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OAK RIDGE NATIONAL LABORATORY
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ORNL/MIT-256

DATE: September 23, 1977

SUBJECT: Analysis of Lime-Slurry Stirred Tank Carbonation Reactor

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ABSTRACT

Gas residence time distributions were determined for a stirred tank carbonation reactor. Empirical correlations for the first and second moments of the residence time distribution (RTD) curves as functions of flow rates and impeller speeds were obtained. Decontamination factors for ^{85}Kr were measured.

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Printed in the United States of America. Available from
National Technical Information Service
U.S. Department of Commerce
5285 Port Royal Road, Springfield, Virginia 22161
Price: Printed Copy \$4.50; Microfiche \$3.00

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1. SUMMARY

Stack gases from nuclear fuel reprocessing plants contain ^{14}C (as $^{14}\text{CO}_2$) and ^{85}Kr , both of which must be removed due to their radiation hazards. The ^{14}C removal system was simulated by a stirred tank containing a calcium hydroxide slurry through which gas containing CO_2 was bubbled. The gas residence time distributions (RTDs) were determined as functions of gas flow rates and impeller speeds for inlet gas compositions of air with about 300 ppm CO_2 and a mixture of 80% CO_2 and 20% O_2 . The carbonation reactor should permit ^{85}Kr to pass through to a subsequent removal system. Mean residence times were found to be inversely proportional to gas flow rates, slightly proportional to impeller speeds for air, and poorly characterized by data for high carbon dioxide feed. Decontamination factors, which are a measure of ^{85}Kr adsorption by the lime slurry, indicated that only a small amount of krypton was removed irreversibly by the slurry.

2. INTRODUCTION

2.1 Background

Carbon-14 and krypton-85 are radioactive components of off-gas streams from nuclear reactor fuel reprocessing plants. Moderate levels of beta and gamma radiation from ^{85}Kr can damage living cells; however, ^{14}C presents a more serious problem as it can become incorporated into genetic material through the food cycle and cause mutations.

When the KALC (Krypton Adsorption in Liquid Carbon Dioxide) system was designed to remove ^{85}Kr from off-gases, the dangers of ^{14}C were not fully recognized (1). Consequently, the carbon dioxide removal unit was later added downstream of the krypton removal unit. The off-gases contain large amounts of CO_2 ; therefore removal of CO_2 before krypton would reduce the amount of the process stream, thus reducing the size and cost of the krypton removal unit. The FASTER (Fluorocarbon Adsorption System for the Treatment of Effluent from Reprocessors) system removes carbon dioxide first by precipitating it as calcium carbonate (1).

The reaction for removal of carbon dioxide from effluent gas proceeds:

The overall reaction is

The high insolubility of calcium carbonate in water drives reaction (4) towards complete conversion. The kinetics and mechanism of these reactions are discussed elsewhere (2, 3, 4, 8, 9).

2.2 Objectives

The objectives were to determine RTDs for gases containing CO_2 flowing through lime-slurry, stirred-tank reactors and to measure decontamination factors for ^{85}Kr in the lime-slurry reactor system.

3. RESIDENCE TIME DISTRIBUTIONS

3.1 Apparatus and Procedure

The apparatus shown in Fig. 1 provides contact between the calcium hydroxide slurry and incoming gases, permits control of the gas flow rates and impeller speeds, and provides a tracer injection and detection system. A one-molal slurry of calcium hydroxide in water was charged to the 17-liter reactor vessel. The slurry was added to the reactor in a batch mode rather than continuous mode for ease of operation. A six straight-blade disc turbine stirred the slurry. Impeller speed was measured to $\pm 5\%$ accuracy using a stroboscope. Gas entered the tank through a four-armed sparger located directly under the impeller disc. Inlet gas flow rates were measured to an accuracy of $\pm 5\%$ using a rotameter and pressure gauge.

Krypton-85 tracer was introduced to the system as an imperfect pulse. To standardize the amount injected and to avoid contamination of the laboratory, the ^{85}Kr was first loaded into a storage loop and then discharged to the feed line leading to the reactor. After leaving the slurry, the gases passed through a knockout bottle to trap any entrained slurry and were sent to a detector system. A bypass line was used for isolating the reactor RTDs by allowing the gas to flow to the detector without passing through the reactor. The detector then produced plots of the exit age distributions on the chart recorder. The slurry pH was monitored continuously, and when it dropped below 12, indicating Ca(OH)_2 exhaustion, the solution was replaced. Table 1 summarizes the ranges of parameters investigated.

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EXPERIMENTAL APPARATUS

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Table 1. Parameter Ranges Investigated

Feed Gas:	air (300 ppm CO ₂) and 80% CO ₂ -20% O ₂
Impeller Speed:	0, 165, 325, 650, 975 rpm
Gas Flow rate:	5, 10, 20, 30 liter/min

3.2 Data Analysis

The exit age distributions from the chart recorder were analyzed using a PDP-11 computer after RTD curves were digitized using a pressure-sensitive digitizer. Mean residence times and variances corresponding to the reactor were then determined by subtracting $\bar{t}$ and σ^2 of the bypass run from $\bar{t}$ and σ^2 of the runs through the reactor (see Table 2) (5, 6, 7, 11).

Table 2. Moments in RTD Studies

$$0^{\text{th}} \text{ moment} = m_0 = \int_0^\infty C \, dt$$

$$1^{\text{st}} \text{ moment} = m_1 = \int_0^\infty Ct \, dt$$

$$2^{\text{nd}} \text{ moment} = m_2 = \int_0^\infty Ct^2 \, dt$$

$$\text{mean residence time} = \bar{t} = \frac{m_1}{m_0}$$

$$\text{variance} = \sigma^2 = \frac{m_2}{m_0}$$

$$\text{mean residence time of the reactor} = \bar{t}_{\text{overall}} - \bar{t}_{\text{bypass}}$$

$$\text{variance due to the reactor} = \sigma_{\text{overall}}^2 - \sigma_{\text{bypass}}^2$$

If excessive tailing is present in RTD curves, the pseudo moments can be used:

$$\text{pseudo - } 0^{\text{th}} \text{ moment} = m'_0 = \int_0^\infty C e^{-t/\bar{t}} \, dt$$

$$\text{pseudo - } 1^{\text{st}} \text{ moment} = m'_1 = \int_0^\infty Ct e^{-t/\bar{t}} \, dt$$

$$\text{pseudo - } 2^{\text{nd}} \text{ moment} = m'_2 = \int_0^\infty Ct^2 e^{-t/\bar{t}} \, dt$$

3.3 RTD Results and Discussion

3.3.1 Air

The effects of impeller speed on mean residence times and standard deviations are shown in Figs. 2 and 3. Within this range of speeds, mean residence time for the two higher gas flow rates exhibit a slight linear increase with impeller speed. Mean residence times for the lower flow rates increased to a maximum after which they decreased. Standard deviations of the RTD curves versus rpm behaved similarly. The spread of the RTD curve increased with impeller speed at all gas flow rates above the critical impeller speed.

The effect of flow rate on RTD was much greater than that of agitator speed. Plots of reciprocal mean residence times and reciprocal standard deviations versus gas flow rates were linear for fixed impeller speed (see Figs. 4 and 5). Mean residence times and standard deviations decreased with increasing gas flow rates. Low flow rates produced long residence times and large spreads in exit age distributions on which agitator speeds above critical flooding speed had little effect.

3.3.2 80% CO₂

The 80% CO₂ feed gas produced RTD curves similar to that of the air. At low flow rates mean residence times and standard deviations increased with impeller speed (see Figs. 6 and 7). However, at higher impeller speeds this trend was no longer apparent. The gas bubbles initially containing 80% carbon dioxide shrank to approximately 20% of their original volume as they passed through the slurry. As smaller bubbles have lower terminal velocities, residence times for carbon dioxide feed gas would be longer than those for air. Thus, it is possible that higher impeller speeds could have increased the rise rate of the bubbles by bulk motion. The increase in the spread of the residence time distribution curve with impeller speed also supports this theory. However, at high impeller speeds there were no apparent trends. The effects of gas flow rates on RTD curves are shown in Figs. 8 and 9. Similar to air, increasing flow rates decreased mean residence times and dispersion, but to a smaller extent. This can be attributed to shrinkage in gas volumes due to CO₂ absorption.

3.3.3 Empirical Correlations

Plots of residence times and standard deviations as functions of inlet gas flow rates and impeller speeds suggest the possibility of an empirical correlation between them. The equation

$$\frac{1}{X} = a \frac{(\log \text{ mean } Q)^m}{(\text{rpm})^n}$$

was found to fit the data well, where Q is the gas flow rate through the reactor, rpm is the impeller speed in revolutions/min, and X is either

- ▽ 5
○ 10
◇ 20
□ 30

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MEAN GAS RESIDENCE TIME
VERSUS IMPELLER SPEED - AIR

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FIG.
2

liters/min

- ▽ 5
- 10
- ◇ 20
- 30

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STANDARD DEVIATION VERSUS
IMPELLER SPEED - AIR

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FIG.
3

liter/min

▽ 5
○ 10
◇ 20

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MEAN GAS RESIDENCE TIME VS
IMPELLER SPEED - 80% CO₂

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FIG.

6

mean gas residence time or standard deviation of the residence time distribution. Table 3 provides values for the empirical constants a , m , and n .

The observed variations in dependence on rpm and Q suggest that feed gas composition may be included in the correlation (besides its implicit presence in log mean Q) for a better fit to the data. The correlation applies only to the system studied but can be generalized by introducing dimensionless groups.

Table 3. Values of Empirical Constants

X	air			80% CO ₂ -20% O ₂		
	a	m	n	a	m	n
t_m	0.079	0.94	0.19	0.052	1.128	0.228
σ	0.12	1.034	0.209	0.075	1.222	0.247

4. DECONTAMINATION FACTORS

4.1 Apparatus and Procedure

The apparatus used for measuring decontamination factors was the same as described in Sect. 3.1, but the experimental procedure was different. In this case, the feed gas contained a small but fixed amount of ⁸⁵Kr and was fed to the system until steady state was reached. The gas and impeller were then shut off and the number of counts from the detector monitored. As the system approached atmospheric pressure, the beta detector reading became constant. The ⁸⁵Kr radioactivity was noted at this "static" level. Runs were made through the reactor and bypass loop using gas compositions of 3% CO₂ and 94% CO₂.

4.2 Procedure for Data Analysis

The decontamination factor (DF) for krypton was defined as the ratio of moles of ⁸⁵Kr entering to moles of ⁸⁵Kr leaving the gas flowing through the reactor. For a fixed concentration of ⁸⁵Kr in the feed gas the DF would be

$$DF = \frac{\text{static bypass counts/min}}{\text{static counts/min}} \left(\frac{1}{1 - V_{CO_2}} \right)$$

where V_{CO_2} is the volume fraction of CO₂ in inlet gas.

4.3 Results and Discussion

A decontamination factor of 1.00 means that no krypton is retained in the slurry after the solubility limit is reached. The concentration gradient driving force would be largest as gas is first introduced into the reactor and decreases with time as saturation is approached. Therefore, the radioactivity of the effluent should increase monotonically towards a steady state saturation value.

The carbonation reaction is very fast; hence, if calcium carbonate precipitation irreversibly removes krypton from the slurry, a loss of krypton at a constant rate would occur. After saturation of the liquid, this would be the only probable explanation of krypton removal.

Krypton-85 may be removed from the gas mixture by: (a) adsorption by the plexiglas walls of the reactor vessel (10), (b) adsorption by the solids present and being formed by the carbonation reaction in the slurry, and (c) dissolution into the liquid. Once quasi-steady state is reached, i.e., (a) and (c) are saturated, the only mode of ^{85}Kr removal could then be by (b).

4.3.1 3% CO_2

The DF values using 3% CO_2 ranged from 1.001 to 1.006. The average number of counts per minute for the runs are shown in Table 4. The decontamination factor values obtained in this case were within 0.3% of the mean and the reproducibility of results was excellent. The mean decontamination factor of 1.003 for the 3% CO_2 gas means that 0.3% of the inlet krypton is lost by adsorption on CaCO_3 , the corresponding mole fraction being 9×10^{-5} or 78 ppm by weight.

Table 4. Detector Static Counts for Decontamination Factor

Run	Feed Gas (% CO_2)	Average Counts Per Minute With Bypass	Average Counts Per Minute Existing Reactor	Calculated Static DF
1	3	116,000	119,055	1.003
2	3	116,000	118,740	1.006
3	3	116,000	119,370	1.001
4	93	618,591	2,955,919 ^a	2.99
5	93	1,580 ^b	255,944 ^{a,b}	0.1

^aSteady state not achieved.

^bEnergy threshold on beta detector was increased which resulted in lower counts.

4.3.2 93% CO₂

The DF values in this case, 0.1 and 2.99, were inconsistent, and are shown in Table 4. The concentration of krypton in the exit gas was 1/0.07, or 14 times krypton concentration in the feed. The reduced flow rate to the beta detector increased the residence time, which made the number of counts per minute 14 times higher for the gas passing through the reactor as compared to the bypass runs.

5. CONCLUSIONS

5.1 Residence Time Distributions

1. Means and variances of the RTD curves were inversely proportional to the gas flow rates at all impeller speeds.
2. Impeller speed had little effect on RTD curves for most flow rates.
3. RTD measurements were reproducible for air, but not for 80% CO₂.

5.2 Decontamination Factors

1. Krypton-85 adsorbs on CaCO₃ in increasing quantities when the CO₂ content of the feed gases is increased.
2. DF measurements for 3% CO₂ gas were reproducible but were not reproducible for 93% CO₂ gas.
3. The "static method" is not accurate in measuring DF values.

6. RECOMMENDATIONS

1. The tracer gas should have a composition similar to that of the feed to avoid concentration problems.
2. Lengths of the transmission lines should be shortened to minimize RTD complications.
3. Flow rates to the detector should be monitored.
4. For high CO₂-containing feeds: (a) continuous operation would eliminate reactor shutdowns and startups, (b) cooling should be provided to eliminate any thermal effects.

5. Additional data should be obtained for decontamination factors for high-CO₂ feed streams.

7. LOCATION OF DATA

Original data are contained in databook A-7557-G, pp. 1-60 on file at the MIT School of Chemical Engineering Practice, Bldg. 3001, ORNL.

8. ACKNOWLEDGMENTS

We would like to thank our consultants, D.W. Holladay and G.L. Haag, for their advice and assistance in all phases of this project. In addition, J.M. Begovich's advice concerning computer-aided analysis of our data and Rick Yates' help with the apparatus were invaluable.

9. APPENDIX

9.1 Sample Calculations

9.1.1 Expected Life of the Slurry

Sixteen and one half liters of 1.0-M solution of Ca(OH)_2 and H_2O has 16.5 moles of Ca(OH)_2 :

Therefore $22.4 \times 16.5 = 370$ liters of CO_2 will be required to exhaust all Ca(OH)_2 , which is $370(1/0.8) = 463$ liters of 80% CO_2 .

<u>Inlet Flow Rate 80% CO_2 (liter/min)</u>	<u>Time to Exhaust Ca(OH)_2 (min)</u>
5	92.6
10	46.3
20	23.15
30	15.44

9.1.2 Decontamination Factor

The decontamination factor is defined by

$$\begin{aligned}
 \text{DF} &= \frac{\text{moles Kr in (feed)}}{\text{moles Kr out (effluent)}} \\
 &= \frac{\text{counts/min/mole feed gas}}{\text{counts/min/mole effluent gas}} \left[\frac{1 \text{ mole feed gas}}{(1 - V_{\text{CO}_2}) \text{ moles effluent gas}} \right] \\
 &= \frac{\text{cpm (static bypass)}}{\text{cpm (static run)}} \frac{1}{1 - V_{\text{CO}_2}}
 \end{aligned}$$

For $V_{\text{CO}_2} = 0.03$,

$$\text{DF} = 1.031 \frac{\text{cpm (static bypass)}}{\text{cpm (static run)}}$$

and for $V_{CO_2} = 0.93$,

$$DF = 14.29 \frac{\text{cpm (static bypass)}}{\text{cpm (static run)}}$$

9.1.3 Amount of ^{85}Kr Retained by CaCO_3

Consider $DF = 1.003$ for 3% CO_2 feed with 0.09% ^{85}Kr . For an inlet flow rate of M moles/min the rate of CaCO_3 formation will be 0.03 M moles/min. Rate of ^{85}Kr retention by CaCO_3 will then be $0.003 \times 0.0009 M$ moles/min. Therefore,

$$(^{85}\text{Kr})_{\text{mole fraction}} = \frac{0.003 \times 0.0009 M}{0.03 M + 0.003 \times 0.0009 M} = 9 \times 10^{-5}$$

$$(^{85}\text{Kr})_{\text{weight fraction}} = 78 \text{ ppm}$$

9.2 Nomenclature

a	empirical coefficient
cpm	counts per minute
C	E , exit age distribution
DF	decontamination factor
m	empirical exponent
m_0, m_1, m_2	zeroth, first, and second moments of the RTD curve
n	empirical exponent
Q	gas flow rate, liters/min
RTD	residence time distribution
rpm	agitator revolutions per minute
$\bar{t}$	mean residence time, sec
V_{CO_2}	volume fraction of CO_2 in feed gas
x	dependent variable: $\bar{t}$ or σ
σ	standard deviation, sec
$\Delta\sigma^2$	variance, sec^2

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