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PROCESSES FOR THE CONTROL OF $^{14}\text{CO}_2$ DURING REPROCESSING*

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PROCESSES FOR THE CONTROL OF $^{14}\text{CO}_2$ DURING REPROCESSING*

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ABSTRACT

The fixation of $^{14}\text{CO}_2$ may be required at some future time because of the significant fractional contribution of ^{14}C , via the ingestion pathway, to the total population dose from the nuclear fuel cycle, even though the actual quantity of this dose is very small when compared to natural background. The work described here was done in support of fuel reprocessing development, of both graphite fuel (HTGRs) and metal-clad fuel (LWRs and LMFBRs), and was directed to the control of $^{14}\text{CO}_2$ released during reprocessing operations. However, portions of this work are also applicable to the control of $^{14}\text{CO}_2$ released during reactor operation. The work described falls in three major areas:

- The application of liquid-slurry fixation with $\text{Ca}(\text{OH})_2$, which converts the CO_2 to CaCO_3 , carried out after treatment of the CO_2 -containing stream to remove other gaseous radioactive components, mainly ^{85}Kr . This approach is primarily for application to HTGR fuel reprocessing.
- The above process for CO_2 fixation, but used ahead of Kr removal, and followed by a molecular sieve process to take out the ^{85}Kr . This approach was developed for use with HTGR reprocessing, but certain aspects also have application to metal-clad fuel reprocessing and to reactor operation.
- The use of solid $\text{Ba}(\text{OH})_2$ hydrate, reacting directly with the gaseous phase. This process is generally applicable to both reprocessing and to reactor operation.

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Processes for the Control of ^{14}C During Reprocessing

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1. INTRODUCTION

During operation of nuclear reactors, some ^{14}C is produced, primarily via neutron activation of ^{14}N , ^{15}N , ^{16}O , and ^{17}O , with activation of ^{13}C becoming significant in HTGRs [1]. The ^{14}C may be formed both in the fuel, from the nitrogen and oxygen reactions, and in the moderator, from oxygen in water-cooled reactors or from carbon (and nitrogen) in graphite-moderated, helium-cooled reactors. Some ^{14}C is also formed in the metal clad and core hardware, but this is retained in the metal and not released [1]. Table 1 summarizes the calculated quantities. The ^{14}C formed in the water of water-moderated LWRs is released during reactor operation, as a mixture of CO_2 and hydrocarbons, with CO_2 predominant in BWRs and CH_4 and C_2H_6 predominant in PWRs [1]. The reported releases of ^{14}C from Russian reactors is much higher, 200 to 800 Ci/GW(e)-yr, apparently due to use of nitrogen gas for pressurization and from the use of hydrazine and ammonium hydroxide in the primary cooling water [1]. In terms of reprocessing plants, the total annual curies of ^{14}C for plants serving 45 GW(e) generating capacity are shown in Table 2. The ^{14}C present in the fuel or in the graphite moderator is released primarily as CO_2 during reprocessing, diluted with varying amounts of air, noble gases, and small amounts of other gases; the ^{14}C in the metal clad and hardware is not released.

Table 1. ^{14}C produced in different reactors

Reactor Type	^{14}C Produced, in Ci/GW(e)-yr*		
	In the fuel	In metal clad and hardware	In the Moderator
LWR water moderated	20	30-60	8-16
LMFBR sodium moderated	6	13	-
HTGR graphite moderated	12	-	37-190

*Based on the nitrogen contents specified in Ref. [1].

Table 2. ^{14}C entering reprocessing plants serving 45 GW(e) generating capacity*

Reactor type	MTHM per yr	^{14}C , in Ci/yr	
		In the fuel	In the hardware or graphite moderator
LWR (Barnwell plant)	1500	~ 800	1400-2700
LMFBR (core and blanket)	1500	~ 300	600
HTGR (highly enriched)	450	500	1700-7300

*Adapted from Ref. [1].

$^{14}\text{CO}_2$ constitutes a small hazard, if released, because it can enter the food chain via photosynthesis [2]. The incremental relative global ^{14}C hazard from this source, if it were released, can be roughly estimated from these two facts: (a) the natural production rate of ^{14}C (from cosmic-ray induced reactions) is about 27,000 Ci/yr, and (b) ^{14}C contributes about 1% of the natural radiation background [3]. Thus, a reprocessing plant of the Barnwell type and size would add about 3×10^{-4} fraction to natural background per year of operation, or about 1% over a 40-yr lifetime. In terms of local impact from ^{14}C release, the effects could be greatly reduced by holding up $^{14}\text{CO}_2$ during the day and releasing at night, when the photosynthetic uptake of CO_2 is essentially nil [4].

This report summarizes developmental studies done at ORNL on the control of $^{14}\text{CO}_2$ which are applicable to the reprocessing of both metal-clad and graphite-matrix fuels. Some aspects of this work, primarily that described in Sections 3 and 4 of this report, are also applicable to the control of $^{14}\text{CO}_2$ released during reactor operation.

Our initial studies were carried out in support of HTGR reprocessing, wherein the off-gas consists of very large amounts of $^{12}\text{CO}_2$ containing trace amounts of $^{14}\text{CO}_2$, small amounts of krypton, xenon, and CO, and varying amounts of oxygen and nitrogen. As originally conceived, burner off-gas (after processing to remove particulates, iodine, water and tritium) would first be treated by the KALC process (Krypton Absorption in Liquid CO_2) to remove ^{85}Kr along with other noble gases [5,6]. The clean CO_2 could then either be discharged or, if required, converted to a stable solid form for isolation. The process developed at ORNL for fixation of CO_2 is conversion to CaCO_3 via slurry reaction with slaked lime. This process was shown to be effective in achieving fixation of >99% of the CO_2 while also attaining

>90% utilization of the slaked lime [7]. Details of this work are described in Section 2 of this report. In a paper study, it was shown that economical disposal of the CaCO_3 requires that it be low-level waste [8], and this in turn requires that the prior steps be effective in removing radioactivities other than ^{14}C .

An alternative concept for processing of HTGR off-gas was considered, wherein the CaCO_3 process precedes ^{85}Kr removal. This approach greatly simplifies the krypton removal step since the gross amounts of CO_2 are no longer present. However, it places a heavy burden on the carbonate fixation process in that >99% of the ^{85}Kr must pass on through, otherwise the CaCO_3 will be escalated out of the low-level category. Therefore, scoping tests were conducted to determine the holdup of ^{85}Kr on the CaCO_3 during CO_2 fixation [9], as summarized in Section 2. It was shown to be feasible to do the carbonate fixation first, keeping the ^{85}Kr retention to <1%, by appropriate sparging.

Since this sequence leaves the krypton diluted primarily by oxygen, the more-complex KALC process, required in the presence of large amounts of CO_2 , is in principle no longer required, if a simpler process is available. The feasibility of using molecular sieves for this last operation was shown in laboratory tests [10], even in the presence of some CO_2 and xenon, using a frontal displacement technique, which is described in Section 3.

Currently, an alternative process for the CO_2 fixation step is under development, based on the gas-phase reaction of CO_2 with $\text{Ba}(\text{OH})_2$ hydrate [11]. The key to this reaction is use of an expanded hydrate, which reacts rapidly and completely at moderate temperature and pressure, and is effective to low CO_2 concentrations. Details of this work are reported in Section 4.

2. FIXATION OF CO₂ IN ALKALINE SLURRIES

The very large volumes of CO₂ arising during reprocessing of HTGR fuel from combustion of the graphite blocks require a process amenable to these large quantities, both technologically and economically. The rate of off-gas generation is about 30 m³/min (1000 sCFM) in a commercial-scale plant (450 MTHM/yr) and this gas is largely CO₂. The reference off-gas cleanup scheme for such a plant followed this sequence [12]:

- oxidation (of any CO or tritium)
- iodine removal (with zeolites)
- radon holdup for decay of ²²⁰Rn (with type 5A molecular sieve)
- tritiated water removal (with type 3A molecular sieve)
- removal of krypton (via the KALC process)

In the reference process, clean CO₂ containing only ¹⁴C radioactivity was discharged to the atmosphere. However, it was recognized that at some future date the fixation of ¹⁴C might be required, and therefore the work described in this section was carried out. It had been determined in a paper study [8] that fixation as CaCO₃ provided a suitable end product, that direct reaction with a Ca(OH)₂ slurry should be acceptable, and that the CO₂ must be essentially free of any radioactivity other than ¹⁴C to avoid escalating the solid product out of the low-level waste category, which would create a major economic impact. Prior work on this reaction had focused on the production of CaCO₃ and not on the efficiency of CO₂ utilization, which was our interest. Therefore, work was done to obtain data on this latter point. In addition, studies were also done to determine the feasibility of fixing the CO₂ as CaCO₃ prior to the removal of ⁸⁵Kr; this requires a high DF for krypton separation from the CaCO₃ but, if this can be achieved, subsequent krypton concentration can be performed on a much smaller gas stream using molecular sieves (see Section 3 of this report) rather than the more complex KALC process. Data were also obtained on dilute CO₂ streams (about 0.1% in air) which will derive from VWR fuel reprocessing. Some studies were also made with Ba(OH)₂ slurries and with other alkalis.

2.1 The Fixation of CO_2 with $\text{Ca}(\text{OH})_2$ from Simulated HTGR Fuel Reprocessing Off-Gas

The feed gases (pure CO_2 down to 5% $\text{CO}_2/95\% \text{O}_2$) were contacted with the $\text{Ca}(\text{OH})_2$ in a single-stage agitated contactor, 19.6 cm ID, with a quiescent slurry volume of 6.7 liters [7]. The contactor, mechanical drive, and impeller were designed according to the standard criteria [13-15]. The contactor schematic is shown in Fig. 1. The CO_2 - $\text{Ca}(\text{OH})_2$ slurry reaction was studied to determine decontamination factors (DFs) and values of the interfacial area as a function of impeller speed, gas composition, gas flow rate, $\text{Ca}(\text{OH})_2$ concentration, and temperature. These operational parameters were studied for the following ranges: impeller speed, 100-1800 rpm; gas composition, 100, 87.5, 33.6, and 4.7% CO_2 (balance as O_2); gas flow rate, 0.85-50 slm; $\text{Ca}(\text{OH})_2$ slurry concentration, 0.50-2.0 molal; temperature, 21-46°C. Gas samples were analyzed by a combination of gas chromatography, infrared spectroscopy, flow metering, and mass balances.

The rate at which CO_2 transferred to the slurry, the DF, and the pH of the slurry (~12.5) remained constant, even at very high gas flow rates, until 90% of the $\text{Ca}(\text{OH})_2$ had been utilized (for batch operation); then the pH and the DF decreased rapidly. The DF for the CO_2 - $\text{Ca}(\text{OH})_2$ reaction varied inversely with gas flow rate and directly with impeller speed and CO_2 concentration in the feed gas. Pure CO_2 was completely reacted at 10 slm for an impeller speed of 1700 rpm and at 5 slm for 800 rpm. The DF was >3000 for 87.5% CO_2 feed at 3.5 slm and 500 for 4.7% CO_2 feed at 1 slm. Results of tests showed that DFs of $>10^4$ were feasible by operating stirred contactors in series.

The rate of reaction was concluded to be liquid-phase controlled for the feed composition studied and the gas flow rates studied. By assuming the applicability of the model for gas absorption accompanied by pseudo-first-order reaction, mass transfer coefficients and interfacial areas were calculated for both the plug flow and perfectly backmixed gas models.

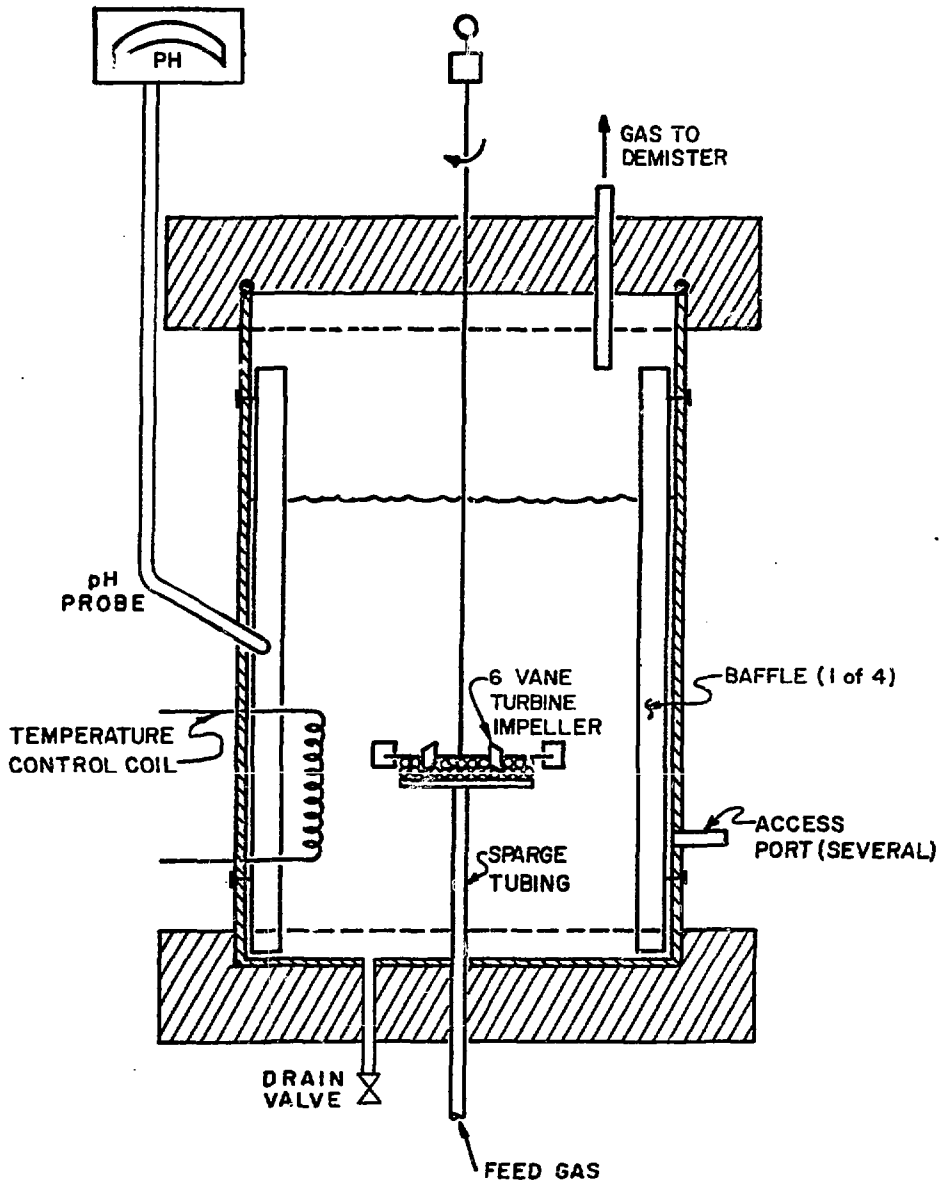


Fig. 1. Cutaway view of stirred-cell contactor.

The interfacial area calculated from the chemical reaction model with plug flow ranged from 0.2 to 3.0 cm^2/cm^3 , depending on superficial velocity and impeller speed. The mass transfer rate was only slightly affected by $\text{Ca}(\text{OH})_2$ concentration from 0.50 to 1.50 molal. The mass transfer rate and the DF were virtually independent of temperature over the range 21-46°C.

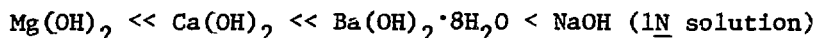
The settling rate of the CaCO_3 product was dependent on operating conditions and was measured to provide a qualitative indication of particle size for estimating its separation from the slurry. The settling rate was found to vary directly with impeller speed and temperature and inversely with gas flow rate.

2.2 The Fixation of CO_2 from Simulated LWR Fuel Reprocessing Off-Gas Using Alkaline Slurries

For this work a dilute CO_2 stream was used (0.03% CO_2 in air; also 3% CO_2). In addition to $\text{Ca}(\text{OH})_2$, the barium and magnesium hydroxides were also tested. The same general approach was used as before, but the analytical technique was modified because of the very low CO_2 content in the effluent gas; a larger stirred tank reactor was also used, with a volume of 16 liters [16].

Decontamination factors and interfacial areas were obtained for the following operating conditions: gas composition, 0.033% ~~to~~ ^{and} 3.0% CO_2 (balance as air); slurry concentration, 0.4 to 1.5 molal; slurry type, $\text{Ca}(\text{OH})_2$, $\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$, and $\text{Mg}(\text{OH})_2$; impeller speed, 325 ~~to~~ ^{and} 650 rpm; and gas flow rate, 10 to 80 slm. Gas samples were analyzed primarily by infrared spectroscopy because it was the more dependable method for measuring CO_2 at the 1 ppm level and below.

Under equivalent operating conditions the DFs for CO_2 increased in the same order as the solubilities:



The DF for $\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$ is about 10 times greater than for $\text{Ca}(\text{OH})_2$,

which is in turn about 10 times greater than for $\text{Mg}(\text{OH})_2$ (see Fig. 2). Although $\text{Ba}(\text{OH})_2$ is more expensive than $\text{Ca}(\text{OH})_2$, the total amount of CO_2 given off during LWR reprocessing is much less than for HTGR reprocessing, thus allowing the economical use of the more expensive reagent. There were no significant differences in DFs obtained for CO_2 removed via either semibatch or continuous slurry operation.

For the same operating conditions (impeller speed, superficial velocity, temperature, etc) the DFs in the dilute (0.033% CO_2) gas were as much as a factor of 5 less than those obtained for a 90% CO_2 -air feed. Based on a plug flow model with a log-mean pressure driving force, interfacial areas varied directly with superficial velocity over the range of 0.2 to $2 \text{ cm}^2/\text{cm}^3$. For fixation of CO_2 from simulated LWR fuel reprocessing off-gases, it appears feasible to obtain DFs for CO_2 of 10^2 to 10^4 ; $\text{Ca}(\text{OH})_2$ *with* ~~and~~ barium hydroxide. It was determined that the DFs for CO_2 removal from LWR-type off gases:

1. Varied directly with impeller speed and impeller diameter;
2. varied inversely with slurry concentration and gas flow rate (however, for $\text{Ba}(\text{OH})_2$ slurries, DF varied directly with slurry concentration);
3. varied directly with temperature for slurries in which the solubility of the solids increases with temperature;
4. varied directly with concentration of CO_2 in the feed.

Again, the rate of CO_2 removal was liquid phase controlled [17,18]. It was possible to model $\text{Ca}(\text{OH})_2$ slurry by accounting for both the interfacial area and degree of mixing as a function of the hydrodynamic parameters. However, $\text{Ba}(\text{OH})_2$ slurries could not be characterized using simple plug flow or backmix models.

Reactant	Impeller speed	Gas composition	Analytical method	Temp
Δ 1 m Mg(OH) ₂	650 rpm	0.033% CO ₂ -air	GC & TCD	21°C
▲ 1 m Ca(OH) ₂	325 rpm	1 and 3% CO ₂ -air	GC & TCD or FID	21°C
○ 1 m Ca(OH) ₂	650 rpm	0.033% CO ₂ -air	GC & FID	15°C
● 1 m Ca(OH) ₂	650 rpm	3% CO ₂ -air	GC & TCD or FID	21°C
∇ 1 m Ca(OH) ₂	650 rpm	0.033% CO ₂ -air	GC & FID	60°C
□ 0.4 and 0.75 m Ba(OH) ₂	650 rpm	0.033% CO ₂ -air	GC & FID	15°C
■ 0.4 and 0.75 m Ba(OH) ₂	650 rpm	3% CO ₂ -air	GC & TCD or FID	25°C
▼ 1.0 N NaOH	650 rpm	3% CO ₂ -air	GC & TCD or FID	25°C

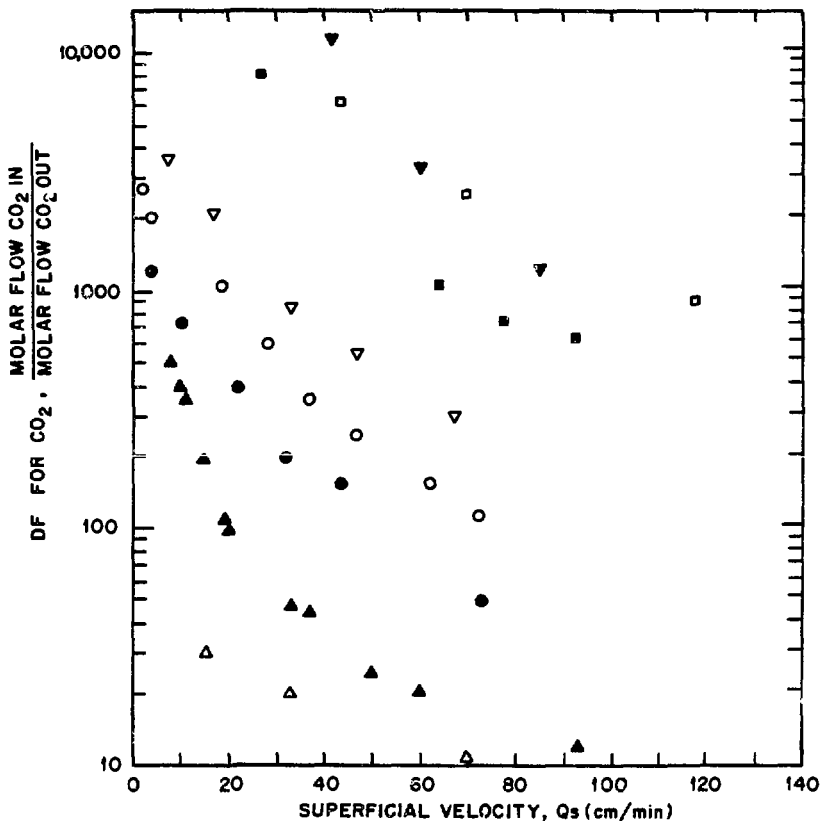


Fig. 2. DF's for Removal of CO_2 from Dilute Streams Under Various Conditions and with Different Reagents.

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2.3 Fixation of CO_2 as CaCO_3 in the Presence of Krypton

These studies were conducted with gas mixtures which approximated the HTGR off-gas composition of 90% CO_2 , 7.5% O_2 , 2.5% N_2 , 16 ppm total Kr, 1.0 ppm ^{85}Kr , and 61 ppm Xe [19]. The ranges of variables studied for the HTGR off-gas processing were: impeller speed, 650 and 800 rpm; CO_2 feed gas concentration, 88 to 97%; superficial gas velocity, 10 to 110 cm/min; $\text{Ca}(\text{OH})_2$ slurry concentration, 0.5, 1.0, and 2.0 M; Kr feed gas concentration, 18 to 180 ppm; temperature, 20 to 60°C; and both batch and single and series continuous stirred tank operation. The stirred tank reactor used was the same as that described in Section 2.1. The xenon concentration was ≤ 60 ppm. It was the specific goal of these studies to determine the feasibility of removing CO_2 from HTGR fuel reprocessing off-gas prior to krypton removal, with conditions of operation developed to minimize the krypton retention in the CaCO_3 slurry. Experiments were conducted to determine the distribution of krypton. These decontamination and separation factors were defined:

$$\text{DF for } \text{CO}_2 = \frac{\text{moles of } \text{CO}_2 \text{ into contactor in feed gas}}{\text{moles of } \text{CO}_2 \text{ out in effluent gas}}$$

$$\text{SF for Kr} = \frac{\text{moles of Kr into contactor in feed gas}}{\text{moles of Kr remaining in the slurry}}$$

Thus, a high DF for CO_2 indicates effective fixation while a high SF for Kr indicates good decontamination of the CaCO_3 from Kr. DFs for CO_2 in the 10^2 - 10^3 range were feasible for CO_2 removal in single-stage contactors and DFs for CO_2 of 10^3 - 10^4 were feasible for two-stage contactor operation. SFs for Kr were 100-200 for the primary contactor operation, and add-on SFs for Kr of an additional 100 could be readily obtained by evacuation or sparging of the stirred product slurry. Thus, total SFs for Kr of 10^4 to 10^5 could be obtained by using a combination of primary processes and add-on treatments.

Experimentally, the following parametric relationships were established:

1. The DFs for CO_2 varied inversely with gas superficial velocity, while the SFs for Kr had a slight direct variation with superficial velocity.
2. The DFs for CO_2 varied inversely with slurry molality, while the SFs for Kr varied directly with slurry molality.

3. The DFs for CO_2 had a slight direct variation with temperature, while the SFs for Kr were not affected.
4. The DFs for CO_2 varied directly with impeller speed.
5. The DFs for CO_2 varied directly with CO_2 mole fraction in the feed gas, while the SFs for Kr varied inversely with CO_2 mole fraction in the feed gas.
6. With two contactors in series, the overall DFs for CO_2 varied directly with the extent of the conversion of CO_2 that occurred in tank 1, while the overall SFs for Kr varied inversely with the extent of CO_2 conversion in tank 2.

The development of the most useful models for prediction of DFs for CO_2 and krypton or for prediction of scaled-up contactor dimensions were dependent on expressions for the interfacial area. Interfacial area could be estimated either from a general hydrodynamic correlation or from an expression constructed from the experimental data of the bench-scale contactors of this study. The general rate expression was patterned after the studies of Juvekar and Sharma [20], in which the reaction is basically pseudo-first order with control in the liquid phase.

3. SEPARATION OF $^{14}\text{CO}_2$ AND ^{85}Kr VIA MOLECULAR SIEVES

Molecular sieves were experimentally investigated for the separation of krypton and carbon dioxide from dry off-gas streams of the type that would result from separations such as those described in Section 2. Molecular sieves are a class of highly inert, inorganic zeolites which can adsorb $\sim 100 \text{ cm}^3$ (STP)/g of certain gases and be regenerated by heating/ or depressurization. A potential difficulty is that CO_2 and Kr have very similar sorptive properties. A series of calculations and experiments were conducted to determine the value of molecular sieves for this application. The two most successful approaches are described below.

For selective removal of carbon dioxide from off-gas streams containing krypton, molecular sieve 4A was found to perform adequately. Adsorption by molecular sieves depends upon the molecule to be adsorbed having both the proper size and geometry to fit within the molecular sieve lattice and having appropriate intermolecular attractive forces between the molecular and sieve. Molecular sieve 3A has too small a lattice to adsorb carbon dioxide while molecular sieve 5A was found to adsorb both carbon dioxide and krypton. Molecular sieve size 4A has been reported to adsorb krypton at high pressures and moderate temperatures [21] but the rate of adsorption appears near zero when operating pressures are 1 to 3×10^5 Pa and the operating temperature is near 0°C .

A series of experiments using a 95-cm long molecular sieve adsorption column were conducted to obtain the above results. The commercial 4A molecular sieve used in these tests was in the bead form as manufactured by Linde. All experiments used a premixed feed gas of 93.1% CO_2 , 5.4% O_2 , and 1.5% Kr. The krypton concentrations were measured using ^{85}Kr tracer while the CO_2 content was measured with an infrared analyzer. Tests were conducted at 0°C over a pressure range of 1.0 to 2.3×10^5 Pa. The measured CO_2 levels in the gas after passing through the molecular sieve were below 10 ppm, the limit of detection for CO_2 of the analytical equipment that was used. The bed was easily regenerated by heating to 200°C .

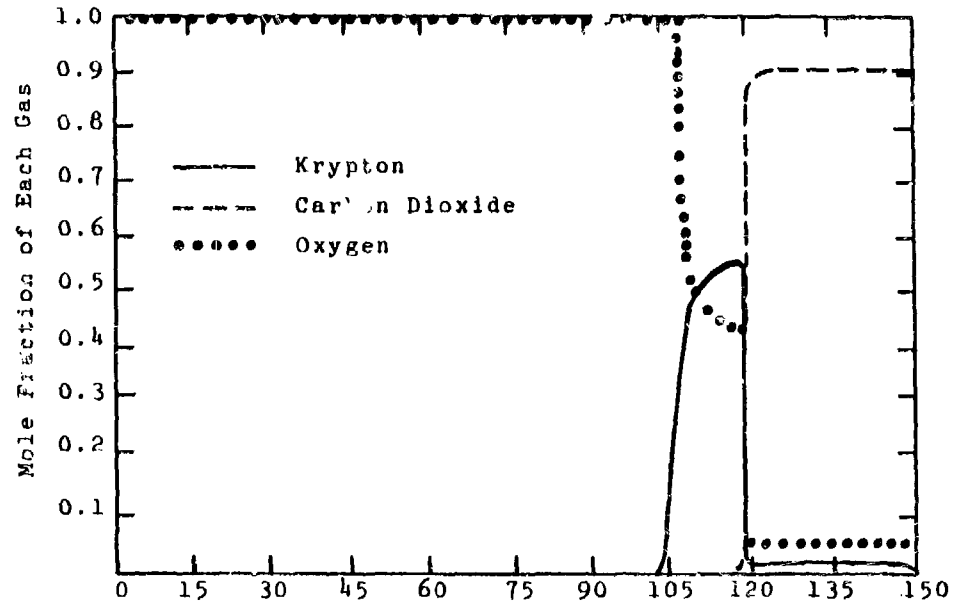
The length of the mass transfer zone for CO_2 adsorption varied from 11.8 cm at a gas flow rate of $7.22 \text{ cm}^3/\text{cm}^2\cdot\text{min}$ at $1.01 \times 10^5 \text{ Pa}$ to 4.3 cm with a flow rate of $10.32 \text{ cm}^3/\text{cm}^2\cdot\text{min}$ at $1.7 \times 10^5 \text{ Pa}$. The mass transfer zone is defined herein as the distance through the bed where the CO_2 concentration in the gas phase changed by 80% of the difference between the feed gas and outlet gas concentrations.

To separate krypton and carbon dioxide from the off-gas and each other, experiments showed that molecular sieve 5A used as a frontal analysis gas phase chromatograph provided good separations. The principle of operation of this device is as follows. If a gas mixture of krypton, oxygen, and carbon dioxide flows through a bed of 5A molecular sieve near atmospheric pressure at 0°C , both carbon dioxide and krypton will be adsorbed. Carbon dioxide is, however, more strongly adsorbed than krypton and thus will displace krypton gas from the bed. In examining a long molecular sieve bed supplied with a feed gas of oxygen, krypton and carbon dioxide, one observes that the zone of the molecular sieve bed nearest the feed point is saturated with CO_2 while the gas phase contains the feed gas. At the end of this zone, there is a transition region where CO_2 is being adsorbed onto the bed and krypton is being displaced from the bed into the gas phase. Beyond this first transition region is a zone where adsorbed krypton is being held by the bed and only oxygen and krypton exist in the gas phase. At the end of this zone lies a second transition region where krypton is being adsorbed onto the bed. Beyond the latter region are found only oxygen and a molecular sieve bed with very little adsorbed gas.

If the gas mixture is continuously fed to the bed and the gas exiting from the bed is analyzed, a "bubble" of oxygen is first observed, followed by and pushed out successively by a bubble of krypton containing some oxygen and by the feed gas. At the end of this process, the bed is saturated with CO_2 . Heat is generated during the process; therefore, provisions for heat dissipation must be included since the bed must be kept at constant temperature to ensure good separations. With two or more beds, continuous operation can be provided.

The above separation approach was experimentally verified with the equipment and feed gas described earlier. The molecular sieve was in the form of 1/16 in. pellets as supplied by Linde. A series of 10 runs were made with pressures from 1.0 to 2.36×10^5 Pa and gas flow rates from 7.6 to $152.9 \text{ cm}^3/\text{cm}^2 \cdot \text{min}$. The results of a typical run are shown in Fig. 3. In the single molecular sieve bed, krypton was concentrated from 1.5% to 52% to 62% depending upon the experiment. The length of the mass transfer zone between the krypton and CO_2 varied from 1.0 to 3.1 cm. Theoretical calculations of Kr, CO_2 , and O_2 separations with this process were made and agreed with the experimental values obtained. Additional experiments with xenon added as an impurity indicated that this impurity presented no problem. As with earlier experiments, CO_2 levels were reduced below 10 ppm in the oxygen and krypton product streams.

Molecular sieves offer a simple way to separate dilute CO_2 from an off-gas stream. When the molecular sieve is regenerated, a concentrated CO_2 stream is generated. For separating CO_2 and Kr from other gases, particularly if the krypton has been partially concentrated, molecular sieves show potential as a separation device for small to intermediate gas flow rates. For large gas flows with high CO_2 levels, molecular sieves may not be appropriate due to excessive bed size and/or heat loads.



Time from Start of Experiment (min) \propto Gas Flow into Bed

Molecular Sieve: Linde 5A
 Feed Gas: 93.09% CO₂, 5.43% O₂, 1.48% Kr
 Bed Conditions: 0°C, 1.16×10^5 Pa (1.14 atm)
 Feed Gas Flow: 48.9 cm³(STP)/cm²-min
 Bed Length: 94.6 cm (37.25 in.)

Fig. 3. Gas composition from molecular sieve bed vs time.

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4. FIXATION OF CO₂ ON SOLID Ba(OH)₂ HYDRATE

Fixation of CO₂ on beds of Ba(OH)₂ hydrate has many attractive features [11]. This process would eliminate the need for liquid-solid separation equipment, the handling of liquid streams, and when operated in a packed bed mode, it would be considerably simpler. Use of Ba(OH)₂ hydrate is superior to other solids, most notably CaO or Ca(OH)₂, as the reaction has been shown to be kinetically possible at ambient conditions with final reactant conversions in excess of 99%. Carbon dioxide removal to concentrations below 100 ppb have been routinely observed. The product, BaCO₃, possesses both the thermal and chemical stabilities desired for long-term waste disposal (thermally stable to 1450°C and water solubility only 0.02 gr/liter at 20°C).

Although the reactivity of Ba(OH)₂ hydrates with CO₂ has been briefly cited in the literature [22], the extent of this reactivity has not been studied. Based upon vapor pressure and x-ray diffraction studies, the known hydrates are Ba(OH)₂·H₂O, Ba(OH)₂·3H₂O, and Ba(OH)₂·8H₂O. The respective water vapor dissociation pressures at 25°C are 0.355 mm, 4.20 mm, and 8.26 mm Hg [23] (47, 560, and 1100 Pa, respectively).

Experimental studies have been conducted on packed and fluidized beds of the monohydrate, a mixture of hydrates with an overall stoichiometry of Ba(OH)₂·5H₂O, and the octahydrate. The packed bed concept is preferred from an operational perspective due to the overall simplicity. Experimental studies have concentrated primarily on the treatment of high volumetric air gas streams containing a low concentration of CO₂ (330 ppm). Brief studies have been conducted on gas streams containing 5% and 88% CO₂.

Results have indicated that although Ba(OH)₂·H₂O is unreactive toward CO₂ in a dry air stream, the material expands and becomes quite active when the water vapor pressure of the surrounding gas exceeds the dissociation vapor pressure of Ba(OH)₂·8H₂O. The resulting formation of Ba(OH)₂·8H₂O has been confirmed by x-ray diffraction patterns. As shown by Run 1C (Fig. 4) a bed of Ba(OH)₂·H₂O undergoes a conditioning period when contacted

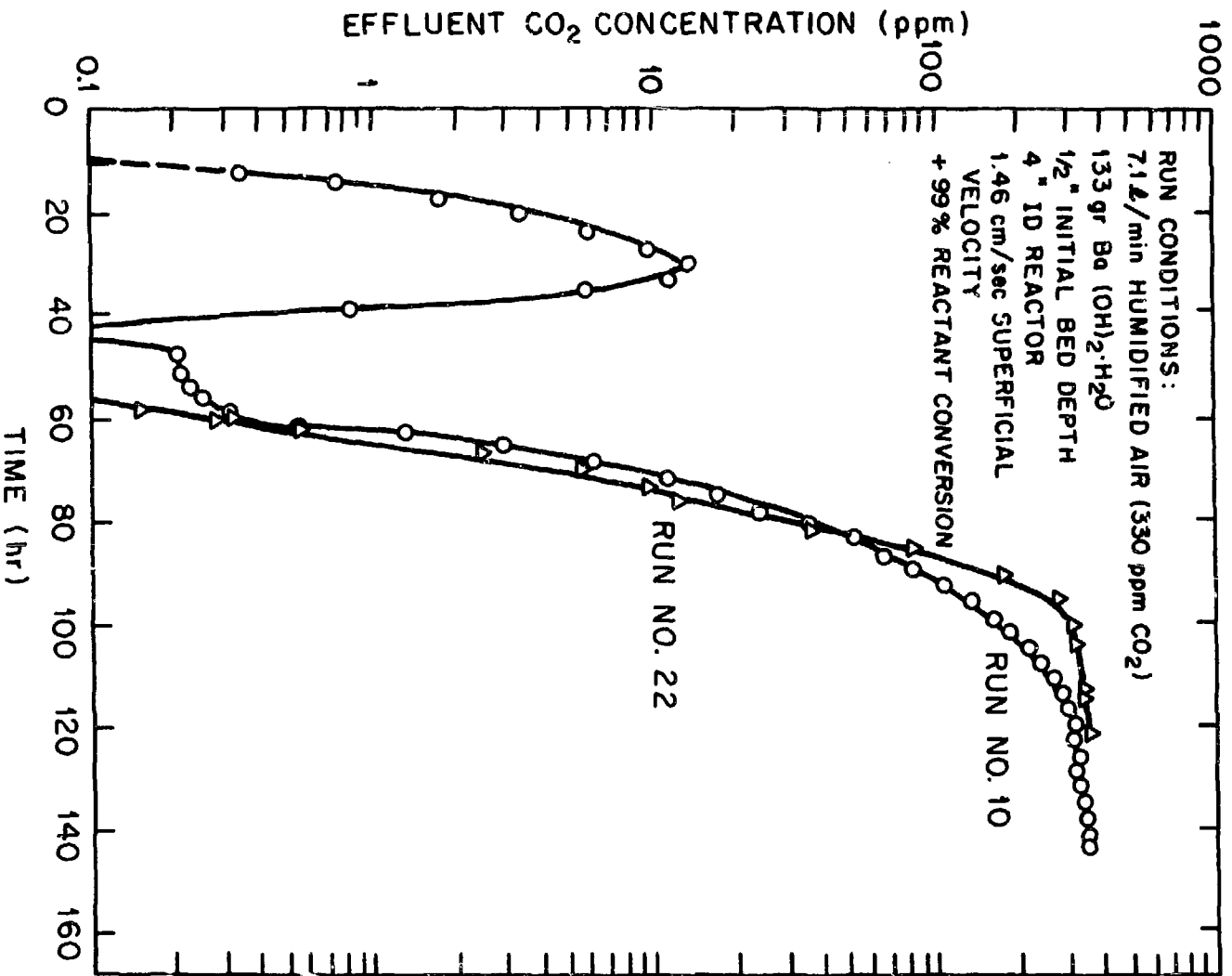


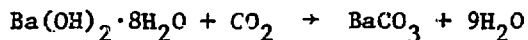
Fig. 4. The effects of preconditioning a $\text{Ba(OH)}_2 \cdot \text{H}_2\text{O}$ bed with humidified nitrogen.

Run 10: Reference Run

Run 22: Preconditioned Run.

with a humid, CO₂-bearing gas. During this period, the activity of the bed decreases and then increases. The initially high reactivity is attributed to residual Ba(OH)₂·8H₂O which may be present in the bed. The subsequent improvement in reactivity is due to the hydration of Ba(OH)₂·H₂O to Ba(OH)₂·8H₂O. As indicated by Run 22, it is possible to precondition a bed by contacting it with a humid, inert gas. In both cases, a bed volume increase of approximately 150% was observed due to the formation of Ba(OH)₂·8H₂O and final reactant conversions in excess of 99% were obtained. The BaCO₃ product is powdery in nature and excessive pressure drop could be an operational problem. Studies conducted in the fluidized bed mode have been promising although the entrainment of fines has been a problem.

A brief examination of gas streams with a higher CO₂ content has been conducted. As shown in Fig. 5, beds of ^{-5 +20} mesh Ba(OH)₂·hydrate containing an inert diluent are capable of high CO₂ removal efficiencies during the treatment of an 88% CO₂ gas stream. However, due to the overall stoichiometry of the reaction,



nine water molecules are released for each CO₂ molecule that reacts. Therefore for the treatment of a CO₂-rich gas stream, the feed gas will quickly become water-saturated. As the remainder of the water product cannot leave the system as vapor, thereby carrying a heat load with it, the reaction shifts from being 81.9 kcal/g-mole endothermic to 12.7 kcal/g-mole exothermic. Cooling capabilities or dispersion of the reactant will then be required during large bed applications to avoid melting of the reactant (MP of the octahydrate is 78°C). Condensed water has been observed within the reactor vessel although no deleterious effect on the overall reaction was observed. For treatment of gas streams rich in CO₂ with beds of Ba(OH)₂·H₂O, no preconditioning step is required; the reaction is driven by the high CO₂ level at the inlet end, liberating water which hydrates (and activates) the downstream end of the bed. Work in progress has shown that intermediate hydration provides a suitable compromise between volume change and chemical reactivity.

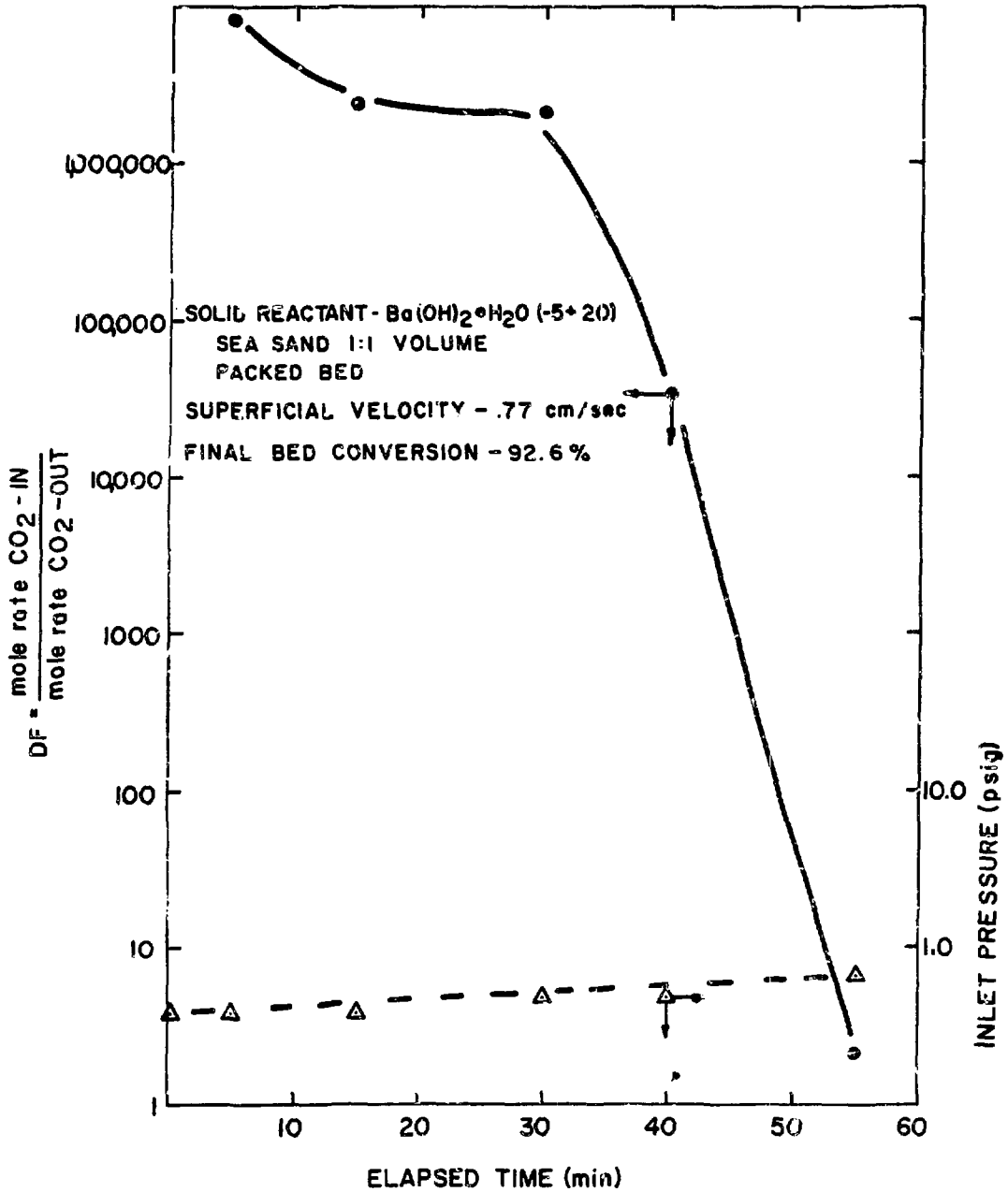


Fig. 5. Reaction of $\text{Ba(OH)}_2 \cdot \text{H}_2\text{O}$ with humidified 88% CO_2 .

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5. SUMMARY

The work described outlines methods applicable to the fixation of ^{14}C -containing CO_2 evolved during the reprocessing of both graphite-based and metal-clad fuel. Some of these methods are also applicable to control of ^{14}C evolved during reactor operation, particularly BWRs.

In summary:

- For CO_2 -rich off-gas from HTGR fuel reprocessing, the wet slurry process using $\text{Ca}(\text{OH})_2$ is both effective and economical. Although initially developed for use after ^{85}Kr removal, it was shown that CO_2 fixation can be done first, leaving a relatively small gas stream to be treated for concentration of the krypton.
- For CO_2 -dilute off-gas from LWR (and LMFBR) fuel reprocessing, the wet slurry process is also effective, with $\text{Ba}(\text{OH})_2$ hydrate being more effective than $\text{Ca}(\text{OH})_2$. The much smaller amount of total CO_2 in this case allows use of the more expensive reagent.
- Molecular sieves can be used to separate Kr and CO_2 from each other in dilute, air-like streams resulting from reprocessing operations. This approach is also suitable to reactor off-gases.
- A solid-gas phase reaction using $\text{Ba}(\text{OH})_2$ hydrates to remove CO_2 from gas streams is very effective. This approach is applicable to all of the sources mentioned above except the high-volume, high-concentration CO_2 from HTGR fuel reprocessing.

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