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Processes for the Control of $^{14}\text{CO}_2$ During Reprocessing

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Nuclear Fuel and Waste Programs

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

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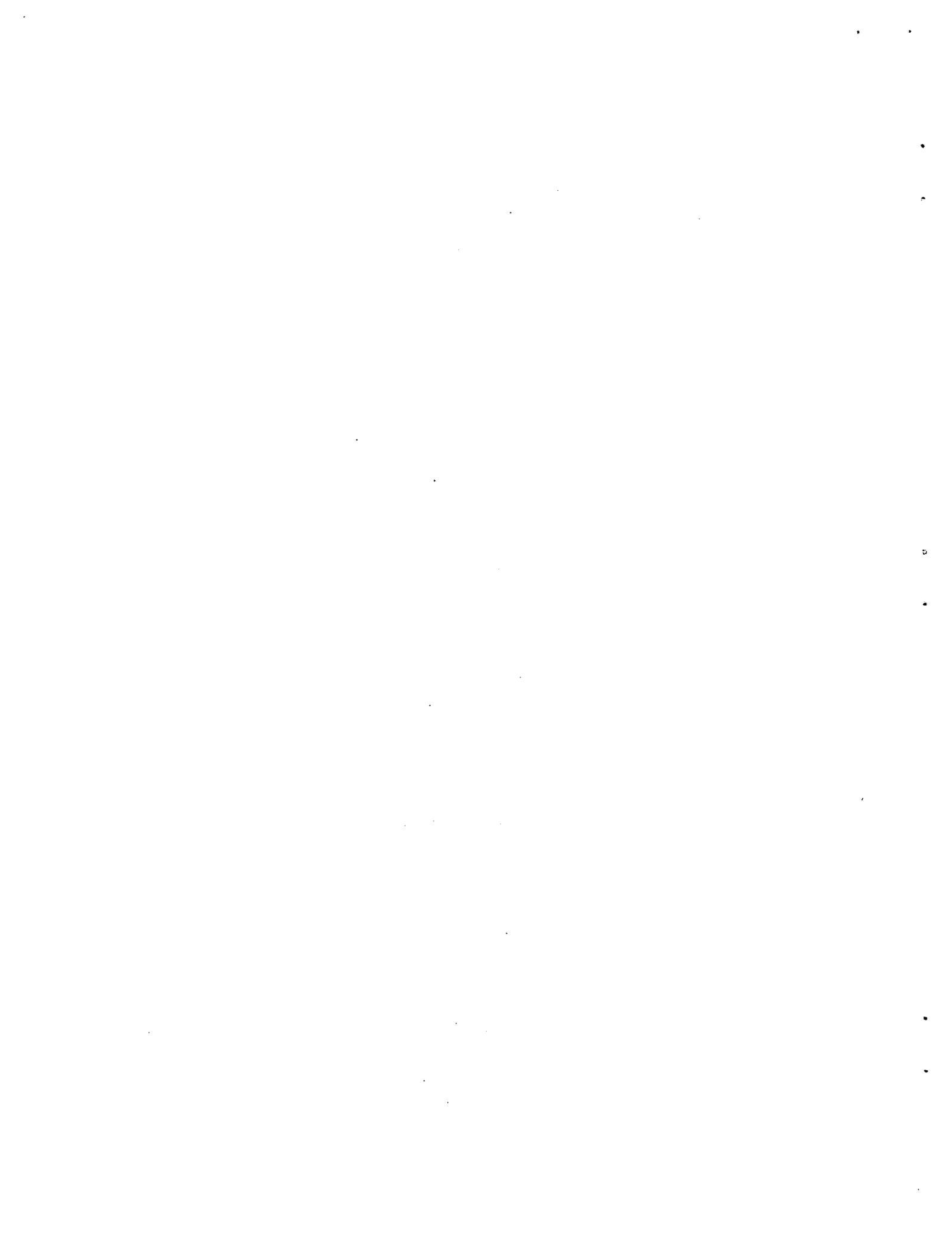
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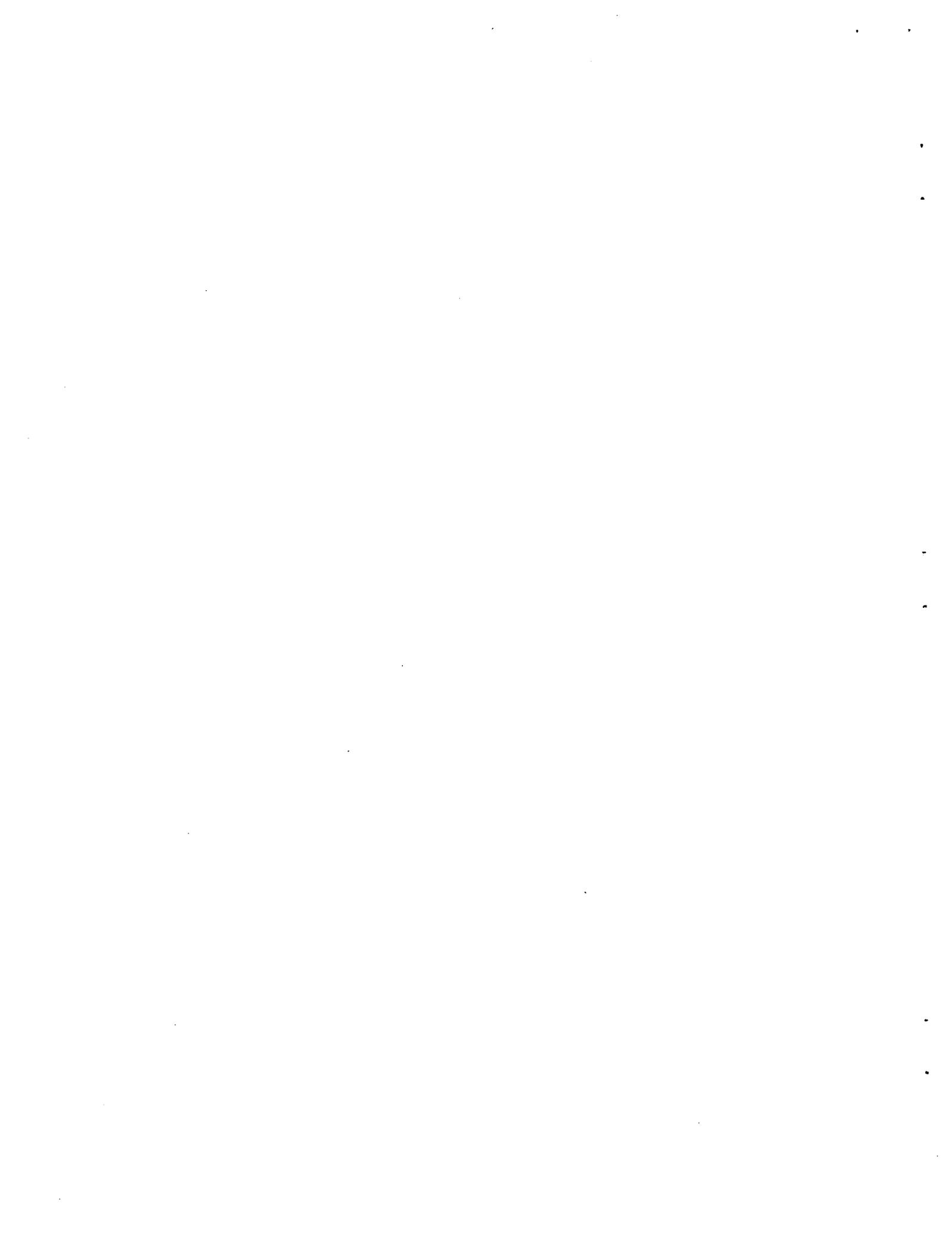
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CONTENTS

	<u>Page</u>
ABSTRACT	1
1. INTRODUCTION	1
2. FIXATION OF CO ₂ IN ALKALINE SLURRIES	5
2.1 Fixation of CO ₂ with Ca(OH) ₂ from Simulated HTGR Fuel Reprocessing Off-gas	6
2.2 Fixation of CO ₂ from Simulated LWR Fuel Reprocessing Off-gas Using Alkaline Slurries	8
2.3 Fixation of CO ₂ as CaCO ₃ in the Presence of Krypton	10
3. SEPARATION OF ¹⁴ CO ₂ AND ⁸⁵ Kr VIA MOLECULAR SIEVES	12
4. FIXATION OF CO ₂ ON SOLID Ba(OH) ₂ HYDRATE	16
5. SUMMARY	20
6. REFERENCES	21



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

K. J. Notz, D. W. Holladay, C. W. Forsberg,
and G. L. Haag

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 krypton 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 reactor operation.

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

(a) in the fuel from the nitrogen and oxygen reactions and (b) 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 are much higher, 200 to 800 Ci/GW(e)-yr, and are apparently due to use of nitrogen gas for pressurization and to 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 and is 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.

If released, $^{14}\text{CO}_2$ constitutes a small hazard 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

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

Reactor type	^{14}C produced [Ci/GW(e)-yr] ^a		
	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

^aBased on the nitrogen contents specified in ref. 1.

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

Reactor type	Metric tons of heavy metal per year	^{14}C (Ci/year)	
		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

^aAdapted from ref. 1.

(from cosmic-ray-induced reactions) is about 27,000 Ci/year, 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-year lifetime. In terms of local impact from ^{14}C release, the effects could be greatly reduced by holding $^{14}\text{CO}_2$ during the day and releasing it 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 Sects. 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 krypton absorption in

liquid CO₂ (KALC) process to remove ⁸⁵Kr along with other noble gases.^{5,6} The clean CO₂ could then either be discharged or, if required, converted to a stable solid form for isolation. The process developed at ORNL for fixation of CO₂ is conversion to CaCO₃ via slurry reaction with slaked lime. This process was shown to be effective in achieving fixation of >99% of the CO₂ while also attaining >90% utilization of the slaked lime.⁷ Details of this work are described in Sect. 2 of this report. In a paper study, it was shown that economical disposal of the CaCO₃ requires that it be low-level waste,⁸ and this in turn requires that the prior steps be effective in removing radionuclides other than ¹⁴C.

An alternative concept for processing of HTGR off-gas was considered, wherein the CaCO₃ process precedes ⁸⁵Kr removal. This approach greatly simplifies the krypton removal step because the gross amounts of CO₂ are no longer present. However, it places a heavy burden on the carbonate fixation process in that >99% of the ⁸⁵Kr must pass through so that the CaCO₃ will not be escalated out of the low-level category. Therefore, scoping tests were conducted to determine the holdup of ⁸⁵Kr on the CaCO₃ during CO₂ fixation,⁹ as summarized in Sect. 2. It was shown to be feasible to do the carbonate fixation first, keeping the ⁸⁵Kr retention to <1%, by appropriate sparging. Because this sequence leaves the krypton diluted primarily by oxygen, the more complex KALC process, required in the presence of large amounts of CO₂, is in principle no longer required. The feasibility of using molecular sieves, even in the presence of some CO₂ and xenon, was shown in laboratory tests¹⁰ using a frontal displacement technique, which is described in Sect. 3.

Currently, an alternative process for the CO₂ fixation step is under development, based on the gas-phase reaction of CO₂ with Ba(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 CO₂ concentrations. Details of this work are reported in Sect. 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 metric tons of heavy metal (MTHM) per year], and this gas is largely CO₂. The reference off-gas cleanup scheme for such a plant followed this sequence:¹²

1. oxidation (of any CO or tritium),
2. iodine removal (with zeolites),
3. radon holdup for decay of ²²⁰Rn (with type 5A molecular sieve),
4. tritiated water removal (with type 3A molecular sieve), and
5. 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 study⁸ 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 decontamination factor (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 (Sect. 3) rather than the more complex KALC process. Data were also obtained on dilute CO₂ streams (about 0.1%) which will derive from LWR fuel reprocessing. Some studies were also made with Ba(OH)₂ slurries and with other alkalies.

2.1 Fixation of CO₂ with Ca(OH)₂ from Simulated HTGR Fuel Reprocessing Off-gas

The feed gases (pure CO₂ down a 5% CO₂/95% O₂) were contacted with the Ca(OH)₂ in a single-stage, 19.6-cm-ID agitated contactor 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 CO₂-Ca(OH)₂ slurry reaction was studied to determine DFs and values of the interfacial area as a function of impeller speed, gas composition, gas flow rate, Ca(OH)₂ concentration, and temperature. These operational parameters were studied for the following ranges: (a) impeller speed, 100 to 1800 rpm; (b) gas composition, 100, 87.5, 33.6, and 4.7% CO₂ (balance as O₂); (c) gas flow rate, 0.85 to 50 standard liters/min (slm); (d) Ca(OH)₂ slurry concentration, 0.50 to 2.0 M; and (e) temperature, 21 to 46°C. Gas samples were analyzed by a combination of gas chromatography, infrared spectroscopy, flow metering, and mass balances.

The rate at which CO₂ 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 Ca(OH)₂ had been utilized (for batch operation); then the pH and the DF decreased rapidly. The DF for the CO₂-Ca(OH)₂ reaction varied inversely with gas flow rate and directly with impeller speed and CO₂ concentration in the feed gas. Pure CO₂ 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% CO₂ feed at 3.5 slm and 500 for 4.7% CO₂ feed at 1 slm. Results of tests showed that DFs of >10⁴ were feasible by operating stirred contactors in series.

The rate of reaction was concluded to be liquid-phase controlled for the feed composition and 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. The interfacial area calculated from the chemical reaction model with plug flow ranged from 0.2 to 3.0 cm²/cm³, depending on

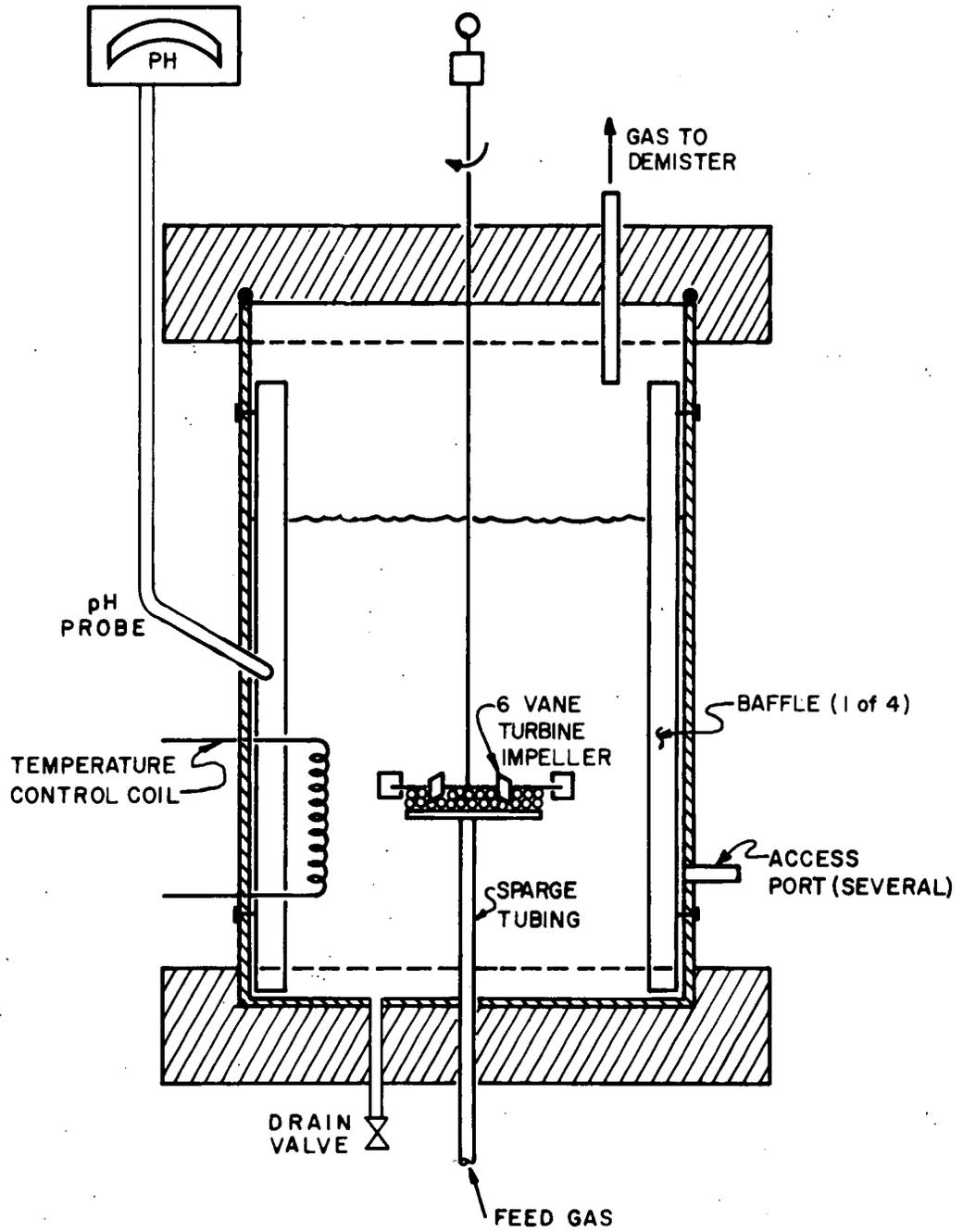


Fig. 1. Cutaway view of stirred-cell contactor.

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 *M*. The mass transfer rate and the DF were virtually independent of temperature over the range 21 to 46°C.

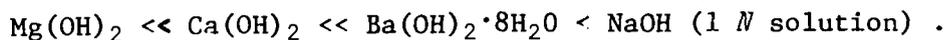
The settling rate of the CaCO_3 product was dependent on operating conditions and was measured to provide a qualitative indication of particle size for estimating its separation from the slurry. The settling rate was found to vary directly with impeller speed and temperature and inversely with gas flow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

2.2 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 (16-liter) stirred-tank reactor was also used.¹⁶

Decontamination factors and interfacial areas were obtained for the following conditions: gas composition, 0.033 and 3.0% CO_2 (balance as air); slurry concentration, 0.4 to 1.5 *M*; 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 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 ten times greater than for $\text{Ca}(\text{OH})_2$, which is in turn about ten times greater than for $\text{Mg}(\text{OH})_2$ (Fig. 2). Although

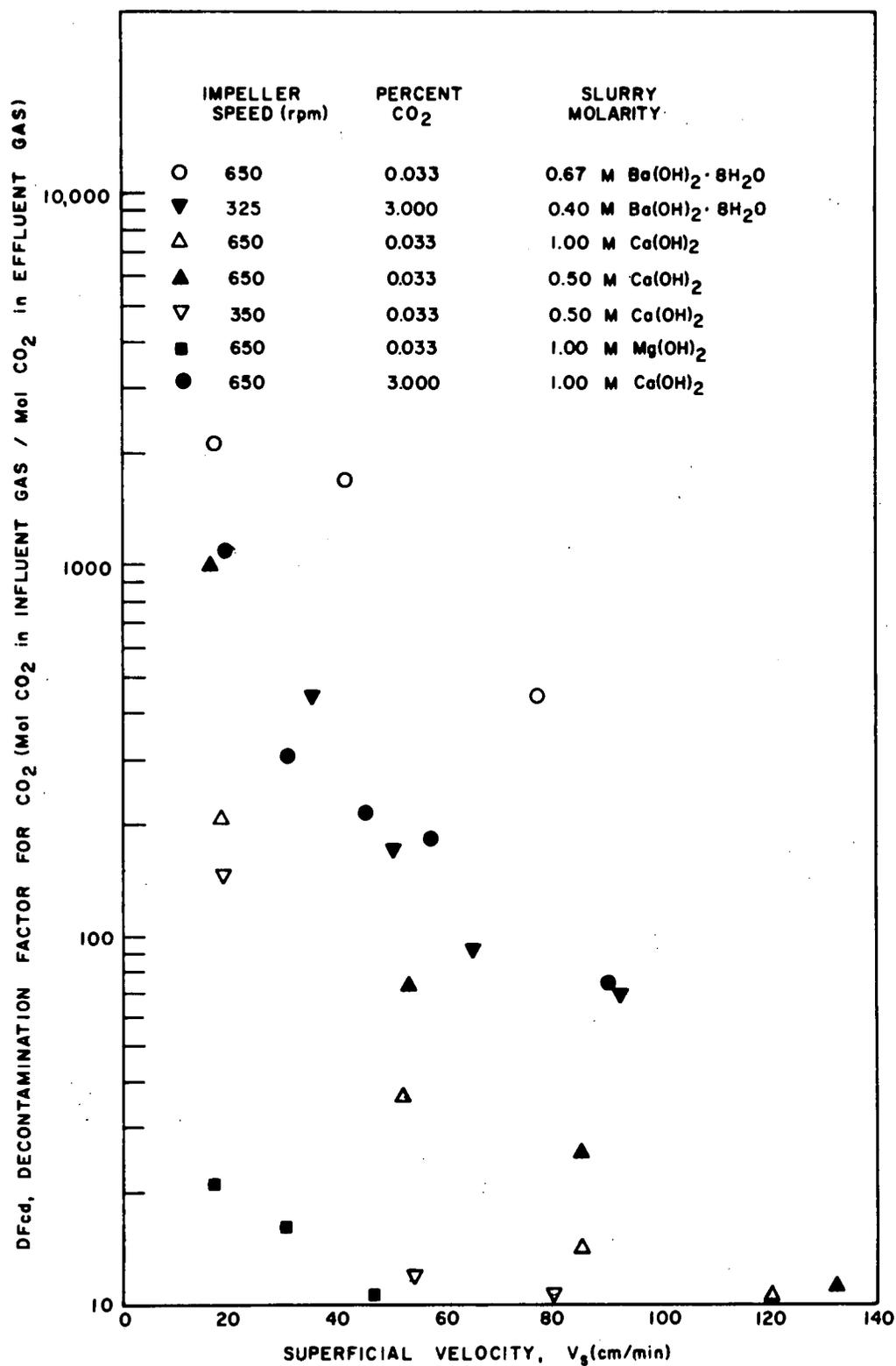


Fig. 2. Decontamination factors for removal of CO₂ from dilute streams under various conditions and with different reagents.

$\text{Ba}(\text{OH})_2$ 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 0.2 to 2 cm^2/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 with $\text{Ca}(\text{OH})_2$ or 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; and,
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 reaction 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.

2.3 Fixation of CO_2 as CaCO_3 in the Presence of Krypton

These studies were conducted with gas mixtures that 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 (a) impeller speed, 650

and 800 rpm; (b) CO₂ feed gas concentration, 88 to 97%; (c) superficial gas velocity, 10 to 110 cm/min; (d) Ca(OH)₂ slurry concentration, 0.5, 1.0, and 2.0 M; (e) krypton feed-gas concentration, 18 to 180 ppm; (f) temperature, 20 to 60°C, and (g) both batch and single and series continuous stirred-tank operation. The stirred-tank reactor used was the same as that described in Sect. 2.1. The xenon concentration was ≤60 ppm. It was the specific goal of these studies to determine the feasibility of removing CO₂ from HTGR fuel reprocessing off-gas prior to krypton removal, with conditions of operation developed to minimize the krypton retention in the CaCO₃ slurry. Experiments were conducted to determine the distribution of krypton. These DFs and separation factors (SFs) were defined:

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

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

Thus, a high DF for CO₂ indicates effective fixation while a high SF for krypton indicates good decontamination of the CaCO₃ from krypton. Decontamination factors for CO₂ in the 10² to 10³ range were feasible for CO₂ removal in single-stage contactors, and DFs for CO₂ of 10³ to 10⁴ were feasible for two-stage contactor operation. Separation factors for krypton were 100 to 200 for the primary contactor operation, and add-on SFs for krypton of an additional 100 could be readily obtained by evacuation or sparging of the stirred product slurry. Thus, total SFs for krypton of 10⁴ to 10⁵ 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 CO₂ varied inversely with gas superficial velocity, while the SFs for krypton had a slight direct variation with superficial velocity.
2. The DFs for CO₂ varied inversely with slurry molality, while the SFs for krypton varied directly with slurry molality.

3. The DFs for CO₂ had a slight direct variation with temperature, while the SFs for krypton were not affected.
4. The DFs for CO₂ varied directly with impeller speed.
5. The DFs for CO₂ varied directly with CO₂ mole fraction in the feed gas, while the SFs for krypton varied inversely with CO₂ mole fraction in the feed gas.
6. With two contactors in series, the overall DFs for CO₂ varied directly with the extent of the conversion of CO₂ that occurred in tank 2, while the overall SFs for krypton varied inversely with the extent of CO₂ conversion in tank 2.

The development of the most useful models for prediction of DFs for CO₂ and krypton or for prediction of scaled-up contactor dimensions was 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 ¹⁴CO₂ AND ⁸⁵Kr VIA MOLECULAR SIEVES

Molecular sieves were investigated experimentally for the separation of krypton and CO₂ from dry off-gas streams of the type that would result from separations such as those described in Sect. 2. Molecular sieves are a class of highly inert, inorganic zeolites which can adsorb ~100 cm³ (STP)/g of certain gases and be regenerated by heating or depressurization. A potential difficulty is that CO₂ and krypton 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 CO₂ from off-gas streams containing krypton, molecular sieve 4A was found to perform adequately. Adsorption by molecular sieves depends on 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 molecule and sieve. Molecular sieve 3A has too small a lattice to adsorb CO₂, whereas molecular sieve 5A was found to adsorb both CO₂ and krypton. Molecular sieve size 4A has been reported to adsorb krypton at high pressures and moderate temperatures²¹, but the rate of adsorption appears near zero when operating pressures are 1×10^5 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 was conducted to obtain the above results. The commercial 4A molecular sieve used in these tests was in the bead form as manufactured by Linde Division of Union Carbide Corporation. All experiments used a premixed feed gas of 93.1% CO₂, 5.4% O₂, and 1.5% Kr. The krypton concentrations were measured using ⁸⁵Kr tracer; the CO₂ content was measured with an infrared analyzer. Tests were conducted at 0°C over the pressure range 1.0×10^5 to 2.3×10^5 Pa. The measured CO₂ levels in the gas after passing through the molecular sieve were <10 ppm — the limit of detection for CO₂ 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 CO₂ adsorption varied from 11.8 cm at a gas flow rate of 7.22 cm³/cm²·min at 1.01×10^5 Pa to 4.3 cm with a flow rate of 10.32 cm³/cm²·min at 1.7×10^5 Pa. The mass transfer zone is defined herein as the distance through the bed where the CO₂ concentration in the gas phase changed by 80% of the difference between the feed gas and outlet gas concentrations.

To separate krypton and CO₂ from the off-gas and from 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 CO₂ flows through a bed of 5A molecular sieve near atmospheric pressure at 0°C, both CO₂ 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 CO₂, one observes that the zone of the molecular sieve bed nearest the feed point is saturated with CO₂ while the gas phase contains the feed gas. At the end of this zone, there is a transition region where CO₂ 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 fed continuously to the bed and the gas exiting 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 CO₂. 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 verified experimentally 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 ten runs was made with pressures from 1.0×10^5 to 2.36×10^5 Pa and gas flow rates from 7.6 to 152.9 cm³/cm²·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 on the experiment. The length of the mass transfer zone between the krypton and CO₂ varied from 1.0 to 3.1 cm. Theoretical calculations of krypton, oxygen, and CO₂ 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, CO₂ levels were reduced below 10 ppm in the krypton and oxygen product streams.

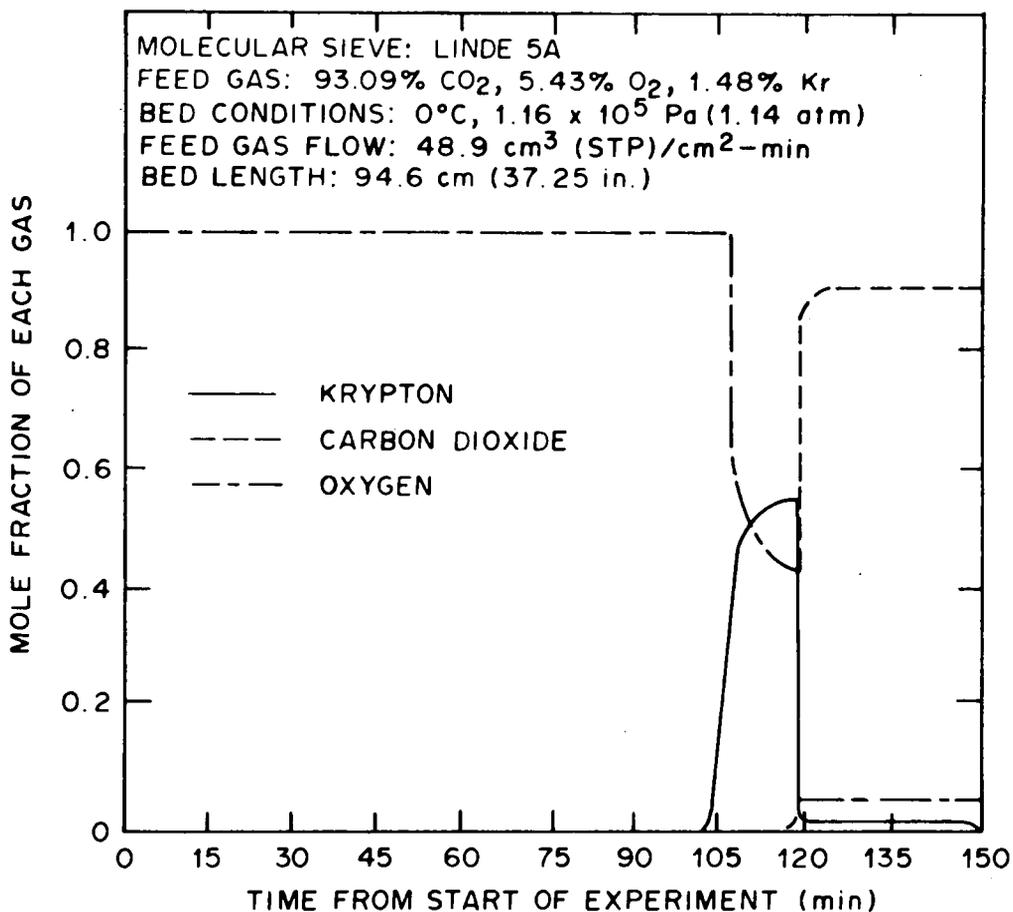


Fig. 3. Gas composition from molecular sieve bed vs time.

Molecular sieves offer a simple way to separate dilute CO₂ from an off-gas stream. When the molecular sieve is regenerated, a concentrated CO₂ stream is generated. For separating CO₂ and krypton 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 CO₂ levels, molecular sieves may not be appropriate because of excessive bed size and/or heat loads.

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 has been observed routinely. The product, BaCO₃, possesses both the thermal and chemical stabilities desired for long-term waste disposal (thermally stable to 1450°C and water solubility of only 0.02 g/liter at 20°C).

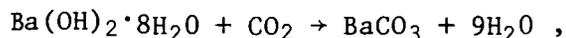
Although the reactivity of Ba(OH)₂ hydrates with CO₂ has been briefly cited in the literature,²² the extent of this reactivity has not been studied. Based on vapor pressure and x-ray diffraction studies, the known hydrates are Ba(OH)₂·H₂O, Ba(OH)₂·3H₂O, and Ba(OH)₂·8H₂O. The respective water vapor dissociation pressures at 25°C are 0.355, 4.20, and 8.26 mm Hg²³ (47, 560, and 1100 Pa).

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 10 (Fig. 4) a bed of $\text{Ba(OH)}_2 \cdot \text{H}_2\text{O}$ undergoes a conditioning period when contacted with a humid, CO_2 -bearing gas. During this period, the activity of the bed decreases and then increases. The initially high reactivity is attributed to residual $\text{Ba(OH)}_2 \cdot 8\text{H}_2\text{O}$ which may be present in the bed. The subsequent improvement in reactivity is due to the hydration of $\text{Ba(OH)}_2 \cdot \text{H}_2\text{O}$ to $\text{Ba(OH)}_2 \cdot 8\text{H}_2\text{O}$. As indicated by run 22, it is possible to precondition a bed by contacting it with a humid, inert gas. In both bases, a bed volume increase of $\sim 150\%$ was observed due to the formation of $\text{Ba(OH)}_2 \cdot 8\text{H}_2\text{O}$, and final reactant conversions in excess of 99% were obtained. The BaCO_3 product is friable, 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 CO_2 content has been conducted. As shown in Fig. 5, beds of -5 +20 mesh $\text{Ba(OH)}_2 \cdot \text{hydrate}$ containing an inert diluent are capable of high CO_2 removal efficiencies during the treatment of an 88% CO_2 gas stream. However, due to the overall stoichiometry of the reaction



nine water molecules are released for each CO_2 molecule that reacts. Therefore, for the treatment of a CO_2 -rich gas stream, the feed gas will quickly become water saturated. Because the remainder of the water product cannot leave the system as vapor, thereby carrying a heat load with it, the reaction shifts from 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 has been noted. For treatment of gas streams rich in CO_2 with beds of $\text{Ba(OH)}_2 \cdot \text{H}_2\text{O}$, no preconditioning step is required; the reaction is driven by the high CO_2 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.

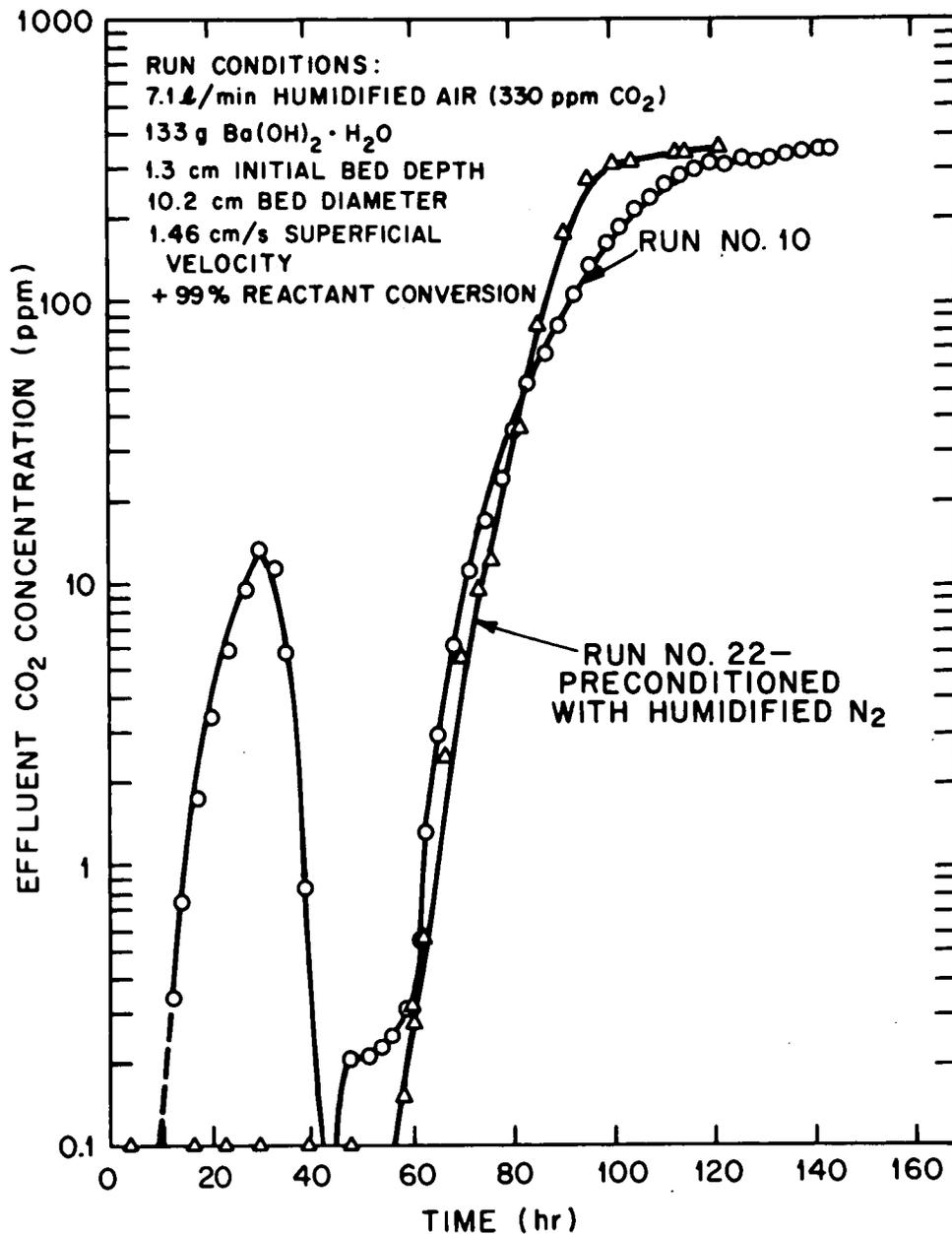


Fig. 4. The effects of preconditioning a Ba(OH)₂ · H₂O bed with humidified nitrogen. Run 10, reference run; run 22, preconditioned run.

ORNL-DWG 78-13722 R2

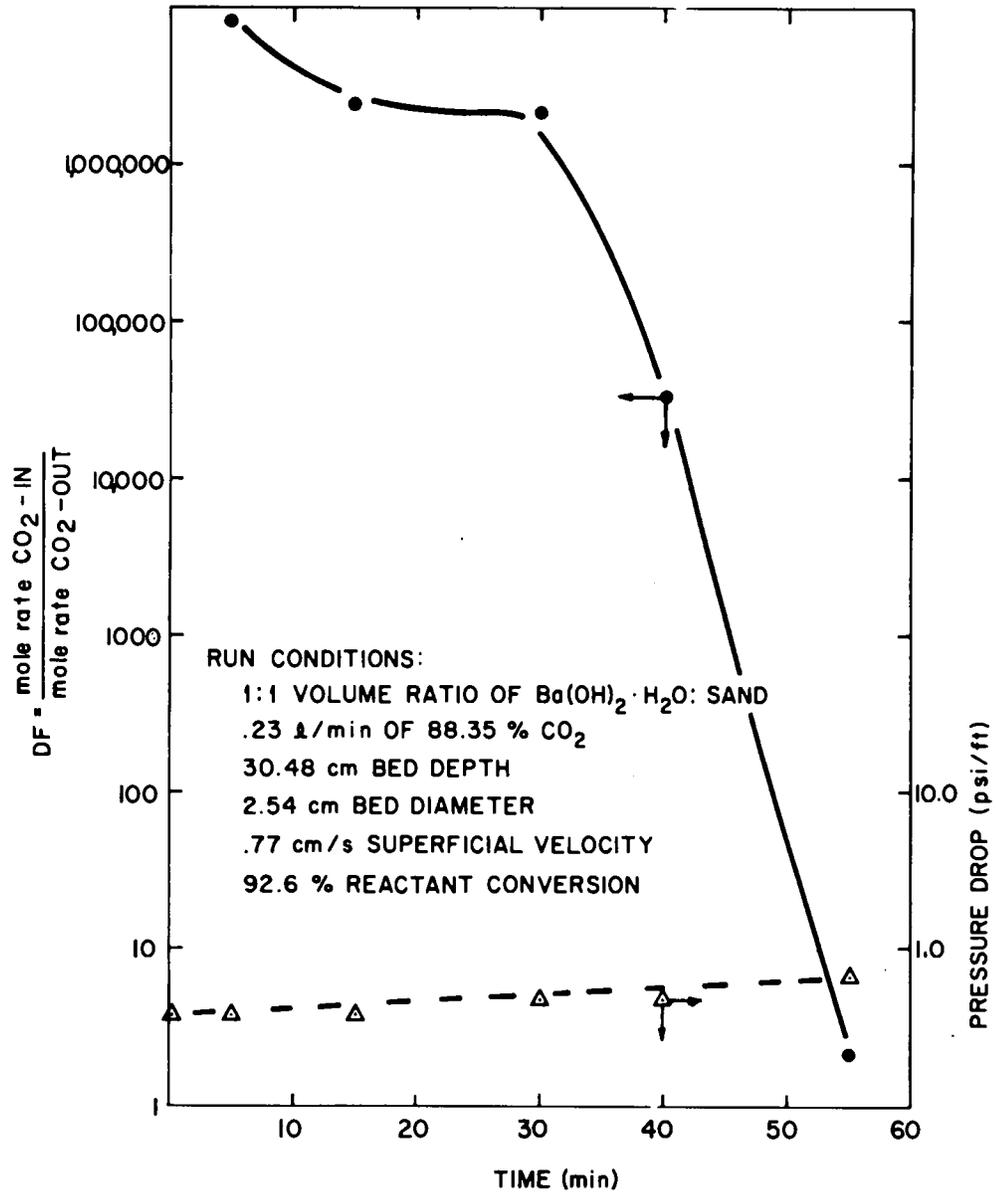


Fig. 5. Reaction of $\text{Ba}(\text{OH})_2 \cdot \text{H}_2\text{O}$ with humidified 88% CO_2 .

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 krypton 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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