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CARBON-14 IMMOBILIZATION VIA THE CO₂-Ba(OH)₂ HYDRATE
GAS-SOLID REACTION*

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Gary L. Haag
Experimental Engineering Section
Chemical Technology Division
Oak Ridge National Laboratory
Oak Ridge, Tennessee 37830

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CARBON-14 IMMOBILIZATION VIA THE $\text{CO}_2\text{-Ba(OH)}_2$ HYDRATE
GAS-SOLID REACTION

G. L. Haag
Oak Ridge National Laboratory
Oak Ridge, Tennessee 37830

Abstract

Although no restrictions have been placed on the release of carbon-14, 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 carbon-14 from various nuclear facilities. The process utilizes the $\text{CO}_2\text{-Ba(OH)}_2$ hydrate gas-solid reaction to directly remove and immobilize carbon-14. 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 greater than 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 $\text{Ba(OH)}_2\cdot\text{H}_2\text{O}$, $\text{Ba(OH)}_2\cdot 5\text{H}_2\text{O}$, and $\text{Ba(OH)}_2\cdot 8\text{H}_2\text{O}$ and analytical-grade $\text{Ba(OH)}_2\cdot 8\text{H}_2\text{O}$ have been examined. Studies at ambient conditions have indicated $\text{Ba(OH)}_2\cdot 8\text{H}_2\text{O}$ to be the active species. Therefore, process operating conditions will likely be required which favor the formation of $\text{Ba(OH)}_2\cdot 8\text{H}_2\text{O}$. The dissociation water vapor pressure for

$\text{Ba(OH)}_2 \cdot 8\text{H}_2\text{O}$ at 25°C is 1.10 kPa (8.26 mm Hg). Although both commercial- and analytical-grade $\text{Ba(OH)}_2 \cdot 8\text{H}_2\text{O}$ have been found to be reactive toward CO_2 , they are considerably less reactive than either $\text{Ba(OH)}_2 \cdot \text{H}_2\text{O}$ or $\text{Ba(OH)}_2 \cdot 5\text{H}_2\text{O}$ which have been hydrated to $\text{Ba(OH)}_2 \cdot 8\text{H}_2\text{O}$. We have observed that during the fixed-bed treatments of humidified-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 two-fold 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 $\text{Ba(OH)}_2 \cdot 8\text{H}_2\text{O}$ flakes possess acceptable CO_2 removal, bed utilization, and pressure drop properties. Under appropriate conditions, we have observed a pressure drop of 3.64 $\text{kPa} \cdot \text{m}^{-1}$ ($0.14 \text{ psi} \cdot \text{ft}^{-1}$) at a superficial gas velocity of $13 \text{ cm} \cdot \text{s}^{-1}$.

I. Introduction

In the radiation field which exists within a nuclear reactor, radioisotope carbon-14 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, carbon-14 poses a long-term health hazard due to its long half-life of 5730 years and the ease with which it may be assimilated into living matter.⁽¹⁰⁻¹⁴⁾

An appreciable fraction of the carbon-14 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 carbon-14 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 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 I.

For the removal and fixation of carbon-14 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 \$100-200/man-rem.

Table I. Approximate Production and Release Rates
of Carbon-14 in the Nuclear Fuel Cycle⁽²⁾

Nuclear Reactors	C1/Gw(e)yr
LWR	8-10
CANDU	500
Reprocessing Plant	
LMFBR	6
LWR	18
HTGR	200

II. Suggested Technologies for $^{14}\text{CO}_2$ Control

Suggested technologies for carbon-14 control have generally followed commercially available technology for 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 $\text{Ca}(\text{OH})_2$, 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 $\text{Ca}(\text{OH})_2$ 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/liter at 25°C).⁽²¹⁾ 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 $\text{Ca}(\text{OH})_2$ 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 carbon-14 removal and fixation existed. However, widely acceptable CO_2 sorbents such as ascarite (NaOH on asbestos) and

$\text{LiOH}\cdot\text{H}_2\text{O}$, which has been used extensively for CO_2 control in life support systems, lack sufficient carbonate stability for final waste disposal. CO_2 removal studies have been conducted on soda lime [$\text{NaOH}-\text{Ca}(\text{OH})_2$ mixture] and baralyme [$\text{Ca}(\text{OH})_2-\text{Ba}(\text{OH})_2$ 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 I (alkali metals) hydroxides (Table II) indicates that they may be categorically classified as possessing excessive solubility in water for long-term waste disposal. However, the higher molecular weight carbonates of the Group II (alkaline earths) are considerably more stable. As shown in Table II, 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 in our lab, that a CaCO_3 coating forms about the $\text{Ca}(\text{OH})_2$ 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 $\text{Ca}(\text{OH})_2$ reactant.(30) Process temperatures were $100-200^\circ\text{C}$. 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

Table II. Solubility and decomposition properties of Group 1 (Alkali Metal) and Group 2 (Alkaline Earth) carbonates at low CO₂ partial pressures (21,22)

	Molal Solubility		Decomposition temperature (°C)
	25°C	100°C	
Group 1 Carbonates			
Li ₂ CO ₃	0.18	0.10	1310
Na ₂ CO ₃	2.80	4.26	--
K ₂ CO ₃	8.10	4.41	--
Rb ₂ CO ₃	19.48	--	740
Cs ₂ CO ₃	8.00	--	610
Group 2 Carbonates			
MgCO ₃	0.00126*	--	350
CaCO ₃	0.00013	0.000375	825
SrCO ₃	0.000075	0.00044	1340
BaCO ₃	0.000124	0.000332	1450

*Cold water.

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

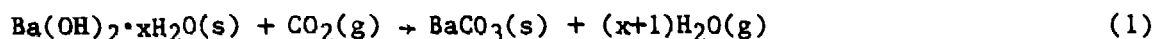
To determine the likelihood of a reactant being coated by a nonporous product which would result in severe diffusional limitations of the gaseous reactant, a comparison of the molar crystal volume ratios of the product and reactant, referred to as the Pilling-Bedworth ratio, is often beneficial. The Pilling-Bedworth ratios for several alkali and alkaline earth hydroxides and their carbonate products are presented in Table III. With the exception of the $\text{Ba}(\text{OH})_2$ and $\text{Sr}(\text{OH})_2$ data, the table was taken from a paper by Markowitz.⁽³¹⁾ A Pilling-Bedworth ratio greater than one indicates a high probability of diffusional limitations, and a value less than one 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 III, one would anticipate that $\text{LiOH}\cdot\text{H}_2\text{O}$, $\text{Sr}(\text{OH})_2\cdot 8\text{H}_2\text{O}$, $\text{Ba}(\text{OH})_2\cdot\text{H}_2\text{O}$, and $\text{Ba}(\text{OH})_2\cdot 8\text{H}_2\text{O}$ would be efficient CO_2 absorbents if the chemical reactions were kinetically favored. One might also predict $\text{Ba}(\text{OH})_2\cdot 8\text{H}_2\text{O}$ to be more efficient than $\text{Ba}(\text{OH})_2\cdot\text{H}_2\text{O}$ for CO_2 removal. The Pilling-Bedworth ratio of 1.18 for $\text{Ca}(\text{OH})_2$ is consistent with the reported formation of an impervious shell about the $\text{Ca}(\text{OH})_2$ particle thus resulting in diffusional limitations. Similarly, work performed by Boryta and Maas⁽³²⁾ and the Naval Research Laboratory⁽³³⁾ have indicated $\text{LiOH}\cdot\text{H}_2\text{O}$, 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.

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

Substance	Formula weight	Density (g/cm ³)	Molar volume (cm ³ /g-mole)	Pilling-Bedworth ratio
LiOH	23.95	1.43	16.75	1.07
LiOH·H ₂ O	41.96	1.51	27.79	0.64
Li ₂ CO ₃	73.89	2.07	35.70	
NaOH	40.01	2.13	18.78	1.47-Na ₂ CO ₃ ·H ₂ O 1.13-Na ₂ CO ₃
Na ₂ CO ₃	106.00	2.51	42.25	
Na ₂ CO ₃ ·H ₂ O	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 ·8H ₂ O	265.76	1.90	139.87	0.29
SrCO ₃	147.63	3.70	39.90	
Ba(OH) ₂ ·8H ₂ O	315.48	2.10	150.23	0.30
Ba(OH) ₂ ·1H ₂ O	189.48	3.65	51.8	0.86
BaCO ₃	197.35	4.43	44.47	

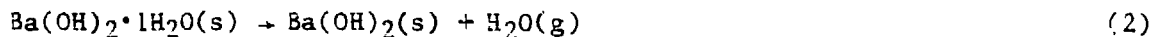
III. Literature Review

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:

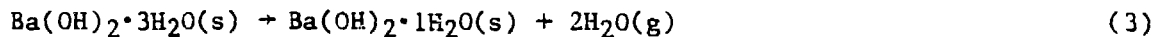


where x is the initial degree of hydration.

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, Kovtunencko, and Bundel.⁽³⁴⁾ The results were published in 1964. In this study, the water vapor pressure of $\text{Ba(OH)}_2 \cdot x\text{H}_2\text{O}$ 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 $\text{Ba(OH)}_2 \cdot \text{H}_2\text{O}$, $\text{Ba(OH)}_2 \cdot 3\text{H}_2\text{O}$, and $\text{Ba(OH)}_2 \cdot 8\text{H}_2\text{O}$ 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:



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



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

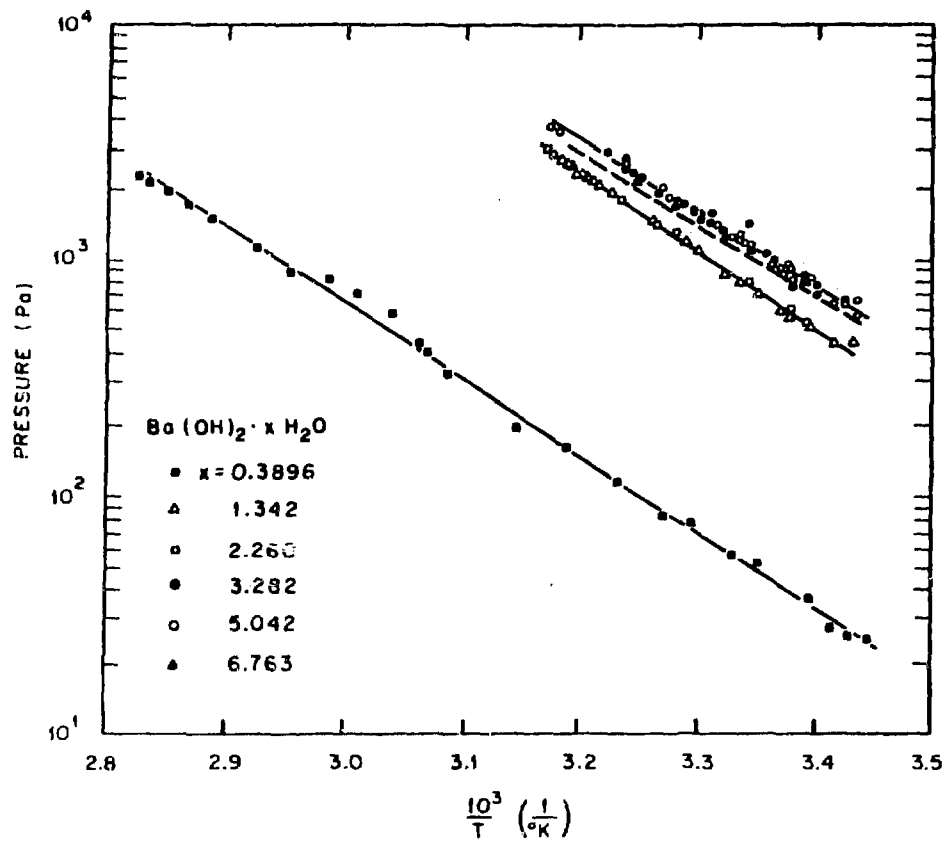
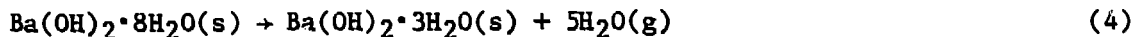


Fig 1 DISSOCIATION VAPOR PRESSURES FOR Ba(OH)₂ HYDRATES



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

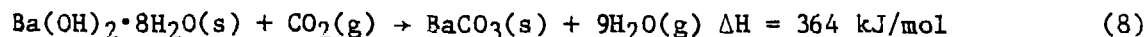
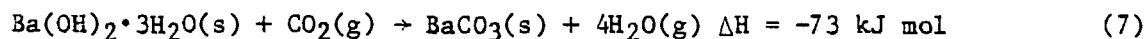
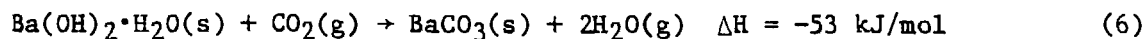
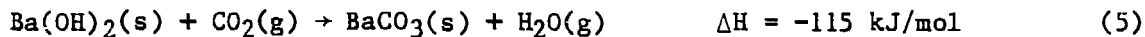
where

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

T = temperature, °K.

Using the Van't Hoff equation, the data was 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 $\text{Ba(OH)}_2 \cdot 2\text{H}_2\text{O}$ and amorphous compounds to exist.

With the exception of $\text{Ba(OH)}_2 \cdot 2\text{H}_2\text{O}$, the thermodynamics of the CO_2 -barium hydroxide hydrate gas-solid reaction may be calculated from published values.⁽³⁴⁻⁴⁰⁾ Presented in Table IV are the thermodynamic calculations for the following reactions:



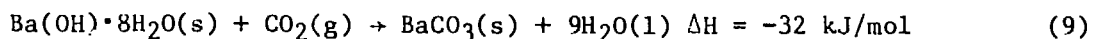
At 298°K and 1 atm, the fugacities of the gas species may be approximated by their partial pressures (atm), and the fugacities of the crystalline species, with respect to their reference states, is approximately equal to one. If the water product is present as vapor, the equilibrium constant, K_{eq} , is

Table IV. Thermodynamic properties of the $\text{CO}_2\text{-Ba(OH)}_2$ hydrate gas-solid reaction at 298.15°K⁽³²⁻³⁷⁾

Reaction	ΔG $\text{kJ}\cdot\text{mol}^{-1}$	ΔH $\text{kJ}\cdot\text{mol}^{-1}$	ΔS $\text{J}\cdot\text{mol}^{-1}\cdot\text{°K}^{-1}$	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	$6.84\cdot 10^{10}$

equal to $[P_{H_2O}]^{x+1} \cdot [P_{CO_2}]^{-1}$ 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 V. 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.

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 (9 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 IV and V for the following reaction.



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

Table V. Equilibrium values for the
 $\text{CO}_2\text{-Ba(OH)}_2$ Hydrate Gas-Solid Reaction

Reaction	K_{eq}	Reactant hydration	P_{CO_2}	
			Pa	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	$1.87 \cdot 10^{-3}$	8	$1.5 \cdot 10^{-6}$	$1.1 \cdot 10^{-8}$
9	$6.84 \cdot 10^{10}$	8	$1.5 \cdot 10^{-6}$	$1.1 \cdot 10^{-8}$

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 CO₂, 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).

IV. Experimental Studies

Experimental studies are being conducted to develop a better understanding of the CO₂ - Ba(OH)₂ hydrate gas-solid reaction and to develop a process capable of treating a high volumetric, low CO₂ 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.

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)₂·8H₂O and commercially available Ba(OH)₂·H₂O,

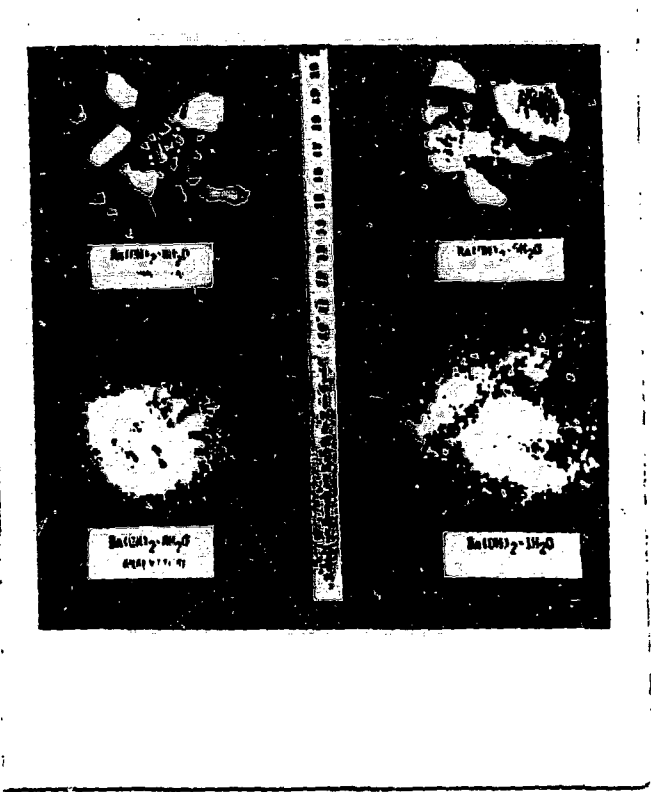


Fig. 2 $Ba(OH)_2$ hydrates

Table VI. X-ray diffraction analyses of $\text{Ba}(\text{OH})_2$ hydrate samples.

Sample	Observed line intensities				
$\text{Ba}(\text{OH})_2 \cdot \text{H}_2\text{O}$	$\text{Ba}(\text{OH})_2 \cdot \text{H}_2\text{O}$ - strongest				
	$\text{Ba}(\text{OH})_2 \cdot 3\text{H}_2\text{O}$				
$\text{Ba}(\text{OH})_2 \cdot 5\text{H}_2\text{O}$	<table border="0"> <tr> <td data-bbox="654 653 825 679">$\text{Ba}(\text{OH})_2 \cdot \text{H}_2\text{O}$</td> <td data-bbox="883 713 1133 739" rowspan="3">- same intensity</td> </tr> <tr> <td data-bbox="763 713 840 739">$\cdot 3\text{H}_2\text{O}$</td> </tr> <tr> <td data-bbox="763 774 840 800">$\cdot 8\text{H}_2\text{O}$</td> </tr> </table>	$\text{Ba}(\text{OH})_2 \cdot \text{H}_2\text{O}$	- same intensity	$\cdot 3\text{H}_2\text{O}$	$\cdot 8\text{H}_2\text{O}$
$\text{Ba}(\text{OH})_2 \cdot \text{H}_2\text{O}$	- same intensity				
$\cdot 3\text{H}_2\text{O}$					
$\cdot 8\text{H}_2\text{O}$					
$\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$ - commercial	Unidentified				
$\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$ - analytical	$\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$				

Table VII. Reactant analyses on commercial $\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$

	Average composition	Standard deviation	Number of samples
Drum #1	$\text{Ba}(\text{OH})_2 \cdot 7.54\text{H}_2\text{O}$	0.0966	12
Drum #2	$\text{Ba}(\text{OH})_2 \cdot 7.47\text{H}_2\text{O}$	0.0830	20

$\text{Ba}(\text{OH})_2 \cdot 5\text{H}_2\text{O}$, and $\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$. 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 VI. Considerable difficulty was encountered in analyzing the diffraction pattern for the commercial $\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$ flakes. Reactant analyses were conducted on two 200 lb drums of the commercial $\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$. These results are presented in Table VII.

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

Discussions with the vendor have indicated that the flakes are prepared by distributing a hot magma solution of $\text{Ba}(\text{OH})_2$ hydrate (approximately .3 mm thick) on a conveyor 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 being very smooth and 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 Floppings in Solidification Processes for a similar solidification process in which eutectic and pure species are present, we speculate the dendritic-like stars to be $\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$.⁽⁴³⁾ This material preferentially crystallizes 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 $\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$ is 47% eutectic, 53% $\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$.

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 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 $\text{Ba}(\text{OH})_2$ 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).

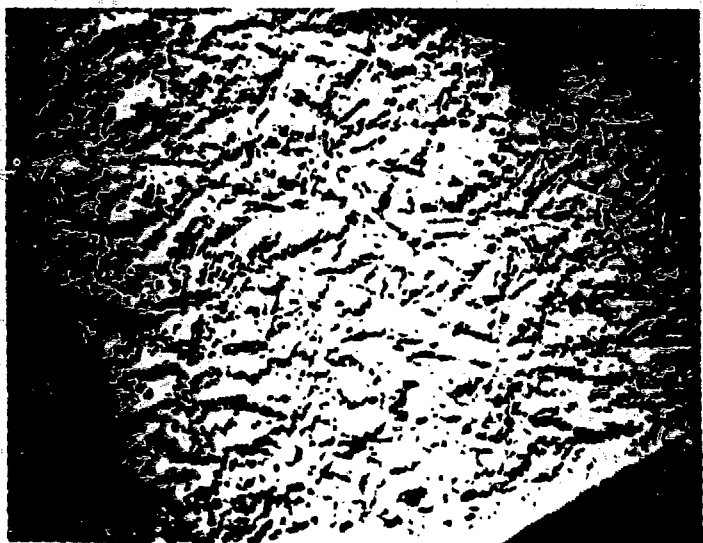
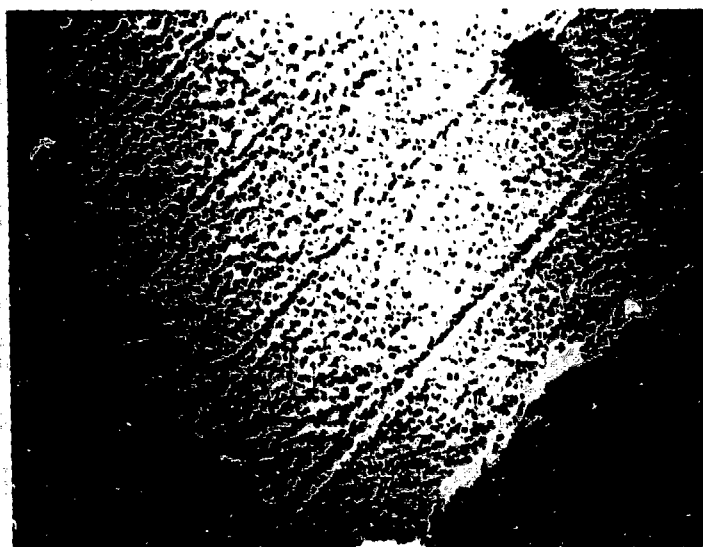


Fig. 3 Top and bottom ~~side~~ of commercial
Ba(OH)₂·8H₂O flakes

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Fig. 4. $\text{Ra}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$ Flake, Magnification - 12.75X
3x5 - Original photo, Magnification - 12.75X

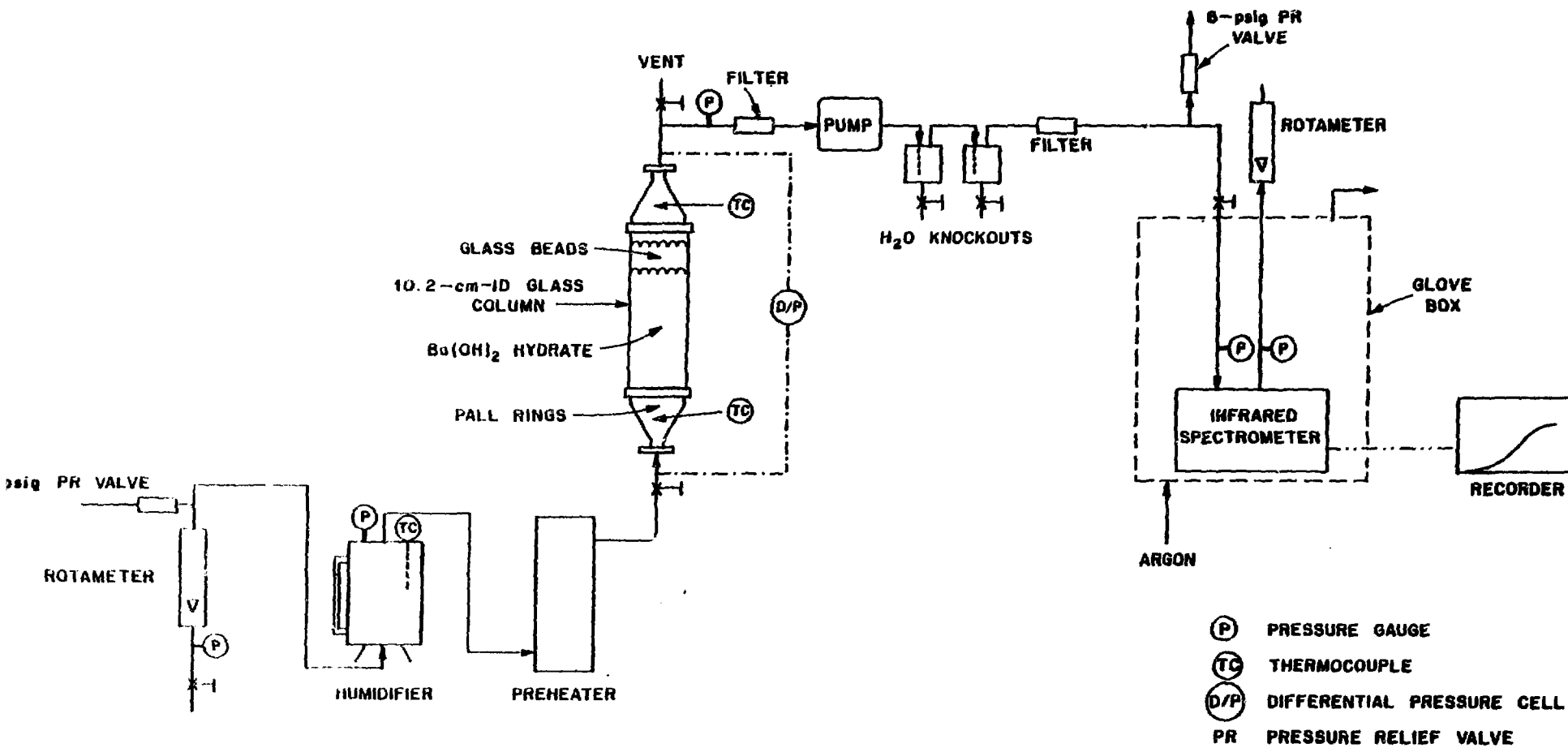


Fig. 5 Schematic of the experimental equipment

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 insure a positive pressure system for gas analyses, the pressure at the top of the bed is maintained at 6.9 kPa (1 psig). A small portion of the effluent gas is passed through a filter and to a metal bellows pump for pressurization to 48 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 infra-red analyzer which 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 CO₂ concentration and hence, the drifting of the baseline. The glove box is continuously purged with argon. The infra-red spectrometer wavelength is set at 4.25 microns and the path-length at 20.25 meters. The cell pressure is maintained at 34.5 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 CO₂ concentrations. The instrument has been calibrated over the concentration range of 100 ppb to 330 ppm CO₂ 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.

$\text{Ba}(\text{OH})_2 \cdot \text{H}_2\text{O}$ Studies

Due to the lack of reactivity and poor product conversion associated with the carbonation of $\text{Ca}(\text{OH})_2$, the prime objective in initial studies on the hydrates of $\text{Ba}(\text{OH})_2$ was to establish the reactivity of the various hydrated species. As indicated in Fig. 6, beds of $\text{Ba}(\text{OH})_2 \cdot \text{H}_2\text{O}$ were superior to either beds of $\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$ or $\text{Ba}(\text{OH})_2 \cdot 5\text{H}_2\text{O}$ for the treatment of a humidified 4.8% CO_2 gas stream. Therefore, initial experimental emphasis was placed upon the use of $\text{Ba}(\text{OH})_2 \cdot \text{H}_2\text{O}$ for CO_2 removal and fixation. The results of these studies indicated CO_2 removal from air (330 ppm CO_2) concentrations to less than 50 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 two-fold increase in bed volume and accompanying increases in pressure drop across the bed. As indicated in Fig. 7, when a bed of $\text{Ba}(\text{OH})_2 \cdot \text{H}_2\text{O}$ 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 $\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$ (Fig. 8 or Fig. 7), the reaction proceeded quite rapidly. The formation of $\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$ was confirmed by x-ray diffraction analysis. As shown in Run 10, Fig. 8, a packed bed of

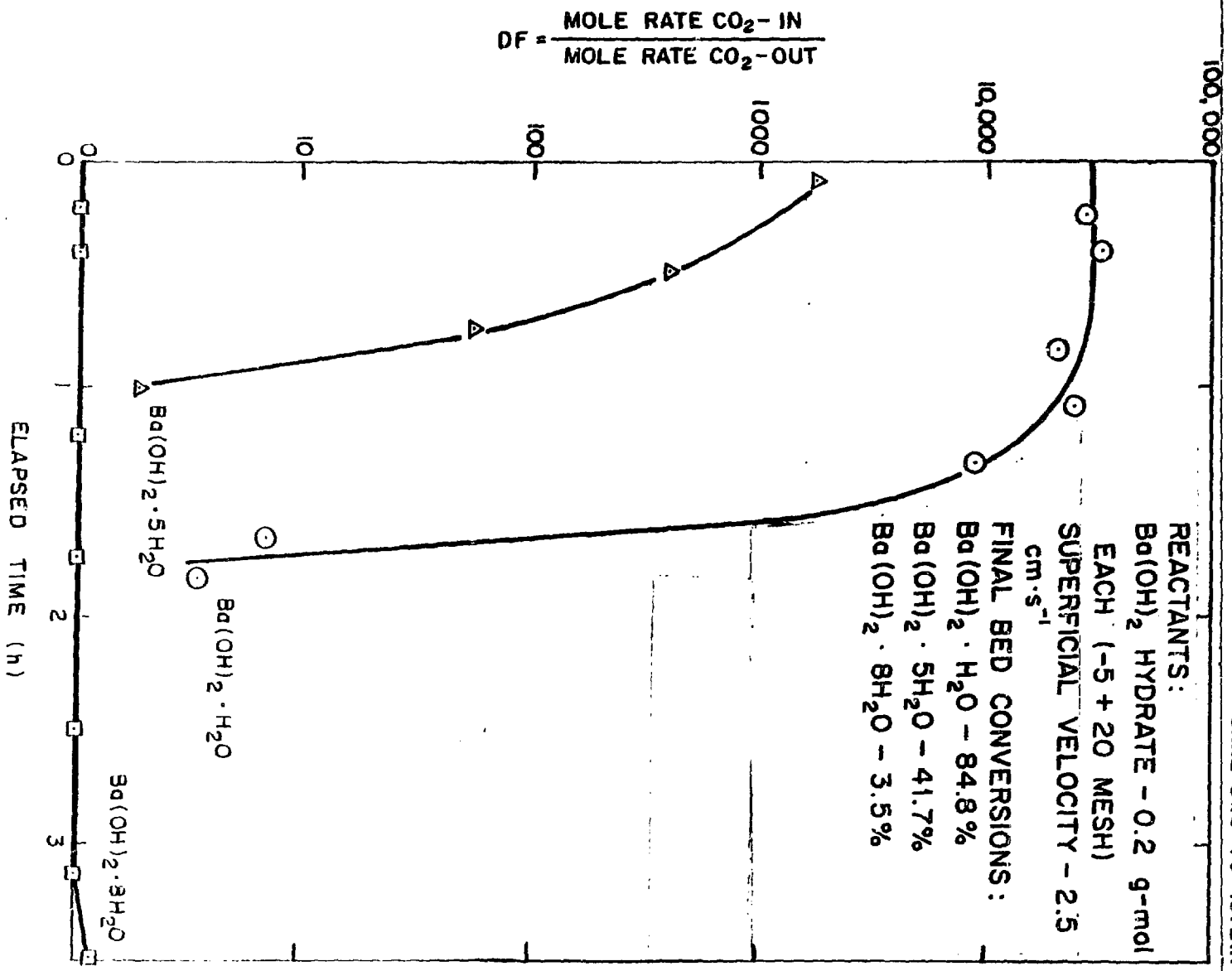


Fig. 6. COMPARISON OF Ba(OH)_2 HYDRATES IN PACKED BEDS WITH A HUMIDIFIED 4.8% CO_2 FEED GAS

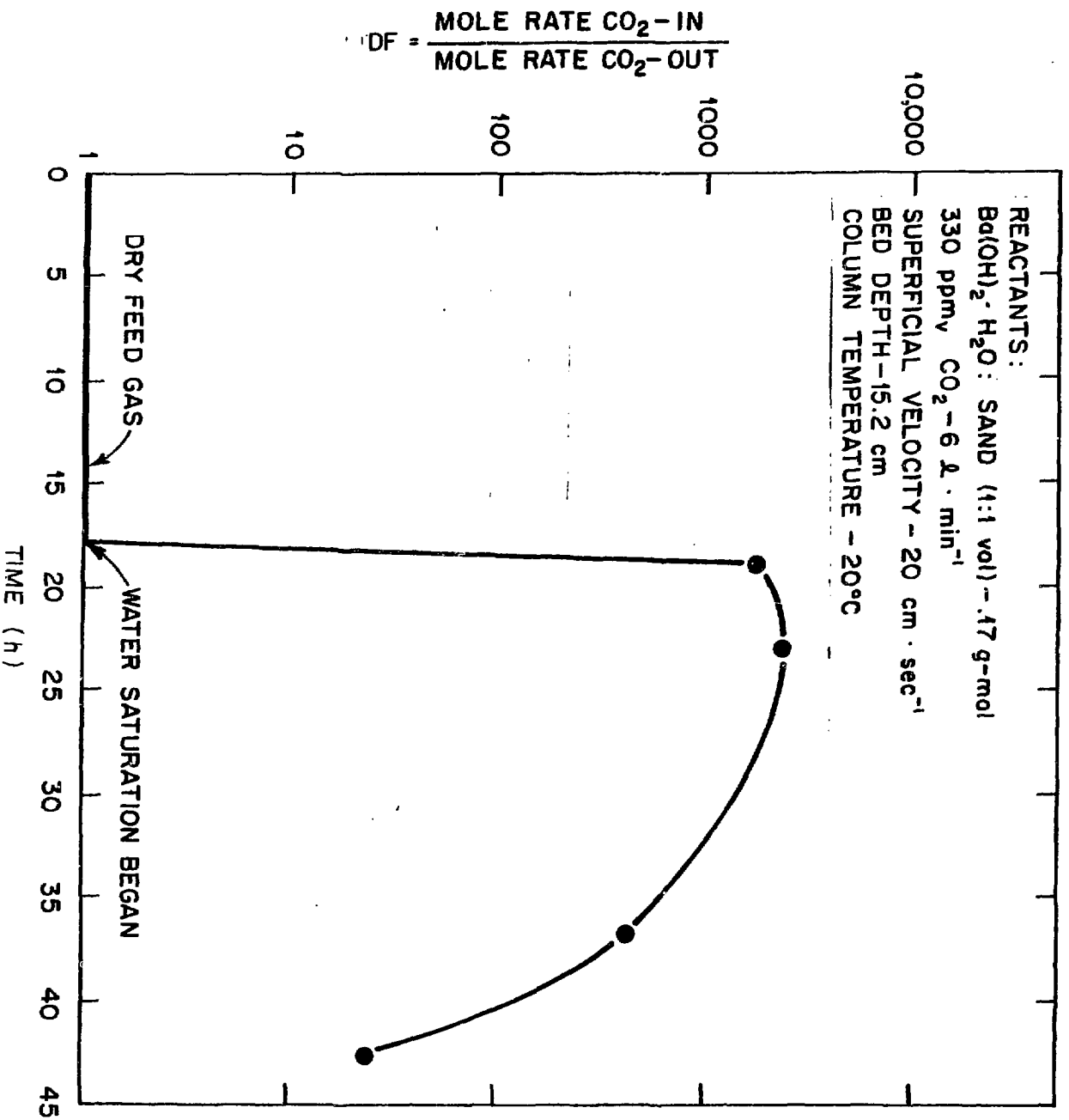


Fig. 7 THE EFFECT OF WATER VAPOR PRESSURE ON THE REACTIVITY OF $\text{Ba}(\text{OH})_2 \cdot \text{H}_2\text{O}$ BEDS

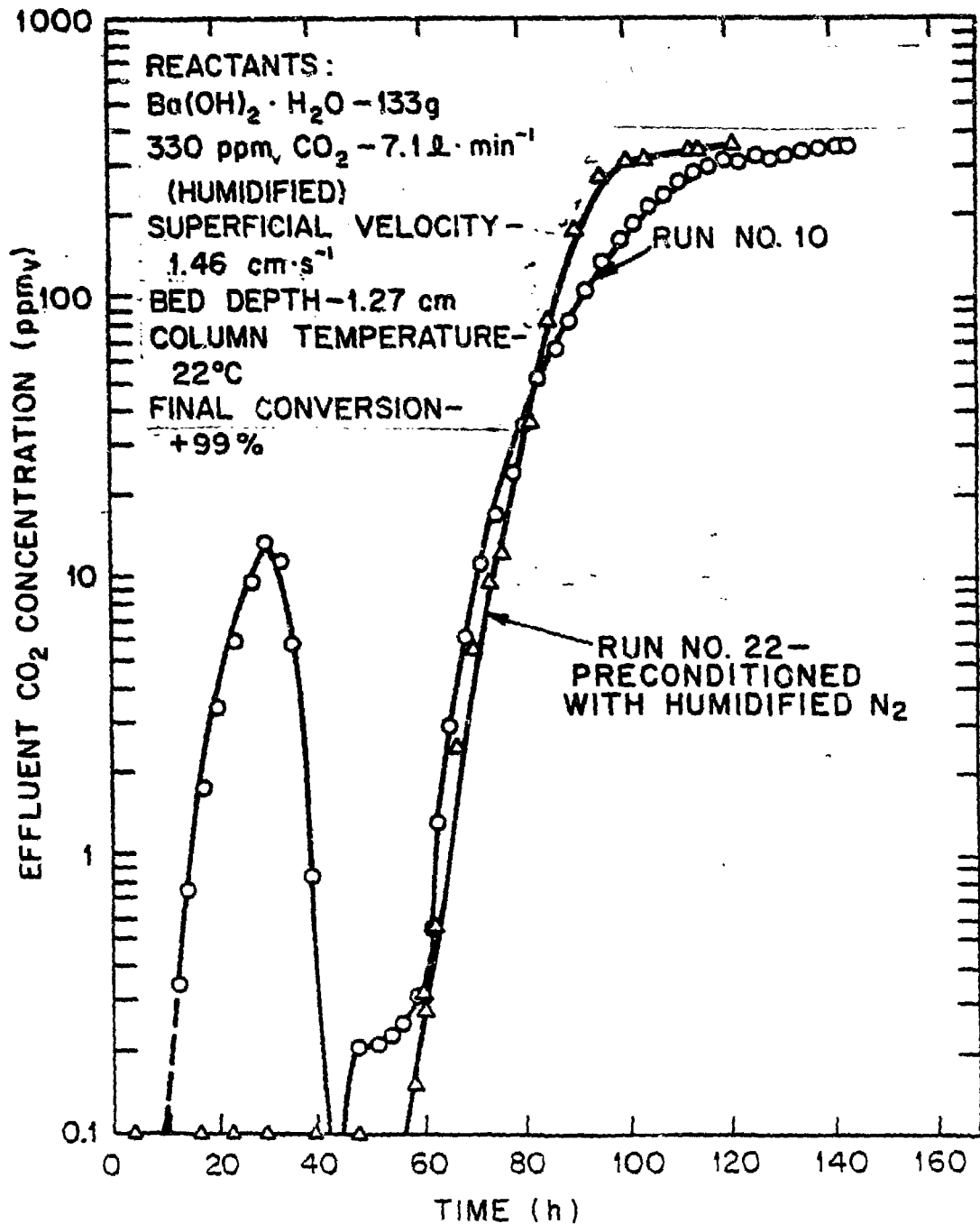


Fig. 8 THE EFFECTS OF BED PRECONDITIONING ON $\text{Ba}(\text{OH})_2 \cdot \text{H}_2\text{O}$ WITH HUMIDIFIED NITROGEN

$\text{Ba(OH)}_2 \cdot \text{H}_2\text{O}$ 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 $\text{Ba(OH)}_2 \cdot 8\text{H}_2\text{O}$ which is gradually depleted. In time, moisture from the air converts the rest of the bed to active $\text{Ba(OH)}_2 \cdot 8\text{H}_2\text{O}$. 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 $\text{Ba(OH)}_2 \cdot 8\text{H}_2\text{O}$ formation was observed, and reactant conversions in excess of 99% were obtained. The bed expansion did result in a significant pressure drop increase across the bed. Therefore, the increase in reactivity of $\text{Ba(OH)}_2 \cdot \text{H}_2\text{O}$ over that of either $\text{Ba(OH)}_2 \cdot 5\text{H}_2\text{O}$ or $\text{Ba(OH)}_2 \cdot 8\text{H}_2\text{O}$ is now attributed to the existence of a more active (greater surface area) form of $\text{Ba(OH)}_2 \cdot 8\text{H}_2\text{O}$. Similar results were obtained on fluidized bed studies with humidified air (330 ppm) CO_2 as a feed gas and $\text{Ba(OH)}_2 \cdot \text{H}_2\text{O}$ 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 $\text{Ba(OH)}_2 \cdot 5\text{H}_2\text{O}$ flakes were discontinued as the material degraded upon conversion to octahydrate. This degradation resulted in severe pressure drop problems. Attempts to press either $\text{Ba(OH)}_2 \cdot \text{H}_2\text{O}$ or $\text{Ba(OH)}_2 \cdot 5\text{H}_2\text{O}$ into pellets also failed as the pellets degraded upon conversion to the octahydrate. As a result of these observations, the direction of the research effort was then redirected toward the development

of a sufficiently active $\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$ species which when placed in a packed bed, resulted in acceptable operational characteristics, particularly with respect to pressure drop.

Commercial $\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$ Flake

Present efforts are directed toward the use of the flakes of commercial $\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$ in packed bed reactors. Although these flakes possess considerably less reactivity than hydrated $\text{Ba}(\text{OH})_2 \cdot \text{H}_2\text{O}$, 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 x 51-cm (4"-ID x 20") length 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 $\text{cm} \cdot \text{sec}^{-1}$ 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 $\text{cm} \cdot \text{sec}^{-1}$. 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

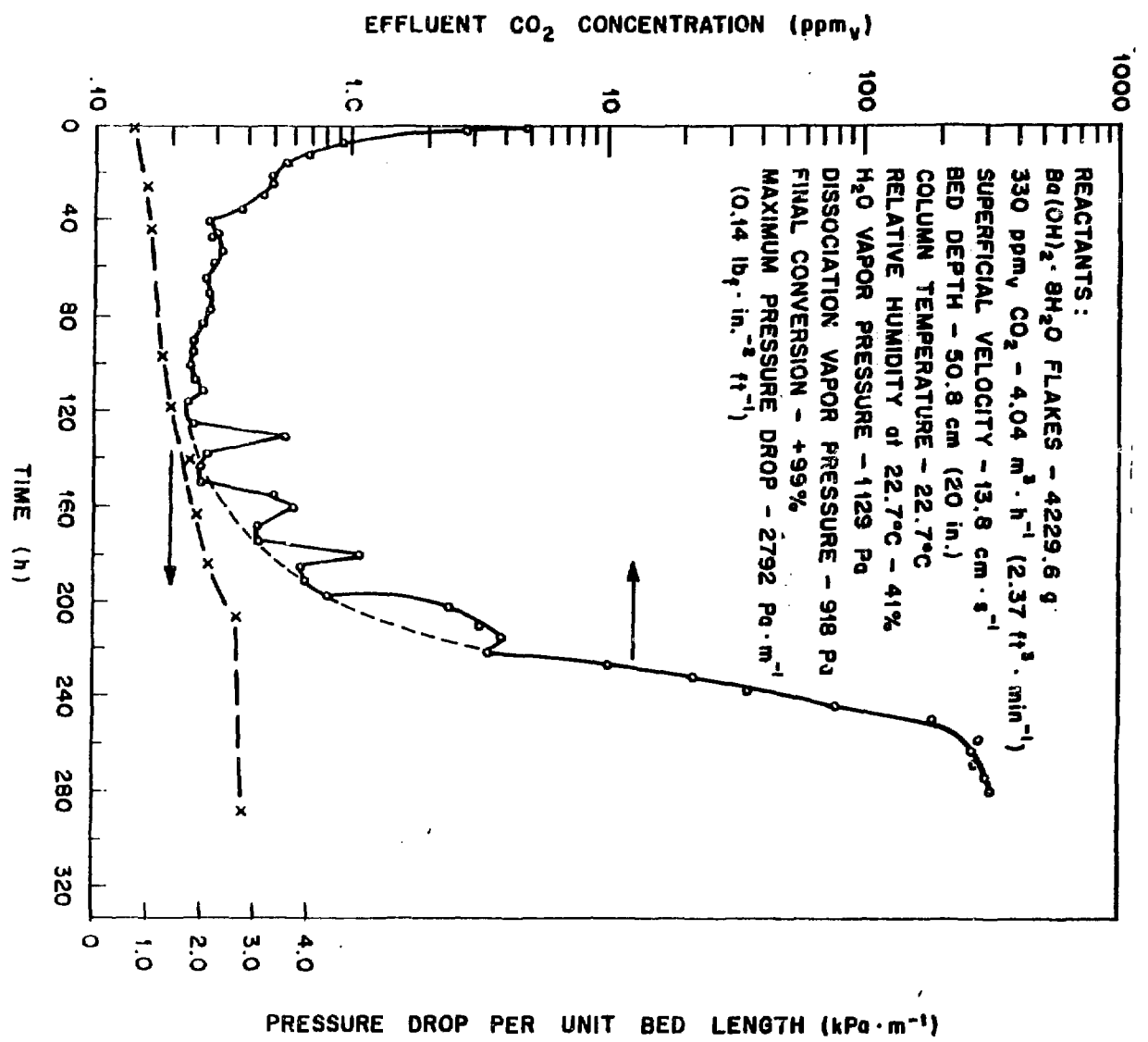


Fig. 9. NEAR OPTIMAL CONDITIONS FOR CO₂ REMOVAL FROM AIR (330 ppm_v) WITH Ba(OH)₂ · 8H₂O FLAKE BED

of approximately 18 cm. The initial pressure drop across the bed was 1.01 $\text{kPa}\cdot\text{m}^{-1}$ ($.04 \text{ lb}\cdot\text{in}^{-2}\cdot\text{ft}^{-1}$) and gradually increased to 3.64 $\text{kPa}\cdot\text{m}^{-1}$ ($.14 \text{ lb}\cdot\text{in}^{-2}\cdot\text{ft}^{-1}$). 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 preceding 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 $\text{Ba}(\text{OH})_2\cdot 8\text{H}_2\text{O}$ 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 $\text{Ba}(\text{OH})_2\cdot 8\text{H}_2\text{O}$ have resulted in bed deactivation and early CO_2 breakthrough, indicating $\text{Ba}(\text{OH})\cdot 3\text{H}_2\text{O}$ to be considerably less reactive than $\text{Ba}(\text{OH})_2\cdot 8\text{H}_2\text{O}$. This deactivation step appears to be kinetically controlled. Studies are presently underway to develop a better understanding of the deactivation phenomenon. Although prolonged operation at vapor pressures below the dissociation vapor pressure of $\text{Ba}(\text{OH})_2\cdot 8\text{H}_2\text{O}$ 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 $\text{Ba}(\text{OH})_2\cdot 8\text{H}_2\text{O}$ are composed of 53 mole % $\text{Ba}(\text{OH})_2\cdot 8\text{H}_2\text{O}$ and 47 mole % $\text{Ba}(\text{OH})_2\cdot 8\text{H}_2\text{O}-\text{Ba}(\text{OH})_2\cdot 3\text{H}_2\text{O}$ eutectic. Results have indicated that when a flake is exposed to a high humidity gas stream, a transformation takes

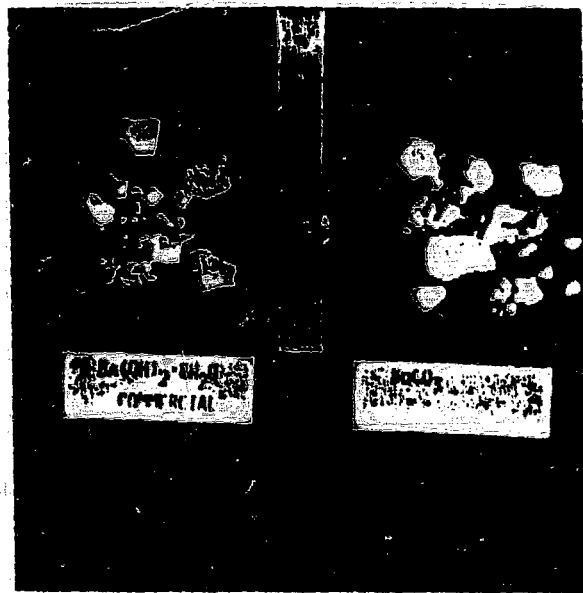


Fig. 10 ^{Commercial} $\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$ reactant and
 BaCO_3 product flakes

place whereby the flake preferentially curls on one side and becomes a more active species (Fig. 11). Studies are underway to develop a better understanding of the mechanism for this transformation although conversion of $\text{Ba(OH)}_2 \cdot 7.5\text{H}_2\text{O}$ to $\text{Ba(OH)}_2 \cdot 8\text{H}_2\text{O}$ and capillary condensation of H_2O vapor within the pores of the flakes appear to be likely candidates. The resulting material is more active, but pressure drop problems are also much greater due to ensuing particle degradation. Studies are underway to determine the severity of the problem as the humidity or water vapor pressure is increased while other system parameters remain constant.

V. CONCLUSION

For the treatment of an air-based off-gas stream, the use of packed beds of $\text{Ba(OH)}_2 \cdot 8\text{H}_2\text{O}$ 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 $\text{Ba(OH)}_2 \cdot 8\text{H}_2\text{O}$, 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 $\text{Ba(OH)}_2 \cdot 8\text{H}_2\text{O}$ to BaCO_3 and not from the hydration of the commercial $\text{Ba(OH)}_2 \cdot 8\text{H}_2\text{O}$ (i.e. $\text{Ba(OH)}_2 \cdot 7.5\text{H}_2\text{O}$) to $\text{Ba(OH)}_2 \cdot 8\text{H}_2\text{O}$.



Fig. 17 Effect of high humidity on $Ba(OH)_2 \cdot 8H_2O$ crystals

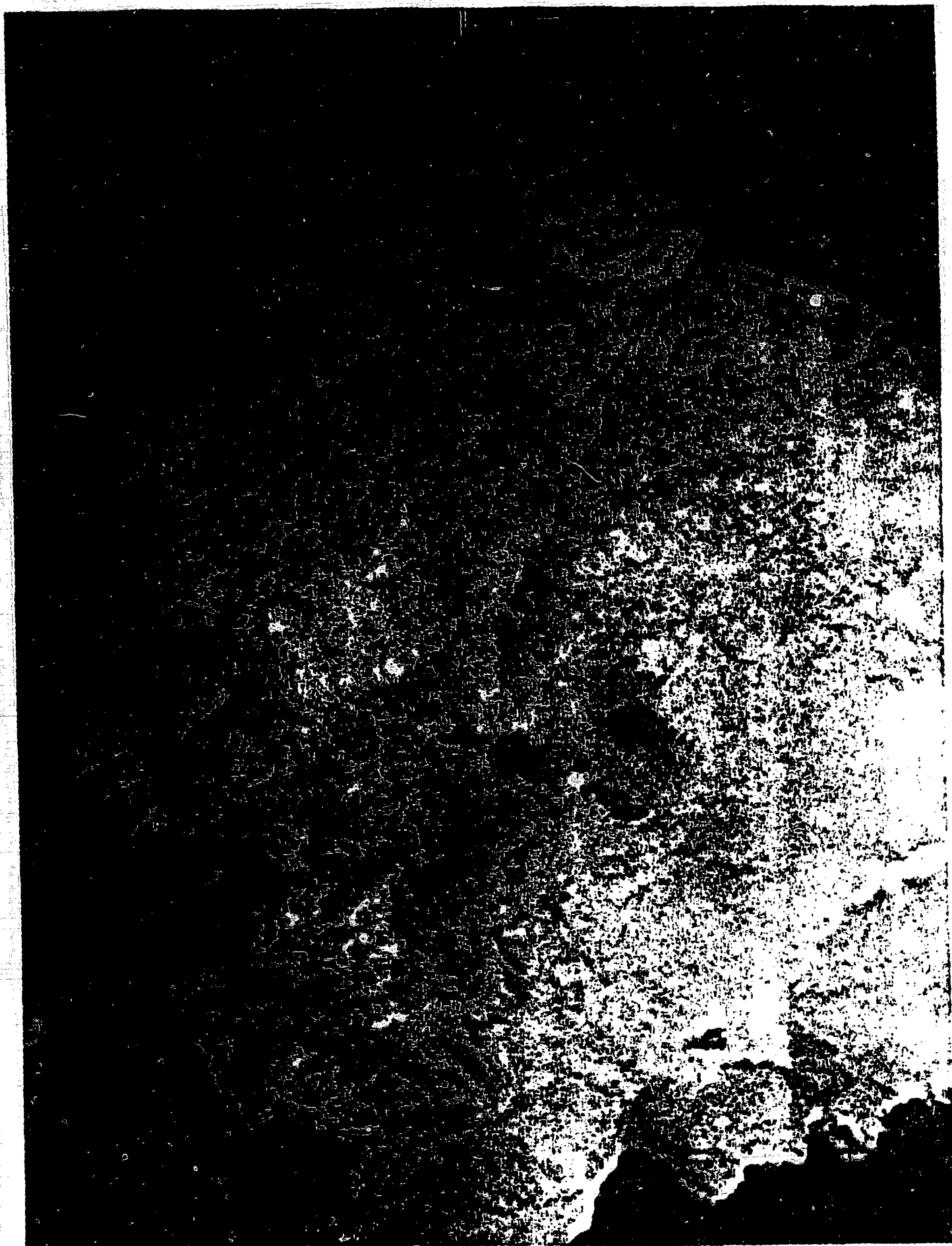


Fig 12 Effect of high humidity on Rasol's B 4.0 flake

8. 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," Proc. Health Phys. Soc. 8th Midyear Symp., Knoxville, Tenn., CONF-741018, pp. 229-234 (1974).
5. M. J. Kabat, "Monitoring and Removal of Gaseous Carbon-14 Species," 15th DOE Nuclear Air Cleaning Conference (August 1978).
6. H. Schuttelkopf, Releases of $^{14}\text{CO}_2$ from Nuclear Facilities with Gaseous Effluents, Kernforschungszentrum 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 (Feb. 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., CONF-740807 (August 12-15, 1974).
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 (August 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 ^{14}C -Contaminated CO_2 as CaCO_3 , 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 - $\text{Ca}(\text{OH})_2$ 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," 15th DOE Nuclear Air Cleaning Conference (August 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 Nuclear Technology (in preparation).
20. K. J. Notz, D. W. Holladay, C. W. Forsberg, and G. L. Haag, "Processes for the Control of $^{14}\text{CO}_2$ 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, 52 Ed., p. B-70, The Chemical Rubber Co., Cleveland, Ohio (1972).
22. W. F. Linke and A. Seidell, Solubilities of Inorganic and Metal Organic Compounds, Fourth Edition, American Chemical Society, Washington, D.C. (1958).
23. R. B. Cook, "Temperature and Pressure Effects on Sodorb 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 CO₂ Scrubber Systems," 1973 Diver's Gas Purity Symposium (Nov. 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 Calcium Hydroxide Mixtures (Baralyme) for Carbon Dioxide Absorption in Anesthetic," Anesthesia and Analgesia, May-June p. 151 (1942).
29. Mellor, "A Comprehensive Treatise on Inorganic and Theoretical Chemistry," Longman, Green & Co., N.Y., vol. III, p. 817, 1923.
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, Moote Prints, 34,9 (1965).
32. D. A. Roryta and H. J. Mass, "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-CO₂ Reaction, Part 1 - Dynamic Isothermal System," NRL Report 6937 (Oct. 1969).
34. B. A. Kondakov, P. V. Kovtunencko, 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, Michigan (updated Nov. 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 (Feb. 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 (Jan. 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 (Nov. 1971).
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. Sa'anc. Acad. Sci. Paris 262.C, 1143 (1966).
43. M. C. Flemings, Solidification Processing, McGraw-Hill, Inc., New York (1974).