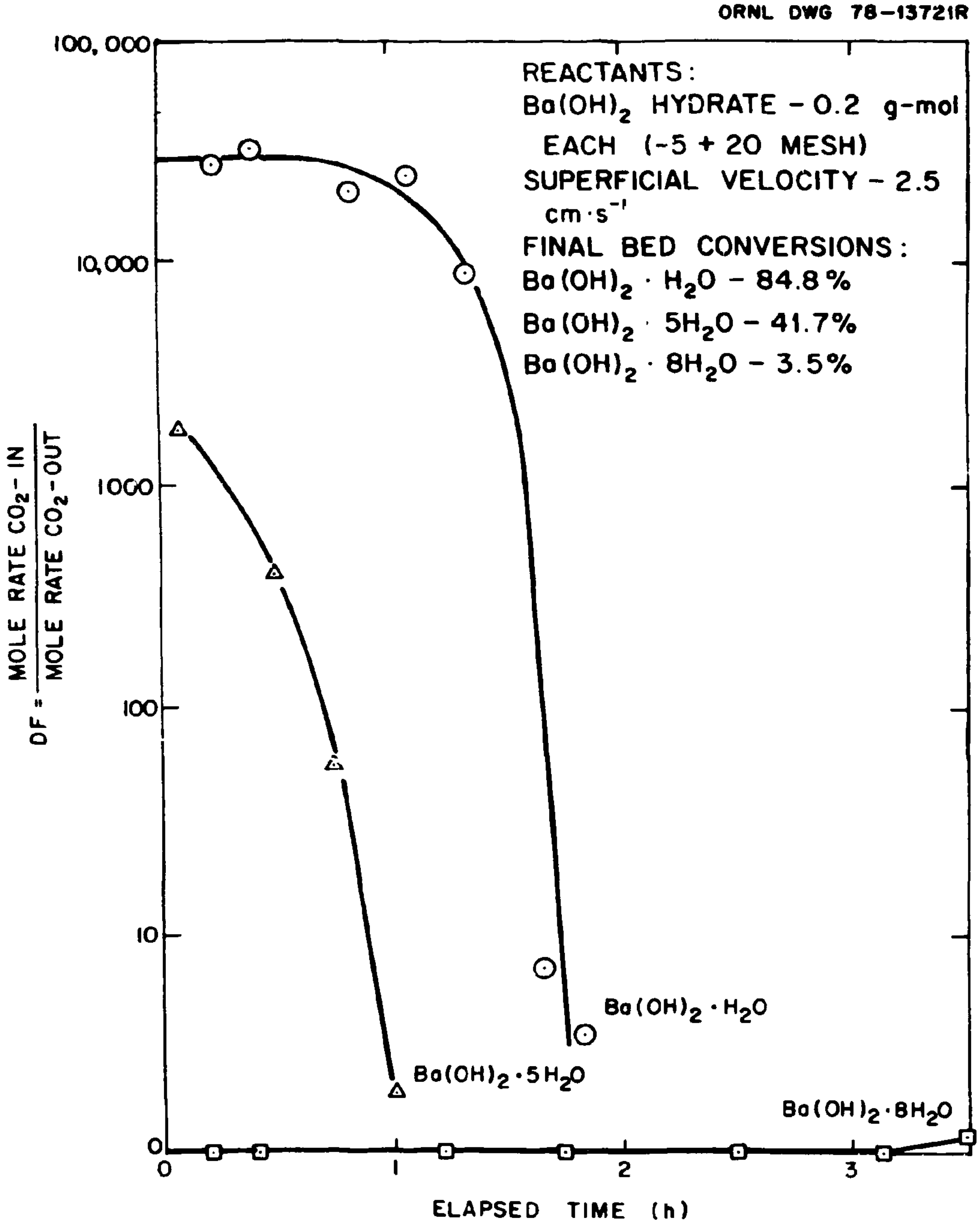

Fig. 6. Comparison of Ba(OH) hydrates in packed beds with a humidified 4.8% CO_2 feed gas.

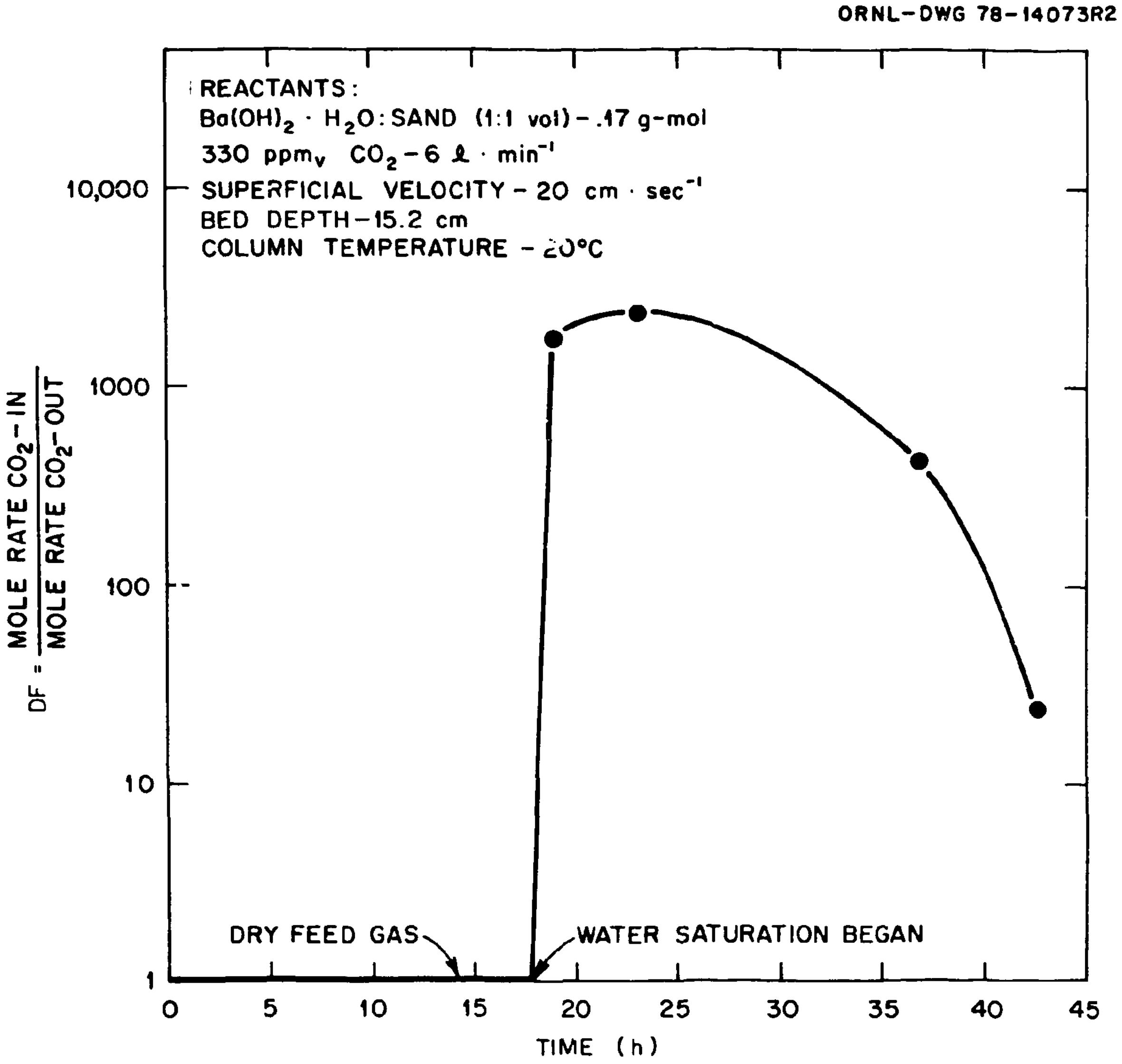

Fig. 7. The effect of water vapor pressure on the reactivity of $Ba(OH)_2$ beds.

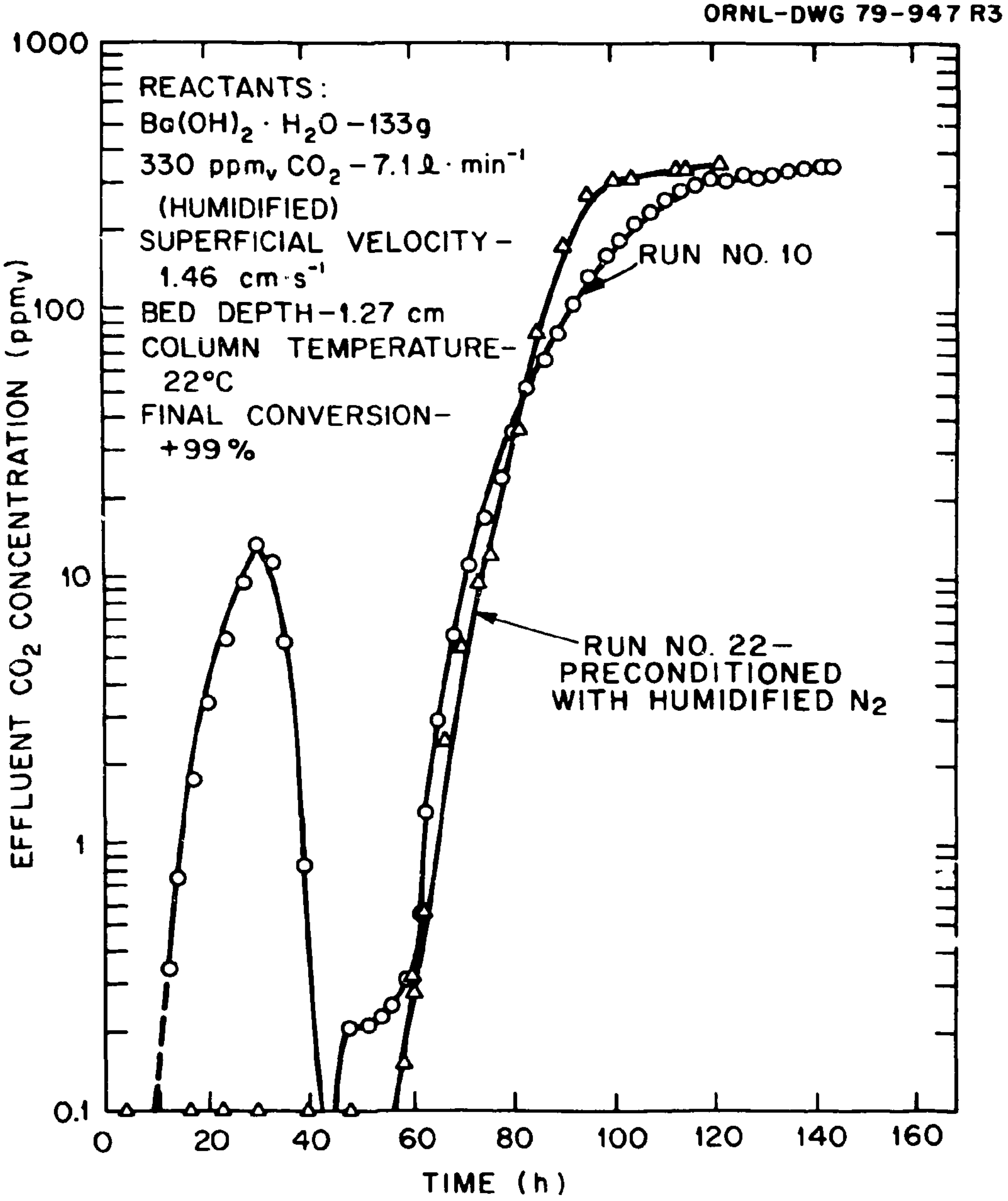

Fig. 8. The effects of bed preconditioning on $Ba(OH)_2 \cdot H_2O$ with humidifed nitrogen.

result in a significant pressure drop increase across the bed. Therefore, the increase in reactivity of $Ba(OH)_2 \cdot 1H_2O$ over that of either $Ba(OH)_2 \cdot 5H_2O$ or $Ba(OH)_2 \cdot 8H_2O$ is now attributed to the existence of a more active (greater surface area) form of $Ba(OH)_2 \cdot 8H_2O$. Similar results were obtained on fluidized-bed studies with humidified air (330 ppm) CO_2 as a feed gas and $Ba(OH)_2 \cdot H_2O$ as a reactant. Initial results were promising although the entrainment of fines in the off-gas presented and will present a considerable problem for process operation. Therefore, because of operational simplicity, the fixed-bed approach has been designated as the desired mode of gas-solid contacting.

For the treatment of an airlike (330 ppm CO_2) gas stream, initial studies on packed beds of commercially designated $Ba(OH)_2 \cdot 5H_2O$ flakes were discontinued as the material degraded upon conversion to octahydrate. This degradation resulted in severe pressure drop problems. Attempts to press either $Ba(OH)_2 \cdot H_2O$ or $Ba(OH)_2 \cdot 5H_2O$ into pellets also failed as the pellets degraded upon conversion to the octahydrate. As a result of these observations, the research effort was then redirected toward the development of a sufficiently active $Ba(OH)_2 \cdot 8H_2O$ species which, when placed in a packed bed, resulted in acceptable operational characteristics, particularly with respect to pressure drop.

4.4 Commercial $Ba(OH)_2 \cdot 8H_2O$ Flake

Present efforts are directed toward the use of the flakes of commercial $Ba(OH)_2 \cdot 8H_2O$ in packed-bed reactors. Although these flakes possess considerably less reactivity than hydrated $Ba(OH)_2 \cdot H_2O$, the material has been found to have sufficient reactivity for the treatment of dilute CO_2 gas streams. The bulk of these runs have been conducted on 10.2-cm-ID by 51-cm-long (4-in.-ID by 20-in.-long) packed beds which contain 4200 g of reactant. The initial void volume of the bed is 52%. However, negligible bed expansion is noted upon complete conversion to carbonate, and the final void volume is 77% due to the lower molar volume of the product. Although several gas superficial velocities have been examined, a nominal superficial velocity of 10 cm/s has been established as a reasonable process standard based upon desired scale-up criteria. The bulk of the data to be presented, however, was obtained at a superficial velocity of 13 cm/s. For these studies, variables of particular interest are the effect of water vapor pressure and column temperature upon the removal efficiency of the bed, and the final pressure drop across the bed upon 100% conversion.

Results of a run operated at near optimal conditions are shown in Fig. 9. The CO_2 breakthrough was reasonably sharp with a mass transfer zone of 18 cm. The initial pressure drop across the bed was 1.01 kPa/m (.04 $lb \cdot in.^{-2} ft^{-1}$) and gradually increased to 3.64 kPa/m (.14 $lb \cdot in.^{-2} ft^{-1}$). The final bulk conversion of the bed upon completion of the run was greater than 99%. The final product was a free-flowing solid which was easily removed from the column (Fig. 10).

As previously mentioned, it is believed that the conditions for the preceeding run were near optimal as results have indicated an operating envelope to exist. The relative humidity for this run was 40%, which corresponded to an inlet water pressure of 1129 Pa (8.47 mm Hg). The dissociation vapor pressure of $Ba(OH)_2 \cdot 8H_2O$ at these conditions is 918 Pa (6.89 mm Hg). Results obtained under similar conditions with water vapor pressures less than that of the dissociation vapor pressure for $Ba(OH)_2 \cdot 8H_2O$ have resulted in bed deactivation and early CO_2 breakthrough, indicating $Ba(OH) \cdot 3H_2O$ to be considerably less reactive than $Ba(OH)_2 \cdot 8H_2O$. This deactivation step appears to be kinetically controlled. Studies are presently under way to develop a better understanding of the deactivation phenomenom. Although prolonged operation at vapor pressures below the dissociation vapor pressure of $Ba(OH)_2 \cdot 8H_2O$ does not appear feasible.

Experimental studies have also indicated that there may be an upper relative humidity or water vapor pressure, above which it may not be desirable to operate as pressure drop problems are compounded. As previously cited, the flakes of commercial $Ba(OH)_2 \cdot 8H_2O$ are composed of 53 mol % $Ba(OH)_2 \cdot 8H_2O$ and 47 mol % $Ba(OH)_2 \cdot 8H_2O$-$Ba(OH)_2 \cdot 3H_2O$ eutectic. Results have indicated that when a flake is exposed to a high-humidity gas stream, a transformation takes place whereby the flake preferentially curls on one side and becomes a more active species (Fig. 11). Work is in progress to develop a better understanding of the mechanism for this transformation, although conversion of $Ba(OH)_2 \cdot 3H_2O$ to $Ba(OH)_2 \cdot 8H_2O$ and capillary condensation of H_2O vapor within the pores of the flakes appear to be

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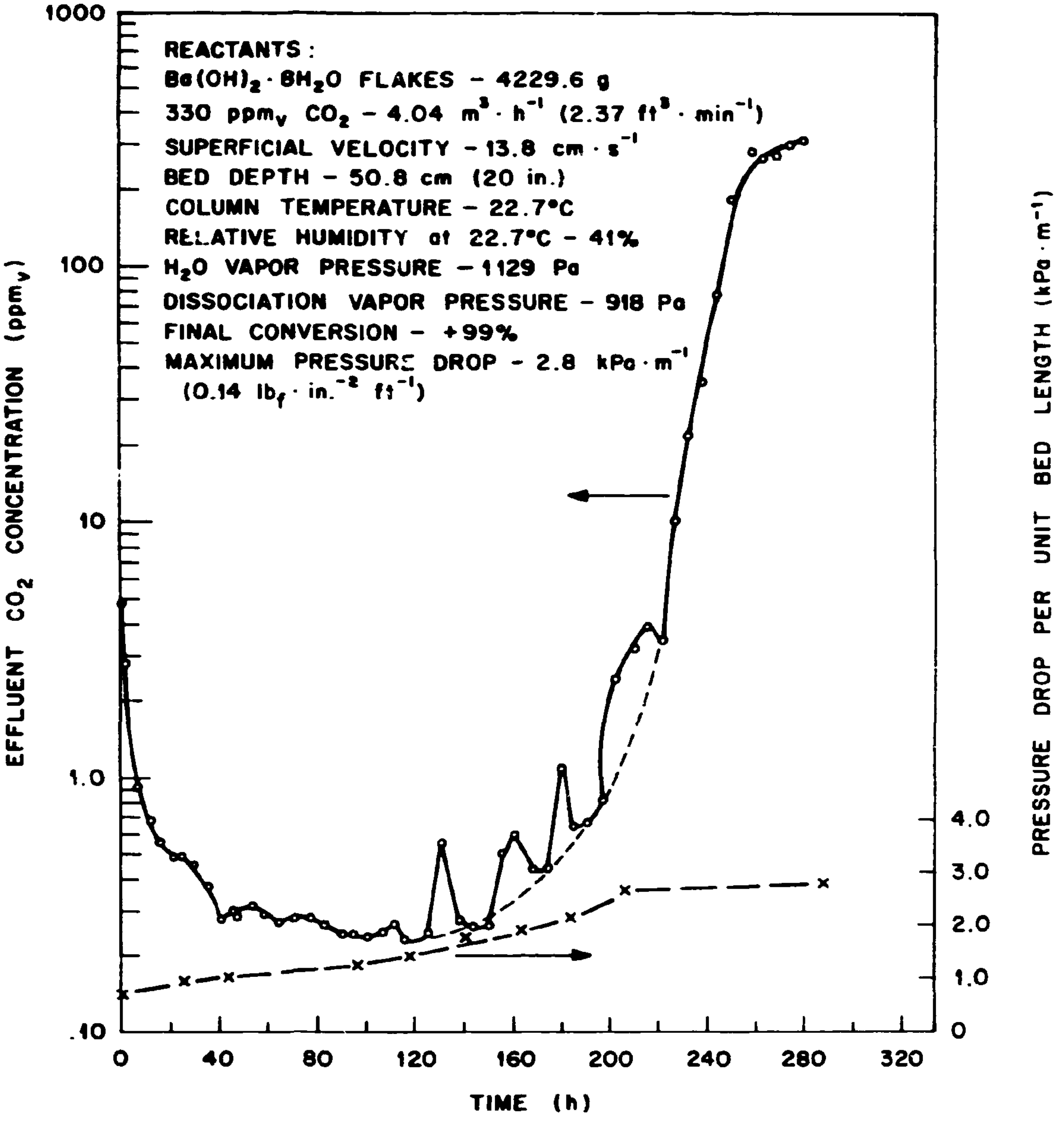

Fig. 9. Near optimal conditions for CO_2 removal from air (330 ppm_v) with $Ba(OH)_2 \cdot 8H_2O$ flake bed.

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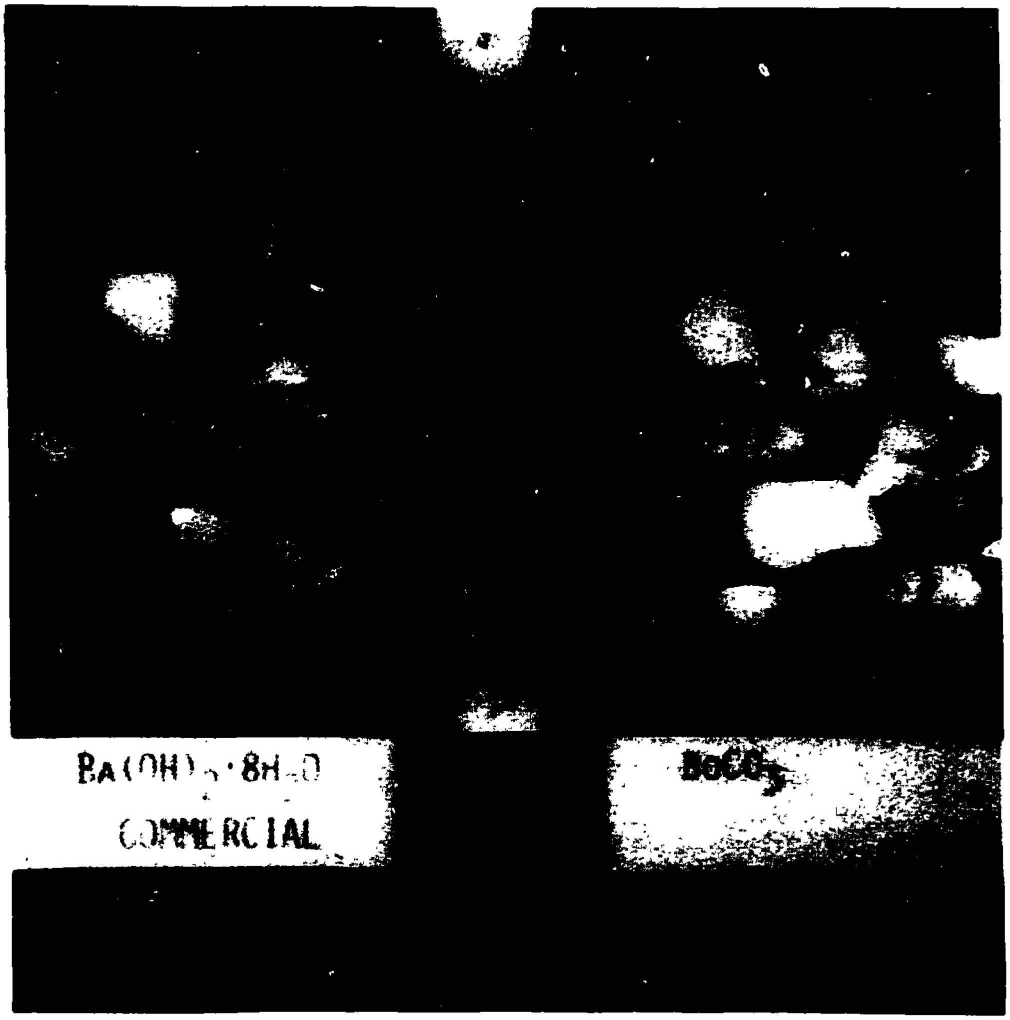

Fig. 10. Commercial $Ba(OH)_2{\cdot}8H_2O$ reactant and $BaCO_3$ product flakes.

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ORNL-PHOTO 4315-81

Fig. 11. Top and bottom views of commercial $Ba(OH)_2 \cdot 8H_2O$ subjected to high humidity; 2.85-by 3.75-in. original photograph, magnification — 16.5 and 13X, respectively.

likely candidates. The resulting material is more active, but pressure drop problems are also much greater due to ensuing particle degradation. Studies are under way to determine the severity of the problem as the humidity or water vapor pressure is increased while other system parameters remain constant.

5. CONCLUSION

For the treatment of an air-based off-gas stream, the use of packed beds of $Ba(OH)_2 \cdot 8H_2O$ flakes to remove CO_2 has been demonstrated. However, the operating conditions must be maintained between certain upper and lower limits with respect to the partial pressure of water. If the water vapor pressure in the gas is less than the dissociation vapor pressure of $Ba(OH)_2 \cdot 8H_2O$, the bed will deactivate. If the vapor pressure is considerably greater, pressure drop problems will increase with increasing humidity as the particles curl and degrade. Results have indicated that when operated in the proper regime, the bulk of the increase in pressure drop results from the conversion of $Ba(OH)_2 \cdot 8H_2O$ to $BaCO_3$ and not from the hydration of the commercial $Ba(OH)_2 \cdot 8H_2O$ (i.e., $Ba(OH)_2 \cdot 7.50H_2O$) to $Ba(OH)_2 \cdot 8H_2O$.

6. REFERENCES

1. H. Bonka et al., "Contamination of the Environment by Carbon-14 Produced in High-Temperature Reactors," *Kernetechnik* 15(7), 297 (1973).

2. W. Davis, Jr., *Carbon-14 Production in Nuclear Reactors,* ORNL/NUREG/TM-12 (February 1977).

3. C. O. Kunz, W. E. Mahoney, and T. W. Miller, "Carbon-14 Gaseous Effluents from Boiling Water Reactors," *Trans. Am. Nucl. Soc. 21,* 91 (1975).

4. C. O. Kunz, W. E. Mahoney, and T. W. Miller, "C-14 Gaseous Effluent from Pressurized Water Reactors," pp. 229-234 in *Proceedings of the Health Physics Society 8th Midyear Symposium,* Knoxville, Tenn., 1974, CONF 741018.

5. M. J. Kabat, "Monitoring and Removal of Gaseous Carbon-14 Species," *Proceedings of the 15th DOE Nuclear Air Cleaning Conference,* Boston, Mass., Aug. 7-10, 1978.

6. H. Schuttelkopf, *Releases of* $^{14}CO_2$ *from Nuclear Facilities with Gaseous Effluents,* Kernsforschungszentrum Karlsruhe KFK 2421, June, 1977 (translated from German) ORNL-tr-4527.

7. *National Strategy Document for Airborne Wastes Management-Draft,* Idaho National Engineering Lab - Allied Chemical Corporation (February 1979).

8. P. J. Magno, C. B. Nelson, and W. H. Ellett, "A Consideration of the Significance of Carbon-14 Discharges from the Nuclear Power Industry," p. 1047 in *Proceedings of the Thirteenth AEC Air Cleaning Conference,* San Francisco, Calif., Aug. 12-15, 1974, CONF-740807.

9. G. G. Killough et al., *Progress Report on Evaluation of Potential Impact of* ^{14}C *Releases from an HTGR Reprocessing Facility,* ORNL/TM-5284 (July 1976).

10. L. Machta, "Prediction of CO_2 in the Atmosphere," *Carbon and the Biosphere,* G. M. Woodwell and E. V. Pecan, eds., Technical Information Center, Office of Information Services, U.S. Atomic Energy Commission (August 1973).

11. G. G. Killough, *A Diffusion-Type Model of the Global Carbon Cycle for the Estimation of Dose to the World Population from Releases of Carbon-14 to the Atmosphere,* ORNL/TM-5269 (1977).

12. J. W. Snider and S. V. Kaye, "Process Behavior and Environmental Assessment of ^{14}C Releases from an HTGR Fuel Reprocessing Facility," *Proceedings of the ANS-AIChE Topical Meeting,* Sun Valley, Idaho, Aug. 5-6, 1976.

13. L. Pauling, "Genetic and Somatic Effects of Carbon-14," *Science 128,* 1183 (1958).

14. J. Schwibach, H. Riedel, and J. Bretschneider, *Studies on the Emission of Carbon-14 from Nuclear Facilities (Nuclear Power Plants and Reprocessing Plants): Its Measurement and the Radiation Exposure Resulting from Emissions,* Series of the Institute for Radiation Hygiene of the Federal Health Office, No. 20, 1979 (translated from German) OLS-80-233.

15. A. G. Croff, *An Evaluation of Options Relative to the Fixation and Disposal of* 14C-Contaminated CO_2 as CaCO3› ORNL/TM-5171 (April 1976).

16. D. W. Holladay, *Experiments with a Lime Slurry in a Stirred Tank for the Fixation of Carbon-14 Contaminated* CO_2 *from Simulated HTGR Fuel Reprocessing Off-Gas,* ORNL/TM-5757 (1978).

17. D. W. Holladay, *An Experimental Investigation of the Distribution of Krypton from Simulated HTGR Fuel Reprocessing Off-Gas During the Removal and Fixation of* CO_2 *by the* CO_2-$Ca(OH)_2$ *Slurry Reaction,* ORNL/TM-6539 (in preparation).

18. D. W. Holladay and G. L. Haag, "Removal of ^{14}C-Contaminated CO_2 from Simulated LWR Fuel Reprocessing Off-Gas by Utilizing the Reaction Between CO_2 and Alkaline Hydroxides in Either Slurry or Solid Form," pp. 547-569 in *Proceedings of the 15th DOE Nuclear Air Cleaning Conference,* Boston, Mass., Aug. 7-10, 1978.

19. D. W. Holladay and G. L. Haag, "Methods for Removing Carbon-14 from Effluent Gases Produced in Nuclear Fuel Reprocessing Plants," to be submitted to *Nucl. Tech.* (in preparation).

20. K. J. Notz, D. W. Holladay, C. W. Forsberg, and G. L. Haag, "Processes for the Control of $^{14}CO_2$ During Reprocessing," paper presented at the International Symposium on Management of Gaseous Wastes from Nuclear Facilities, Vienna, Austria, Feb. 18-22, 1980.

21. *Handbook of Chemistry and Physics,* 52nd ed., The Chemical Rubber Co., Cleveland, Ohio, 1972, pp. 13-70.

22. W. F. Linke and A. Seidell, *Solubilities of Inorganic and Metal Organic Compounds,* Fourth ed., American Chemical Society, Washington, D.C. , 1958.

23. R. B. Cook, *Temperature and Pressure Effects on Sodasorb and Baralyme,* U.S. Naval Academy - TSPR No. 25 (1972).

24. L. J. Nuhn, "Acid-Gas Absorbent," U.S. Patent 2,997,445, Aug. 22, 1961.

25. T. C. Wang, "Temperature Effects on Baralyme, Sodasorb, and Lithium Hydroxide," *Ind. Eng. Chem. Process. Dev., 14(2),* 191 (1975).

26. J. G. Smith, "Low Temperature Performance of CO_2 Scrubber Systems," 1973 Diver's Gas Purity Symposium (November 1973).

27. J. Adriani and D. H. Bolten, "The Efficiency of Mixtures of Barium and Calcium Hydroxides in the Absorption of Carbon Dioxide In Rebreathing Appliances," *Anesthesiology,* 3(1), 1 (1942).

28. D. H. Batten and J. Andriani, "Clinical and Experimental Studies of Barium and Hydroxide Mixtures (Baralyme) for Carbon Dioxide Absorption in Anethesic," *Anesth. and Analg.,* May-June, 151 (1942).

29. J. W. Mellor, *A Comprehensive Treatise on Inorganic and Theoretical Chemistry,"* vol. III. Longman, Green and Co., N.Y., 1923, p. 817.

30. R. Engel, B. Decken, Claus (Brown Boveri) Krupp Reaktorvbau G.m.b.H.), "Removing Carbon Dioxide and Water from a Gas Stream," U.S. 3, 519, 384, Ger. Appl. 8/19/65. CA73:68063k.

31. M. M. Markowitz, *Foote Prints, 34,9 (1965).*

32. D. A. Boryta and H. J. Maas, "Factors Influencing Rate of Carbon Dioxide Reaction with Lithium Hydroxide," *Ind. Eng. Chem. Process Des. Develop. 10(4), 489 (1971).*

33. D. D. Williams and R. R. Miller, *The Effect of Water Vapor on the LiOH-CO_2 Reaction, Part 1 - Dynamic Isothermal System,* NRL Report 6937 (October 1969).

34. B. A. Kondakov, P. V. Kovtunenko, and A. A. Bundel, "Equilibria Between Gaseous and Condensed Phases in the Barium Oxide - Water System," *Russ. J. Phys. Chem. 38(1), 99-102 (1964).*

35. *JANAF Thermochemical Data,* calculated and compiled by the Dow Chemical Company, Thermal Laboratory, Midland, Mich. (updated November 1979).

36. F. D. Rossini, D. D. Wagman, W. H. Evans, S. Levine, and I. Jaffe, *Selected Values of Chemical Thermodynamic Properties — Circular 500,* U.S. Dept. of Commerce (February 1952).

37. D. D. Wagman, W. H. Evans, V. B. Parker, I. Halow, S. M. Bailey, and R. H. Schumm, *Selected Values of Chemical Thermodynamic Properties - Tables for the First 34 Elements in the Standard Order of Arrangement,* U.S. Dept. of Commerce/NBS Technical Note 270-3 (January 1968).

38. V. B. Parker, D. D. Wagman, and W. H. Evans, *Selected Values of Chemical Thermodynamic Properties - Tables for the Alkaline Earth Elements,* U.S. Dept. of Commerce/NBS Technical Note 270-6 (November

39. O. Kubaschewski and E. L. Evans, *Metallurgical Thermochemistry,* Pergamon, London, 1958.

40. P. I. Barin and O. Knacke, *Thermochemical Properties of Inorganic Substances,* Springer-Verlag, New York, 1973.

41. M. Michaud, "Contribution to the Study of the Hydroxides of Potassium and Barium," *Revue de Chimie Minerale, t.5, 89 (1968).* Translated from French by ORNL Translations Department.

42. M. Michaud, "Inorganic Chemistry - Study of the Binary Water-Barium Hydroxide System," *C. r. hepd. Se'anc. Acad. Sci. Paris 262.C, 1143 (1966).*

43. M. C. Flemings, *Solidification Processing,* McGraw-Hill, Inc., N.Y., 1974.