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HR. 1985
ORNL/TM-5757

**Experiments with a Lime Slurry in a
Stirred Tank for the Fixation of
Carbon-14-Contaminated CO₂ from
Simulated HTGR Fuel Reprocessing Off-Gas**

D. W. Holladay

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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 \$6.50; Microfiche \$3.00

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ORNL/TM-5757
Dist. Category UC-77

Contract No. W-7405-eng-26

CHEMICAL TECHNOLOGY DIVISION

HTGR FUEL RECYCLE PROGRAM (189a OH045)

In-Plant Waste Treatment - Task 600

↓ EXPERIMENTS WITH A LIME SLURRY IN A STIRRED TANK FOR THE
FIXATION OF CARBON-14-CONTAMINATED CO₂ FROM SIMULATED
HTGR FUEL REPROCESSING OFF-GAS

D. W. Holladay

Date Published: March 1978

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EXPERIMENTS WITH A LIME SLURRY IN A STIRRED TANK FOR THE
FIXATION OF CARBON-14 CONTAMINATED CO₂ FROM SIMULATED
HTGR FUEL REPROCESSING OFF-GAS.

D. W. Holladay

ABSTRACT

The fixation of CO₂ with a lime slurry in a stirred tank reactor appears to be feasible. The rate of reaction is fast, and virtually complete removal of CO₂ can be attained. At a gas residence time of <1 min, the decontamination factor (DF) is >100 in a single stage reactor for CO₂ concentrations ranging from 5 to 100%. It has been determined that two-stage contacting sequences which result in a cumulative DF >10⁴ are feasible. The reaction rate is constant up to 90% utilization of the lime and then rapidly decreases, as does the pH for the remainder of the reaction. The reaction appears to be liquid-phase-controlled, and the overall gas-side mass transfer coefficient ($K_G a$) increases with impeller speed and gas flow rate, ranging from 0.4×10^{-6} to 6×10^{-6} g-moles of CO₂ per (cm³-sec-atm). The reaction rate data are also correlated by a model of mass transfer accompanied by a fast pseudo first-order chemical reaction from which good agreement of calculated and predicted interfacial area is obtained. It was noted that temperature (21 to 46°C) and lime concentration (0.5 to 1.5 M) had very little effect on mass transfer rate and DF. The settling rate of the CaCO₃ product increased significantly with impeller speed and temperature and decreased with gas flow rate. Scale-up calculations indicate that reasonably sized equipment would provide adequate removal of CO₂ for a full-scale reprocessing plant.

1. INTRODUCTION

For many years it has been assumed that the ¹⁴C contamination of carbon compounds contained in the nuclear fuel reprocessing off-gases was so insignificant that discharge of such gaseous compounds in stack gases would be permitted. This exhaustion through off-gas stacks would occur primarily at fuel reprocessing plants.^{1,2} However, recent environmental studies,³ which included the ingestion pathway,⁴ have resulted in the

tentative conclusion that the long-range effects of ^{14}C discharge to the atmosphere could be quite significant; for example, the ^{14}C cumulative effect (half-life of 5730 years) may be a more serious hazard than the effects of ^{85}Kr (half-life of 10.70 years).

Carbon-14 is produced during the operation of nuclear power reactors as an activation product by the reaction between neutrons and the minor components ^{14}N , ^{13}C , and ^{17}O . Although the ^{14}C could be present in methane and other organic gases, it is assumed here that the bulk of the ^{14}C will appear during reprocessing as carbon in the carbon dioxide produced by the combustion of the HTGR graphite fuel blocks. Croff has written a thorough review of the options available for packaging and long-term burial of the carbonate produced from the fixation of the CO_2 .⁵ This article should be consulted for information relative to prediction with the ORIGEN code of ^{14}C production as a function of hypothesized ^{14}N and ^{13}C levels in the fuel elements, consideration of various packaging and burial options, transportation of the radioactive product, and classification of the activity levels of the product.

Also utilizing the ORIGEN code, Davis⁶ has recently updated the calculated quantities of ^{14}C that may be formed in the fuel and core structural materials of HTGRs. According to these calculations, the ^{14}C content of HTGR fuel entering a fuel reprocessing plant which processes 450 metric tons of heavy metal (MTHM) was estimated to consist of 5600 Ci/year produced by 30 ppm nitrogen in the graphite, 530 Ci/year produced by 25 ppm nitrogen in the fuel, and 1700 Ci/year produced solely by the ^{13}C in the graphite. The $^{14}\text{CO}_2$ produced in a reprocessing plant of this size would be included with more than 50,000 kg of normal CO_2 per day.

Because it may be eventually required that this large quantity of CO_2 be processed in order to dispose of all of the $^{14}\text{CO}_2$ produced in HTGR fuel reprocessing off-gas, studies were conducted to determine an efficient classical engineering process for CO_2 fixation.

In order to clarify the options available for the kinds of processes that are candidates for the fixation of the CO_2 , a fairly extensive literature survey was conducted to determine the extractive processes most used in industry for the isolation of CO_2 . These CO_2 removal processes may be divided into three broad categories:⁷ (1) physical absorption - absorption in water, absorption in methanol, fluorocarbon solvent process, etc.; (2) absorption with chemical reaction - absorption in alkaline liquids such as ethanolamines, caustic soda, hot potassium carbonate, etc.; (3) removal by use of molecular sieves.

The method chosen for removal of CO_2 in a large-scale industrial operation, at least until the early 1970s, would have been either the Giammarco-Vetrocoke process (hot potassium carbonate with an arsenious oxide catalyst) or some combination of ethanolamine followed by a caustic scrub. Such procedures have been used to process as much as 9.5×10^6 scfh of gas containing from 16.5% CO_2 to as little as 10 ppm CO_2 (ppm $\times 10^{-4}$ is equal to mole %).^{8,9} However, due to the industrial requirement for an absorbent recycle capability, none of the wet processes provide an absorbent that reacts with CO_2 to yield a stable compound suitable for long-term storage.

The utilization of molecular sieves for CO_2 removal has experienced rapid growth in the seventies to the extent that banks of molecular sieve columns are now being employed industrially for the large-scale purification

of process gas streams. Linde type-A (4A and 5A) molecular sieves have been used in packed towers to sweeten 1.3×10^5 scfd of natural gas containing H_2S in the range of 0.47 to 0.57% and CO_2 in the range of 6.93 to 10%.¹⁰ The Proceedings of the Third International Conference on Molecular Sieves provides a list of references which are representative of the processes known to be in commercial use at that time.¹¹ Additional publications relating to molecular sieve technology include a general review of the field,¹² a description of natural gas purification by removal of CO_2 , water vapor, and sulfur compounds using 4A, 5A, and 13X sieves,¹³ and a description of a process in which 13X sieves were used to remove CO_2 and water vapor from air in a single absorption step prior to the liquefaction of air.¹⁴

If a large quantity of gas containing CO_2 as an undesirable component is the stream which is to be processed for CO_2 removal, without regard to the ultimate disposal of the CO_2 , then the method chosen would be one of the wet tower stripping processes or the application of molecular sieve columns. However, if the CO_2 must be captured for permanent storage (likely only if the carbon is radioactive), it is necessary to develop other contacting schemes. This report presents the results of bench-scale studies conducted to show the feasibility of using a slaked-lime slurry in an agitated contactor for direct fixation of CO_2 from CO_2 -rich gas streams. Based on an analysis of the acceptable kinetics of the gas-lime slurry reaction, scale-up proposals are made concerning the initial concepts of the size and type of contacting equipment which should be studied in the future.

Section 9, Nomenclature, is included for the reader's convenience. Terms used in this report are listed and defined.

2. MASS TRANSFER: THEORY OF GAS-LIQUID ABSORPTION ACCOMPANIED BY CHEMICAL REACTION

2.1 General Literature and Theory

2.1.1 Background

After many years of development, Higbie, Danckwerts, and Sharma¹⁵⁻¹⁷ (among others) have proposed several simplified expressions to describe mass transfer rates when gas absorption is accompanied by chemical reaction. Relationships are available that describe conditions where the chemical reactions may be first, second, or m th order, reversible or irreversible, slow or fast. The simplest explanation for the necessity of these expressions is found in the realization that during a typical physical absorption, the true liquid- and gas-side mass transfer coefficients, k_L and k_G , can be safely assumed to be fairly constant throughout the contacting equipment, with the local rate variations being primarily due to driving force changes. However, for absorption with chemical reaction, the mass transfer coefficient may itself be a function of the local variations in the concentration of the reactants. This dependency of the mass transfer coefficient on reactant concentration leads to an "enhancement" of mass transfer when there is chemical reaction between a constituent of the liquid and the gas being absorbed. That is, for equal hydrodynamic conditions, the mass transfer rate for simple physical absorption is normally several times slower than for mass transfer in the presence of chemical reaction.

2.1.2 Simple first-order irreversible reaction

The mass transfer coefficient is normally represented by an expression similar to $R/(C^* - C^0)$ only for physical absorption. It is informative to consider one or two cases of mass transfer with varying chemical reactions. For absorption accompanied by simple first-order irreversible reaction, the simplified rate expression is:

$$R = k_L C^* [1 + Dk_1/(k_L)^2]^{0.5} \quad (1)$$

But if $\sqrt{M} \gg 1$, where $M = Dk_1/(k_L)^2$, then

$$R = k_L C^* (M)^{0.5}, \quad (2)$$

or

$$R = C^* (Dk_1)^{0.5}, \quad (3)$$

where

R = rate of absorption, g-moles/(cm²-sec);

k_L = true liquid-side mass transfer coefficient, cm/sec;

C^* = equilibrium concentration of gas being absorbed, g-moles/cm³;

D = diffusivity of dissolved gas reacting in liquid phase,
cm²/sec; and

k_1 = first-order reaction rate constant, sec⁻¹.

2.1.3 Fast pseudo-first-order reaction

As a second example, the concentration of solution anion (the reactant), [B], which reacts with the gas in the neighborhood of the surface may differ very slightly from that in the bulk of the solution under appropriate conditions; hence, the dissolved gas is said to undergo a pseudo-first-order reaction. The Danckwerts model then gives the specific rate of

absorption as:

$$R = C^* (Dk_2[B] + k_L^2)^{0.5}, \quad (4)$$

where

k_2 = second-order reaction rate constant, liters/(g-mole-sec).

If $Dk_2[B] \gg k_L^2$, we have

$$R = C^* (Dk_2[B])^{0.5}. \quad (5)$$

The specific rate of absorption is then independent of the hydrodynamic characteristics and becomes a unique function of the physicochemical properties. Two chemical systems that are often assumed to display pseudo-first-order reactions are the absorption of lean CO_2 in aqueous solutions of either sodium hydroxide or monoethanolamine.

2.1.4 Applications of the fast pseudo-first-order reaction theory

An obvious benefit of an analytical expression which can adequately describe the mass transfer rate for absorption with chemical reaction is that it allows for acceptable theoretical calculations of tower heights (T_H) required for product conversions when overall mass transfer coefficients are unavailable. If an accurate expression for the rate of gas absorption with chemical reaction can be written, then the differential equation describing the mass transfer operation conforming to Eq. (5) can be integrated to provide very reasonable predictions of practical operating tower dimensions. For example, for gas absorption accompanied by a pseudo-first-order reaction in a packed tower contactor, the tower height is predicted by:

$$T_H = \frac{U_L}{Za} \int_{\text{out}}^{\text{in}} \frac{dB_h}{C^* (Dk_2[B_h])^{0.5}}, \quad (6)$$

where

U_L = superficial liquid velocity, cm/sec;

Z = moles of solvent [B] reacting per mole of gas;

a = effective interfacial area, cm^2/cm^3 ; and

B_h = molar concentration of reactant at any height in the tower, moles/ cm^3 .

The theory of absorption accompanied by fast pseudo-first-order reaction is also frequently utilized for determining the effective interfacial area under various hydrodynamic conditions. However, in the absorption of CO_2 from dilute CO_2 in air mixtures, there is often significant gas-side resistance. The relationship for the mass transfer coefficient is then:

$$\frac{1}{K_G a} = \frac{1}{k_G a} + \frac{1}{H k_{LR} a}, \quad (7)$$

where

$K_G a$ = overall gas-side mass transfer coefficient, g-mole/($\text{cm}^3\text{-sec-atm}$);

$k_G a$ = gas-side mass transfer coefficient, g-mole/($\text{cm}^3\text{-sec-atm}$);

H = solubility of solute gas in solution, g-mole/($\text{cm}^3\text{-atm}$); and

k_{LR} = mass transfer coefficient with chemical reaction, cm/sec.

If the model, Eq. (5), for the pseudo-first-order reaction is used, then the expression for k_{LR} can be derived as follows:

$$R = C^* (Dk_2[B])^{0.5} ,$$

also

$$R = k_{LR} C^* ,$$

$$k_{LR} C^* = C^* (Dk_2[B])^{0.5} ,$$

and

$$k_{LR} = (Dk_2[B])^{0.5} . \quad (8)$$

A bench-scale experiment is necessary to obtain $K_G a$, and $k_G a$ must either be measured or obtained from the literature. The solubility of the gas in the ionic solution can be estimated accurately from:¹⁵

$$\log \frac{H}{H_w} = - K_s I , \quad (9)$$

where

H_w = solubility in water, g-mole/(cm³-atm);

I = ionic strength; and

$K_s = i_+ + i_- + i_G$, contributions due to cation, anion, and gas respectively.

When the values of H , k_{LR} , $K_G a$, and $k_G a$ are used in Eq. (7), the value of a may be determined.

2.2 Relevant Literature for the Carbon Dioxide-Calcium Hydroxide Reaction

After a fairly comprehensive literature search, only one study was located which treated specifically the carbonation of Ca(OH)_2 in an agitated contactor.¹⁸ This study, published in three parts, was directed

toward describing the mechanism of chemical reaction between the CO_2 and the Ca(OH)_2 during the absorption process. The general model assumed equality between Davidson's predictions for the mass flux across a spherical gas bubble and Danckwert's expression for the mass flux corresponding to absorption in the presence of a fast first-order chemical reaction. Since they were input parameters for the model, it was necessary to determine bubble rise velocities (12 to 22 cm/sec), the Sauter mean bubble diameter (0.2 to 0.5 cm), interfacial area (dependent on operating conditions), and mean bubble residence times (1 to 5 sec).

Experimental runs for the CO_2 - Ca(OH)_2 reaction were conducted for two agitated contactors (8.5-in. ID and 15.25-in. ID) using only one feed gas composition, which was 10% CO_2 and 90% air. The total gas flow rate for the 8.5-in. ID contactor varied from 5 to 25 liters/min, with impeller speeds of 1500 and 2500 rpm. The chemical analysis method used was the standard technique for titrating hydroxyl and carbonate ions, as described in Sect. 4.1. However, a greater uncertainty in the data was produced by using this method instead of determining CO_2 concentrations in the influent and effluent streams by gas chromatography. Scatter in Morris's¹⁸ fractional conversion data amounted to as much as 10%, so that there was uncertainty in the DF values by as much as a factor of 2.

In general, there was excellent agreement between our results for the fractional conversions obtained for similar total gas flow rates (and similar gas compositions) and those of Morris. However, the specific results were of little value to the overall scope of our work because our studies required information concerning the reduction of CO_2 from streams

with a concentration of 90% CO_2 to less than 1% in the effluent. However, key operational characteristics of the CO_2 - $\text{Ca}(\text{OH})_2$ reaction described during Morris's work served as confirmation to the rather exceptional observations resulting from our own studies. Among these conclusions was the observation that the fixation of CO_2 with $\text{Ca}(\text{OH})_2$ consisted of two regimes: (1) the initial regime that existed for about eight-tenths of the total reaction time, during which the mass transfer rate and the soluble hydroxyl ion level were constant; and (2) the final regime which was a period of decreasing rate where the mass transfer control was a complex transient function of hydroxyl concentration. The consideration of the phase location of mass transfer resistance is discussed in further detail in Sect. 5.

2.3 Kinetics and Thermodynamics of the Carbon Dioxide-Calcium Hydroxide Reaction

The reaction between CO_2 and $\text{Ca}(\text{OH})_2$ is:

The heat of reaction is ~ -25 kcal/g-mole; it is irreversible under normal conditions and requires a temperature of 700 to 800°C before calcination occurs. The reaction is assumed to occur by the following steps:

The first equation, Eq. (11), is the rate-controlling step and is second order in the forward direction. The value of the second-order rate

constant, k_{OH} , at infinite dilution can be estimated by:

$$\log k_{OH} = 13.635 - \frac{2895}{T} \quad (13)$$

Danckwerts¹⁵ has cautioned that the value for k_{OH} is strongly affected not only by temperature, but also by ionic strength and solution composition. The rate constant, k_{OH} , at 20°C has been shown to differ by a factor of 4 (5000 to 20,000) for a variation in ionic strength from 0 to 5.

2.4 A Question of Mass Transfer Control

2.4.1 Background literature and theory

For those mass transfer operations involving absorption of CO_2 into solutions in which first- and second-order reactions can occur, there continues to be considerable controversy over the location of the major mass transfer resistance. One of the first studies describing the absorption of CO_2 by an aqueous NaOH solution was the packed column work of Tope and Dodge.¹⁹ The absorption of CO_2 by NaOH was studied using air containing from 2 to 5% CO_2 as the feed to a 6-in. ID by 36-in. column packed with 1/2-in. carbon Raschig rings. When the log-mean pressure driving force was used in the calculation, the variation of gas flow rate over the operational range did not affect the $K_G a$ for sorption of CO_2 into 2 N NaOH. This $K_G a$ value was found to vary with the liquid phase (NaOH) flow rates. Thus, it was concluded that very little of the mass transfer resistance was in the gas phase. However, it was noted that if the NaOH concentration could be increased sufficiently to cause

reaction at the interface, then the gas film resistance would constitute the only resistance to mass transfer.

In a subsequent study of CO_2 absorption from less concentrated streams,²⁰ the absorption of CO_2 from air was investigated to elucidate an operation which has long demanded considerable industrial attention. The CO_2 influent concentration of ~ 300 ppm was reduced to an effluent concentration of 1 to 40 ppm, depending on the Q_L/Q_G ratio. For this study, $K_G a$ was found to vary as the 0.35 power of the gas flow rate, 0.20 power of the liquor flow rate, and the 0.5 power of the pressure. Thus for the processing of air, there obviously was appreciable gas-phase resistance to mass transfer. It was speculated that for higher liquid flow rates, the increase in the mass transfer coefficient could be partly attributed to an increase in wetted interfacial area. For the Tepe and Dodge studies,¹⁹ it is obvious that a decrease in the CO_2 concentration in feeds from 5 to 0.03% resulted in a considerable shift of mass transfer resistance from the liquid to the gas phase.

Danckwerts^{15,16,21} has addressed the question of mass transfer control for the absorption of CO_2 by NaOH using various types of contacting equipment. Under certain specific conditions (usually in a packed tower), the dissolved gas undergoes a pseudo-first-order reaction; hence, the rate is given, as previously shown, by Eq. (5):

$$R_a = aC^* (Dk_2[B])^{0.5} \quad (5)$$

Danckwerts has suggested that in the case of mass transfer of CO_2 from air to caustic alkali solutions, his model would have predicted that the absorption process would be liquid-film-controlled and, thus, would be

described by Eq. (5). However, the work of Spector and Dodge (above) had shown clearly that there is considerably gas-phase control of CO_2 sorption from air by NaOH in packed towers. Furthermore, it had been concluded by Greenwood and Pearce²² that the sorption of CO_2 from air by NaOH was a completely gas-film-controlled process.

Additional complications arise when the studies of Morris¹⁸ are considered. Although the total slurry hydroxyl ion concentration obviously must decrease as the Ca(OH)_2 dissolves and reacts with CO_2 , the soluble hydroxyl ion concentration is always constant during 80% of the reaction period. It is therefore practically impossible to investigate the rate dependence, as in Eq. (5), on the hydroxyl ion concentration in the slaked-lime slurry. Thus, the lime slurry was replaced by a NaOH solution in a stirred contactor. The absorption of CO_2 was studied for 0.1 to 2 N NaOH concentrations and inlet CO_2 levels ranging from 15 to 60%. The rate over these widely varying conditions was found to be zero order for hydroxyl concentration, and it was concluded that the mass transfer control was somewhere other than the liquid phase. It has been suggested that the effect on the rate of a decrease in diffusivity with an increase in viscosity (due to the presence of Na_2CO_3) may not be correctly observed due to improper temperature control. However, Morris's studies were made with the temperature of the dispersion carefully controlled to within 0.5°C , so that any change in viscosity should have resulted in a change in the rate of CO_2 sorption. Such a rate increase was not observed.

An example from Danckwerts¹⁵ excellent study is offered to clarify the concept of liquid-phase control. In a study of the absorption of CO_2 from pure CO_2 streams utilizing a 18-in.-ID by 10-ft column packed with

1.5-in. Raschig rings, pure CO_2 saturated with water vapor was cocurrently contacted with a solution of NaOH. It was observed that the CO_2 absorption rate was independent of a wide range of flow rates of pure CO_2 . For example, when CO_2 was being absorbed at a rate of $500 \text{ cm}^3/\text{sec}$, the total gas input to the tower varied from 850 to $2300 \text{ cm}^3/\text{sec}$. This variation in gas flow rate did not change the net CO_2 absorption rate of $500 \text{ cm}^3/\text{sec}$. The obvious conclusion was that mass transfer control was in the liquid phase.

In summation, the fixation of CO_2 in alkaline solutions (NaOH, KOH) by contacting in packed towers appears to involve considerable gas-phase control when the feed gas is air or the feed used contains a CO_2 concentration similar to that of air. For feed solutions containing $>1\%$ CO_2 , the controlling mechanism for the sorption of CO_2 by an alkaline solution in packed columns apparently switches from the gas phase to either the interfacial area or the liquid phase.

2.4.2 Gas-side mass transfer coefficients

There is a dearth of information in the literature concerning gas-side mass transfer coefficients for mass transfer with chemical reaction in mechanically agitated gas-liquid contactors. In the most definitive study of this subject to date, Mehta and Sharma²³ utilized the theory of absorption with pseudo-mth-order (m not necessarily an integer) irreversible reaction to obtain effective interfacial area as a function of such variables as speed, type, and diameter of the impeller, ionic strength, nature of ions, viscosity, surface tension of the liquid, and of particular interest for our study, the presence of solids.

It was concluded that values of a and $k_L a$ cannot be predicted a priori because they are profoundly affected by system properties.

In the course of their study, Mehta and Sharma calculated the mass transfer coefficient for sorption of SO_2 (sulfur dioxide) from lean air mixtures into 2 M NaOH in a gas-liquid stirred contactor. The experimental conditions were established for a 20-in.-ID contactor at an impeller speed, n , of 750 rpm, with the physical design of tank, baffles, and impeller based on the same criteria as those used for our studies. For $n = 750$ rpm and 11% SO_2 in air, the overall gas-side mass transfer coefficient was calculated, based on a perfectly backmixed gas model, to be 1140×10^{-5} g-mole/(cm³-sec-atm). The percentage of SO_2 that reacted in the experiment exceeded 99.9. Thus, there was uncertainty in the effluent gas composition and resulting uncertainty in the value of $K_G a$. It would have been informative for the SO_2 -NaOH system if $K_G a$ had been calculated over a range of total gas flow rates and varying SO_2 compositions; nonetheless, this very large value for $K_G a$ (1.14×10^{-2}) was observed to be a factor of 10^3 larger than the $K_G a$ values (2×10^{-5}) calculated for the sorption of CO_2 from lean air mixtures into aqueous NaOH solutions in the same contactor and for the same hydrodynamic conditions. That is, it was concluded that if overall gas-side mass transfer coefficients were in the range of 10^{-5} to 10^{-6} , the control was virtually all in the liquid phase (or interfacial area), since the gas-side resistance could only contribute $\sim 0.1\%$ for $K_G a = 10^{-5}$ or $\sim 0.01\%$ for $K_G a = 10^{-6}$.

Thus, the overall gas-side mass transfer coefficient for gas-phase control of SO_2 sorption in NaOH would be 1.0×10^{-2} g-moles/(cm³-sec-atm) at a minimum. The diffusivity of CO_2 in air is slightly different from

that of SO_2 in air; hence, the diffusivity corrections can be applied assuming that²⁴

$$K_G a \propto D^{0.5} \quad (14)$$

Based on diffusivity values for CO_2 and SO_2 of 0.165 and 0.151 cm^2/sec respectively, at 21°C , the diffusivity correction results in a calculated value of $K_G a$ for gas-phase control of CO_2 sorption into alkaline solution of $\sim 1.2 \times 10^{-2}$ g-mole/ $(\text{cm}^3\text{-sec-atm})$. As will be evident later in the discussion of the mass transfer coefficients of our experiments, the coefficient can be expected to become very large when all the CO_2 is removed for any feed gas composition. Therefore, if all the CO_2 which can be reacted is removed, then the control for the mass transfer of the last few gas molecules cannot be in the liquid phase.

2.5 Calculation of Mass Transfer Coefficients

2.5.1 Theoretical models: backmixed, log-mean

Regardless of the location of mass transfer control, net mass flux for gas sorption accompanied by chemical reaction is given by:

$$N_G = F_{T,I} \frac{p_I}{p_T} - F_{T,O} \frac{p_O}{p_E} \quad (15)$$

where

N_G = moles of reacting gas G absorbed per time;

F_T = total molar gas flow rate;

p = partial pressure of reacting gas G, atm;

p_T = total influent stream pressure, atm;

p_E = total effluent stream pressure, atm;

and subscripts I and O represent influent and effluent.

If the flow rate of the insoluble component, F_{IN} , is used, then Eq. (15) can be written as:

$$N_G = F_{IN} \left[\frac{P_I}{P_T - P_I} - \frac{P_O}{P_E - P_O} \right] \quad (16)$$

The overall gas-side mass transfer coefficient can be defined by the expression:

$$N_G = K_G a V_D p_{DF} \quad (17)$$

where

V_D = volume of gas-slurry dispersion, and

p_{DF} = pressure driving force.

Although there were variations in V_D for the flow rate and composition ranges studied, the difficulty in accurately determining these variations led to the utilization of a value of 7600 cm^3 for all experiments.

Mehta and Sharma strongly suggest that if the impeller speed is in excess of the minimum speed defined by Westerterp,²⁵ then the gas phase is best represented by a perfectly backmixed model. However, their data were obtained for an experimental system with a CO_2 concentration in air of 10 to 14% and with DFs <10 (e.g., inlet CO_2 pressure - 0.139 atm, outlet CO_2 pressure - 0.017 to 0.067 atm). In this study, the effluent partial pressures were quite low (0.0001-atm range) for very high DFs, so that there was some concern about their accuracy. Thus, to average out these uncertainties, the mass transfer coefficients were calculated by utilizing for the p_{DF} term in Eq. (17), (1) the effluent CO_2 partial pressure, (2) the log-mean CO_2 partial pressure driving force, and (3) an arithmetic mean of the inlet and effluent CO_2 partial pressures.

2.5.2 Gas absorption accompanied by fast pseudo-first-order reaction

Based on the previous literature discussion of Sects. 2.4.1 and 2.4.2, the most applicable chemical reaction model for CO_2 sorption in $\text{Ca}(\text{OH})_2$ appears to be the fast pseudo-first-order irreversible reaction theory, as expressed by Eq. (4):

$$Ra = aC^*(Dk_{\text{OH}}[\text{OH}] + k_L^2)^{0.5} \quad (4)$$

One of the conditions to be satisfied for the accuracy of Eq. (4) is:

$$\frac{(Dk_{\text{OH}}[\text{OH}])^{0.5}}{k_L} \ll \frac{[\text{OH}]}{2C^*} \quad (4a)$$

In the CO_2 - $\text{Ca}(\text{OH})_2$ system, for values of $D = 0.69 \times 10^{-5} \text{ cm}^2/\text{sec}$, $k_{\text{OH}} = 6000 \text{ liters}/(\text{g-mole-sec})$, $[\text{OH}] = 0.032 \text{ g-mole/liter}$ [solubility of $\text{Ca}(\text{OH})_2$ at 21°C], $k_L = 0.05 \text{ cm/sec}$, and $C^* = H p_0 = 0.038 \text{ g-mole}/(\text{liter-atm}) \times p_0$, Eq. (4a) is only approximately satisfied for pure CO_2 feeds. However, for other feed gas compositions from 87.5 to 4.74% CO_2 , the effluent partial pressure of CO_2 is sufficiently small (thus, C^* is sufficiently small) to increase the right side of Eq. (4a) so as to produce the desired inequality. Further, the simplified form, Eq. (5), is not quite applicable since the inequality $Dk_{\text{OH}}[\text{OH}] \gg k_L^2$ is not satisfied.

An alternative model for the sorption of CO_2 from rich gas mixtures into alkaline solutions is the instantaneous rate model of Danckwerts:¹⁵

$$\frac{R}{k_L C^*} = \left(1 + \frac{D_{\text{OH}}}{D} \frac{[\text{OH}]}{2C^*} \right) \left(\frac{D}{D_{\text{OH}}} \right)^{0.5} \quad (18)$$

However, the necessary condition for the applicability of Eq. (18) is:

$$(Dk_{\text{OH}}[\text{OH}])^{0.5} \gg 10k_L (1 + [\text{OH}]/2C^*) \quad (18a)$$

This condition was not satisfied by our experimental parameters.

Normally, the equality of Eq. (4) is utilized to produce the elements of the Danckwert's plot, $(Ra/C^*)^2$ vs $k_{OH}[OH]$, so that a and k_L can be obtained. However, this technique is dependent on the variation of Ra with the hydroxyl concentration. Because the constant rate period in the CO_2 - $Ca(OH)_2$ system resulted in the Ra value remaining constant until at least 90% of the total $Ca(OH)_2$ was reacted (pH 12.5), the Danckwert's plot was not useful for our case. In order to utilize the complete expression, Eq. (4), to predict effective interfacial area for our experiments as a function of impeller speed and gas flow rate, it was necessary to obtain a value of k_L from the literature. For sorption of CO_2 into NaOH in an agitated contactor with hydrodynamic conditions similar to ours, Mehta obtained a k_L value of 0.05 cm/sec. The assumption of a constant k_L is reasonable because Mehta has shown that for a pseudo-first-order reaction in an agitated tank, k_L is not a function of impeller speed.

Now, in general, as stated previously in Sect. 2.1.4:

$$\frac{1}{K_G a} = \frac{1}{k_G a} + \frac{1}{H k_{LR} a} \quad (7)$$

For a $k_G a$ value of 1.2×10^{-2} g-moles/(cm³-sec-atm), Eq. (7) can be simplified, based on the results of our experiments ($K_G \ll k_G$) to:

$$\frac{1}{K_G a} = \frac{1}{H k_{LR} a} \quad (19)$$

Thus, Eq. (17), describing the mass transfer rate for CO_2 sorption as a function of system parameters, becomes

$$N_{CD} = K_G a V_D P_{DF} = H k_{LR} a V_D P_{DF}, \quad (20)$$

where

N_{CD} = mass transfer rate of CO_2 .

However,

$$k_{LR} = (Dk_{OH}[OH] + k_L^2)^{0.5}, \quad (21)$$

hence,

$$N_{CD} = a H V_D P_{DF} (Dk_{OH}[OH] + k_L^2)^{0.5}, \quad (22)$$

2.5.3 Estimate of physical properties

The method of estimating each physicochemical property follows. The solubility was calculated from the technique outlined by Danckwerts.¹⁵ The saturated concentrations of $Ca(OH)_2$ and $CaCO_3$ were utilized instead of the total slurry concentrations (~ 1.0 m), although the presence of the slurry apparently could have a significant effect on the CO_2 solubility in the lime-carbonate solution. A solubility value of 0.038 g-mole/(liter-atm) was adopted throughout these calculations. (It is noteworthy that if the 1.0 m concentrations for $Ca(OH)_2$ and $CaCO_3$ were used, H would be reduced to 0.018 units.)

The diffusivity of the CO_2 in the $Ca(OH)_2$ - $CaCO_3$ slurry was estimated from the assumption that $D\mu/T$ was constant. Based on a value for the diffusivity of CO_2 in water of 1.92×10^{-5} cm²/sec at 25°C and a viscosity for a 1.0 m $Ca(OH)_2$ solution of 2.8 cP, a diffusivity at 21°C in the 1.0 m $Ca(OH)_2$ - $CaCO_3$ system was calculated to be 0.69×10^{-5} cm²/sec. This constant value was utilized, although it was recognized that the diffusivity may vary with temperature and viscosity during the reaction.

The rate constant, k_2 (or k_{OH}), has already been discussed (pp. 11,12). If the ionic strength for saturated $Ca(OH)_2$ and $CaCO_3$ solutions were used (a net ionic strength of ~ 0.05), then a reasonable value for k_{OH} is ~ 6000 liters/(g-mole/sec).¹⁵ However, if the total molal concentrations of $Ca(OH)_2$ and $CaCO_3$ were used, so that the "slurry" ionic strength varied between 3 and 4, k_{OH} would be as much as 15,000 liters/(g-mole/sec). For consistency, the value of 6000 liters/(g-mole/sec), for soluble ionic strength, was utilized for k_{OH} in our calculations.

3. EQUIPMENT DESIGN

3.1 Background and Equipment Options

Many factors must be considered in selecting the most appropriate gas-liquid contactor design which will provide the desired quantity and quality of economic processing.²⁶ Among these factors are the determination of the separate contributions of the liquid and gas phases to the mass transfer resistance and, depending on the controlling phase, the relative ratio of interfacial area to the liquid-phase volume. Diffusion transport must occur in both phases, and for most practical commercial gas-liquid interactions, the diffusion is accompanied by complex chemical reactions. Key kinetic parameters are diffusion and rate coefficients.

An a priori review of the various kinds of continuous and discrete contacting equipment may sometimes indicate which process would have the most appropriate set of reaction-diffusion characteristics. When absorption is accompanied by a fast chemical reaction, a large interfacial area is desired, since the reaction zone is most likely to be near the physical

gas-liquid interface. Hence, the most suitable type of contactor is one which maximizes effective interfacial area. When the reaction rate is slow, so that the liquid phase holdup is very important, the equipment chosen is most likely to be either the sieve or bubble cap column. In cases where backmixing is unimportant and there is a low liquid reaction velocity constant, the most economic contactor may be a bubble column (i.e., an unpacked tower stirred only by the gas passing through it). A significant disadvantage of the bubble column is that the gas being processed may experience a considerable pressure drop in its flow through the continuous liquid phase.

Attractive features of spray column operation are low pressure drop, low maintenance cost, and a wide range of liquid-to-gas phase loading ratios.²⁷ Spray towers are particularly effective for operations entailing dust-laden gases and gases which produce solid deposits upon reaction with the liquid phase. The spray column may also be appropriate for the absorption of gases entailing an exothermic chemical reaction, or for the absorption of highly soluble gases, since large volumes of liquid may be circulated through the tower to avoid an excessive temperature rise. Contrary to the general opinion that the spray tower is plagued by low contact efficiency, the short spray column is almost as efficient as the packed column for moderate-to-high liquid rates.

It was previously indicated that the interfacial area is a key parameter in determining the rate of mass transfer whenever a chemical reaction is taking place. Packed towers have often been selected for contacting processes due to their high interfacial area characteristics. A recent

review of the literature²⁸ concerning interfacial areas and mass transfer coefficients in various gas-liquid contactors serves as a good source for comparison of mass transfer characteristics of the various types of contactors. For the multistage equipment, a was in the range of 0.5 to 3.0 cm^2/cm^3 for packed beds (14 different experiments), 0.5 to 2.0 cm^2/cm^3 for cap plates (four studies), 0.5 to 4.0 cm^2/cm^3 for perforated plates (three studies), 0.5 to 3.0 cm^2/cm^3 for simple bubble columns (four studies, 15 different chemical systems), 0.5 to 6.0 cm^2/cm^3 for packed bubble columns (five studies), and 0.1 to 1.0 cm^2/cm^3 for spray columns (one study). Although considerable controversy continues over the appropriate methods of measurement to obtain interfacial areas, Reith²⁹ has reported values of a as high as 30 cm^2/cm^3 for agitated gas-liquid contactors.

3.2 Theory of the Agitated Contactor

3.2.1 Design criteria

The agitated gas-liquid contactor was chosen as the initial bench-scale equipment for our study because of its simplicity and ease of construction and its obvious advantages for the processing and handling of slurries. Other advantages of the stirred tank are the magnitude of interfacial areas which are produced, the simplicity of varying these areas through adjustment of the impeller speed, the simplicity of adjusting the residence time of both gas and liquid phases, and the facility for delivering high heat transfer rates. Previous investigators²³ have discussed the possibility that the stirred vessel may be superior to other types of process equipment when gas absorption into viscous liquids and slurries is accompanied by a chemical reaction. The backmixing

characteristic of the single-stage agitated contactor is unimportant if a pure gas stream is being processed.

In their studies of mass transfer with a chemical reaction in a mechanically agitated gas-liquid contactors, previous investigators²³ have established several design criteria for achieving the most effective operation of the agitated contactor. Valentin³⁰ has also discussed, in general, the operational criteria for optimum contactor design for a gas-liquid agitated system, not necessarily including chemical reaction. Based on these studies, the commonly suggested criteria are listed as follows: (1) effective interfacial area is inversely proportional to h_T/d_T (h_T is liquid height, d_T is tank diameter); (2) interfacial area increases directly with impeller speed; (3) the impeller heights h_I above the contactor base should be 0.3 to 0.5 d_T ; (4) the liquid-side mass transfer coefficient, $k_L a$, decreases when the tank diameter is increased at a constant impeller speed; (5) highest mass transfer coefficients are obtained for six flat-blade turbine and six curved-blade turbine impellers, with the least power consumption by the latter; (6) high concentrations of solids serve to increase interfacial area; and (7) impeller diameter should be equal to 0.4 to 0.5 d_T .

According to Valentin,³⁰ the general rule for tank construction is that liquid heights be roughly equal to the tank diameter; however, the liquid height can be somewhat greater than the diameter without adverse effects, but it should not exceed about twice the diameter since bubble coalescence in the poorly agitated upper zone results in decreased effective interfacial area. It is generally agreed that the best mixing is provided by the inclusion of baffles to minimize agitation vortexing. Bates et al.³¹

have investigated the relationship between number and dimension of baffles and effective mixing and power consumption. The general conclusion is that the optimum case for tolerable power consumption with effective mixing is provided by four baffles, equally spaced, with dimensions of either 1/10 or 1/12 of d_T . The baffles should be mounted at a distance from the wall of 1/6 the baffle width.

3.2.2 Correlations for power consumption and interfacial area

Operating the stirred tank at the maximum stirrer speed which can be tolerated is usually desirable since the speed has a direct effect on the mass transfer rate. However, the obvious penalty for high speed operation is cost. Rushton³² and others have developed correlations that make it possible to predict the power required to attain impeller speeds for a wide range of impeller designs.

Utilizing the Buckingham-Pi techniques of dimensional analysis, based on the assumption of geometric, kinematic, and dynamic similarity, Rushton concluded that an expression for the power number could be developed which would correlate a great deal of data for typical industrial mixing operations; this expression is:

$$n_p = K(N_{Re})^e, \quad (23)$$

or

$$\frac{\rho P_A g_c}{n^3 d_I^5} = K(N_{Re})^e, \quad (24)$$

where

$$N_{Re} = \frac{d_I^2 n \rho}{\mu}; \quad (25)$$

K = dimensionless constant;

ρ = fluid density, lbm/ft^3 ;

P_A = power dissipated with agitation only, ft-lbf/sec ;

g_c = lbm-ft/lbf-sec^2 ;

d_I = impeller diameter, ft ;

n = impeller speed, rps ; and

μ = fluid viscosity, lbm/ft-sec .

For agitation without aeration, Rushton generated curves of power number as a function of agitation Reynolds number over a wide range of agitation conditions, including variations in the number of impeller blades and impeller geometry, variations in the dimensions and number of baffles, and variation in tank geometry. These curves can be used to predict fairly accurately the power required to deliver a desired impeller speed for a wide range of contactor designs and liquid systems.

However, if the agitation operation includes the mixing of a gas with the liquid during blending, it is necessary to first consult a curve relating the ratio of the power dissipated with aeration to the power dissipated without aeration in the same vessel with the same impeller speed. This ratio, P_{MS}/P_A , has been plotted as a function of Q_G/nd_I^3 by Calderbank³³ for air sparging into agitated vessels.

Calderbank's correlations are applicable for agitated and sparged systems with power consumptions of 0 to 0.2 hp/ft^3 and gas superficial velocities of 0 to 60 cm/min . Miller³⁴ has updated Calderbank's correlations for interfacial area and gas holdup so they may be adapted to gas sparging rates $>2 \text{ cm/sec}$. Power input is estimated by:

$$\frac{P_A}{V_R} = \frac{n_P}{V_R} n^3 d_I^5 \rho, \quad (26)$$

where

V_R = volume of agitated liquid, ft^3 ; and

n_P = factor obtained from Rushton's work.

Further,

$$\frac{P_{MS}}{V_R} = \frac{0.706}{V_R} \left[\frac{P_A^2 n d_I^3}{Q_G^{0.56}} \right]^{0.45}, \quad (27)$$

where

P_{MS} = mechanical power input for sparged-agitated system.

Miller also included a factor to account for power input due to sparging effects, which can generally be neglected for the normally encountered ranges of impeller speed. The effective power input is:

$$\frac{P_E}{V_R} = \frac{P_{MS}}{V_R} + C_1 \frac{P_S}{V_R}. \quad (28)$$

The interfacial area can then be estimated by:

$$a = 1.44 \left[\frac{\left(\frac{P_E}{V_R} \right)^{0.4} (\rho)^{0.2}}{\sigma^{0.6}} \right] \left(\frac{U_G}{U_T + U_G} \right)^{0.5} \quad (29)$$

The fractional gas holdup can be estimated by:

$$h = \left(\frac{U_G h}{U_T + U_G} \right)^{0.5} + 0.015a. \quad (30)$$

Equations (27) and (29) are dimensionally consistent in the CGS system.

$P_{MS}, P_A, P_E, P_S = \text{g-cm}^2/\text{sec}^3$;

$V_R = \text{liquid volume, cm}^3$;

Q_G = volumetric flow rate, cm^3/sec ;

ρ = liquid density, g/cm^3 ;

σ = interfacial tension, g/sec^2 ;

U_G = superficial gas velocity, cm/sec ; and

U_T = bubble terminal rise velocity, cm/sec .

There is some uncertainty about the applicability of these correlations for predicting the mixing characteristics of slurries where the mass transfer also involves a chemical reaction. The expressions for a and h were derived for the sparging of air into various liquids for which there was simple absorptive mass transfer. The expression for h is of little value for the absorption of gas from a pure or nearly pure gas stream since there may be 80 to 100% shrinkage of the gas stream in its transfer through the contactor. As noted previously, considerable controversy continues concerning the best method of estimating the effective interfacial area in agitated gas-liquid contactors.

3.3 Practical Design of the Agitated Gas-Liquid Contactor

The bench-scale contactor was designed according to the literature criteria discussed previously. The contactor (7.72-in. ID and 13 in. in height) was fabricated from plexiglass except for the top flange, which was fabricated from stainless steel. As shown in Fig. 1, the contactor was fitted with four equally spaced baffles having widths equal to $0.1 d_T$. The impeller was fabricated as a turbine having six flat blades, with a total tip-to-tip width of $\sim 0.5 d_T$. The six-bladed turbine impeller was modeled after that of Westerterp's.²⁵ The height and width of each blade measured 0.2 and $0.25 d_T$, respectively.

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

The blades were attached to a disk with a diameter of $0.7 d_I$. The impeller was located above the contactor base at a distance equal to about four-tenths the slurry height. The gas sparger, a cross tube configuration containing $\sim$ twenty 1/32-in. holes, was located 2.0 cm directly below the impeller eye. Impeller, shaft, and sparger were fabricated from stainless steel.

A pH probe was inserted through a Swagelok fitting in the wall of the contactor to provide continuous monitoring of the hydroxyl ion concentration. A cooling coil, fabricated from 1/4-in. copper tubing, was located inside the contactor in a concentric arrangement, so that its outer surface coincided with the baffles. Process water was used to provide coolant fluid of $\sim 17^\circ\text{C}$. The seal on the impeller shaft was the standard packed stuffing box utilizing Teflon O-rings which could be tightened by the adjustment of a packing gland. The packing was located in the bottom section of the stainless steel flange, so that above the packing section the shaft was encased in a ball bearing sleeve. The stainless flange dissipated excess heat generated from shaft rotation. Initially, the upper flange was fabricated from plexiglass, but this material proved incapable of tolerating the heat buildup. The seal was virtually 100% leakproof at the low pressure (slightly above atmospheric, 0 to 1 psig) which was produced in the contactor above the slurry. An overall layout of the experimental operation is shown in Fig. 2. Gas mixtures were either blended during operation or purchased preblended with guaranteed analysis.

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Fig. 2. Schematic of experimental layout.

4. EXPERIMENTAL METHODS AND ANALYTICAL TECHNIQUES

4.1 Adjunctive Instrumentation

Power for agitation was provided by a Gast pneumatically driven motor, capable of delivering speeds in the range of 0 to 5000 rpm, with a maximum drive pressure of 100 psig. The true shaft speeds were determined using a Strobotac type 1538-A (General Radio Co.). Gas samples were analyzed using a Tracor gas chromatograph, which detects gas thermal conductivity. The volumetric flow rate of effluent gas from the contactor was measured by a wet-test meter, model 802 American Meter Co. The composition of the slurry was obtained by titrating with standard 1 N HCl, so that the first endpoint, as indicated by phenolphthalein (pH 8 to 9), represented the dissolution of all available Ca(OH)_2 . The second endpoint, as indicated by bromocresol green (pH 3 to 4.5), represented the dissolution of all available CaCO_3 . The very limited solubility of CaCO_3 precluded any interference of the carbonate in the hydroxyl ion titration.³⁵

4.2 Reagents

Both reagent-grade and commercial-grade (available in bulk quantities) hydrated limes [Ca(OH)_2 , slaked lime] were utilized in these studies. The reagent-grade Ca(OH)_2 was obtained from Fisher Scientific Co. Commercial slaked lime was obtained from Williams Lime Co. of Knoxville, Tenn., Foote Mineral Co. of Exton, Pa., and Mississippi Lime Co. of Alton, Ill. Since bulk quantities of commercial lime would be required to provide the large amount of reagent necessary to fix the CO_2 that would be produced in a full-scale HTGR fuel reprocessing plant, the investigation of the

kinetics and physicochemical properties of the various limes was an important facet of the overall study.

4.3 Typical Experimental Operation

For the semibatch operation, a one molal slurry of slightly less than 6.7 liters was prepared in a 10-liter vessel. Precaution was taken to minimize the time of exposure of the slurry to ambient air. (The addition of 1 g-mole of $\text{Ca}(\text{OH})_2$ to 1.0 liter of water resulted in a volume of 1035 ml.) Slurry analysis indicated that exposure times of <1 hr resulted in minimal reaction of the $\text{Ca}(\text{OH})_2$ with the CO_2 in the air. Magnetic stirring was maintained while the slurry was loaded through one flange port into the contactor with the aid of vacuum applied to a second flange port. The balance of the 6.7 liters was provided by wash water from cleanup of the feed reservoir. When pure CO_2 was supplied to the contactor, the wet-test meter was utilized to determine the effluent flow rate. When a mixed gas was studied, the effluent gas line was analyzed by collecting gas bomb samples. Effluent flow rates were determined by both measurement with rotameters and mass balances based on the insoluble O_2 flow rate. All influent flow rates were measured with rotameters. Carbon dioxide in effluent streams could be accurately detected by gas chromatography for concentrations as low as 10 ppm. For all runs, water vapor accompanying the effluent gas from the contactor was removed with Drierite columns. Any sorption or desorption of CO_2 by Drierite (CaSO_4) involved concentrations too low to be discriminated in the normal measurements made with gas chromatography (lower detection limit 10 ppm).

Coolant water was started and the desired impeller speed was set by utilizing the Strobotac while the air pressure to the motor was adjusted. After the gas stream was admitted to the agitated contactor, the shaft speed was readjusted, because less power was required to deliver a set impeller speed whenever agitation was accompanied by gas stream flow.

When the valve controlling the gas stream flow to the sparger was opened, the time was recorded. Gas samples were collected for mixed gas feeds after serial sampling indicated that sufficient time had elapsed to ensure a collection of a steady-state operation sample. For the wet-test meter, the total effluent volume was recorded and divided by the run time to yield an average value for the effluent gas flow rate. The constant rate portion of the reaction period ended whenever the pH began to decrease rapidly from a value of ~ 12.5 . The reaction was normally allowed to continue until the pH reached ~ 6.0 , after which there was no further absorption of CO_2 . The CaCO_3 slurry was then quickly drained from the contactor, either into a plastic container for determination of the settling rate, or into a 55-gal disposal drum. The residual carbonate scale and pockets of carbonate slurry were easily removed from the contactor after each run by rinsing the contactor with a 0.1 M HCl solution.

All studies were made at a speed exceeding the minimum speed above which the impeller is able to disperse the gas effectively. It is assumed that the impeller tip velocity must exceed the gas rising velocity a certain number of times so that all the large gas bubbles can be broken up into smaller bubbles. The minimum impeller speed is obtained from:²⁵

$$\frac{n_o d_I}{\left(\frac{\sigma g}{\rho}\right)} = A_c + \frac{B_c d_T}{d_I} \quad (31)$$

For a 4.0-in. impeller diameter, a minimum n_o of 348 rpm was indicated for the 7.72-in.-ID contactor in this study.

5. EXPERIMENTAL RESULTS

5.1 Reaction Characteristics

The kinetic behavior of the CO_2 -lime slurry always followed the same pattern. For an operating slurry temperature of $\sim 22^\circ\text{C}$, the initial slurry pH was ~ 12.5 , representing the very limited solubility of $\text{Ca}(\text{OH})_2$ at that temperature. As the feed gas containing the CO_2 (either pure or dilute in CO_2) was continuously supplied to the contactor sparger, the pH always remained constant at 12.5, indicating that the $\text{Ca}(\text{OH})_2$ particle dissolution rate matched the hydroxyl ion removal rate.

The net mass transfer rate also remained constant for a fixed gas flow rate. This "constant period" of mass transfer persisted until at least 90% of the $\text{Ca}(\text{OH})_2$ was reacted (as determined by assaying slurry samples and also from gas flow mass balances). After the 90% reaction of the $\text{Ca}(\text{OH})_2$, the pH began to decrease rapidly toward the value associated with a completely saturated solution of CaCO_3 (pH 8.8), with all the $\text{Ca}(\text{OH})_2$ reacted. Any further addition of CO_2 resulted in the formation of $\text{Ca}(\text{HCO}_3)_2$, which led finally to an equilibrium solution of CaCO_3 and $\text{Ca}(\text{HCO}_3)_2$ (pH 6.0). This kinetic behavior is explained by interpreting the constant rate period of mass transfer to be controlled by either the CO_2 -OH rate of reaction or interfacial area. The falling rate period, during which the pH is seen to decrease rapidly from 12.5, was interpreted to be obviously liquid-phase-controlled. The control

for the latter falling rate period may be primarily due to limitations on diffusion of the reactants in the liquid phase. Because the latter phase of the reaction (at least in semibatch operation) always resulted in a rapid decrease in net mass transfer of CO_2 for a constant feed rate, it was not investigated in detail. Further justification of the above mechanism interpretation is given by the data analysis that follows.

5.2 Typical Mass Transfer Rates for Pure Carbon Dioxide as a Function of Total Gas Flow Rates

Mass transfer rates were obtained for the fixation of pure CO_2 in the CO_2 -slaked lime slurry contactor at two different impeller speeds, 800 and 1700 rpm. As shown in Fig. 3, the percentage of CO_2 absorbed was >99% for a wide range of flow rates. Over this range, the net mass transfer rate increased linearly with CO_2 flow rate. The percent conversion decreased to <99% for flow rates >20 reference liters per minute (rlm) at $n = 800$ rpm and >35 rlm at $n = 1700$ rpm. (Reference liters per minute is being defined as gas flow rate at 70°F and 1 atm.) However, in the range of flow rates investigated, even though an increase in flow rate could result in a lower DF, the net mass transfer rate of CO_2 to the lime slurry always increased. It seems likely, however, that a gas rate could be provided at which the net mass transfer rate would decrease as the gas rate was increased. Also, an increase in impeller speed resulted in an increase in net mass transfer rate for any gas flow rate. If it is established that mass transfer is liquid-phase-controlled over a wide range of the gas flow rates, then the increase in mass transfer rate with increasing n and Q_G can most plausibly be attributed

Fig. 3. Mass transfer rate, constant rate period, for sorption and fixation of pure CO_2 in the gas- $Ca(OH)_2$ slurry contactor.

to an increase in interfacial area. An additional factor might be improved dissolution of the Ca(OH)_2 slurry.

5.3 Mass Transfer Rates and Decontamination Factors for the Fixation of Carbon Dioxide from Streams both Concentrated and Dilute in Carbon Dioxide

5.3.1 Fixation rates and decontamination factors for pure carbon dioxide feed gas

For the fixation of pure CO_2 in the gas-slurry contactor, DFs as large as 800 were achieved for flow rates of 3 to 8 rlm and impeller speeds of 1700 and 800 rpm (curves 1 and 2 in Fig. 4, respectively). In actuality, if pure CO_2 were supplied to the contactor, for flow rates up to 10 rlm, the CO_2 stream could be dead-ended into the contactor, with no appreciable buildup of pressure in the contactor until ~90% of the Ca(OH)_2 was reacted. However, the typical KALC process (Krypton Absorption in Liquid CO_2) off-gas has a concentration of ~90% CO_2 -10% O_2 , so that there would always be a net purge of oxygen through the contactor.

For curve 1, the two sets of points in the high flow rate range represent data obtained with two different impeller designs. Much better mixing (but higher power consumption) was obtained with a turbine impeller having six flat blades (4 in. tip to tip) than with the four-bladed turbine impeller. This superior mixing was evidenced in the improved removal efficiencies at every gas flow rate. Data points for flow rates <10 rlm are of little interest because, as previously noted in this flow rate range, the gas can be dead-ended into the contactor.

Fig. 4. Mass transfer rate and decontamination factors for the constant rate period of the removal of CO_2 from simulated ETGR off-gases.

The data of curve 2 indicated the strong effect of impeller speed on the removal efficiency for the CO_2 at all flow rates and the effect on the mass transfer rates at high gas flow rates.

5.3.2 Fixation rates and decontamination factors for 87.5% CO_2 -12.5% O_2 feed gas

A gas with a composition very similar to the KALC off-gas was investigated in the gas-slurry contactor for a range of gas flow rates at an impeller speed of 800 rpm. The results obtained with this feed gas composition are shown in curve 3, Fig. 4. For a fixed gas flow rate and impeller speed, the DF obtained for the pure CO_2 stream was always larger than that obtained for the less concentrated 87.5% CO_2 stream. This trend was consistent for all studies; that is, for fixed total gas flow, the DF decreased as the mole fraction (m.f.) of CO_2 in the gas stream decreased.

Because of the obvious interest in a gas stream with a composition similar to that of the KALC off-gas, flow rates of the 87.5% CO_2 were decreased until very significant DFs were obtained. In the flow rate range of 3-4 rlm, there was an asymptote in the DF curve. Hence, the DF increased very rapidly for flow rates below this limit. Values for the DF as high as 3600 were obtained.

5.3.3 Fixation rates and decontamination factors for 4.74% CO_2 -95.26% O_2 feed gas

A feed gas dilute in CO_2 , containing 4.74% CO_2 and 95.26% O_2 , was also processed in the bench-scale gas-slurry contactor. This dilute feed was studied to provide single-stage kinetic information for the

gas-lime slurry reaction for processing a gas stream dilute in CO_2 . Such a dilute stream could occur during processing if operation with multi-staged contactors (in series) proved to be the most efficient process scheme. For this 4.74% CO_2 feed, DFs were obtained that were less than those of the rich CO_2 feed streams at equal total gas flow rates. Apparently when the gas stream is very dilute in CO_2 (e.g., <0.5%), the DFs obtained are comparable with those of a 5% CO_2 stream at equal total gas flow rates. This is somewhat surprising in view of the trend shown in Fig. 4.

The data obtained for the fixation of CO_2 from the various feed gases are listed in the tables in the following manner: pure CO_2 , $n = 1700$ rpm, Table 1; pure CO_2 , $n = 800$ rpm, Table 2; 87.5% CO_2 -12.5% O_2 , Table 3; 33.6% CO_2 -66.4% O_2 , Table 4; and 4.74% CO_2 -95.26% O_2 , Table 5.

5.3.4 Prediction of multistage contacting

An analysis of the data in Tables 1 to 5 provides guidelines for a number of practical combinations for series operation of gas-lime slurry contactors. For example, from Table 3 it is seen that for an inlet KALC-type gas flow rate of ~ 15 rlm of CO_2 (~ 17.6 total rlm or ~ 0.65 g-moles CO_2/min), a DF of 100 was obtained, producing an outlet gas of $\sim 7\%$ CO_2 . The 0.0065-moles/min CO_2 effluent from the first contactor could be processed in a second contactor of equal diameter to yield a DF of 265 (Table 5, $Q_G = 3.22$ rlm). Both operations in sequence would thus provide a DF of $\sim 26,000$. If this sequential operation was faithfully reproduced in full-size equipment (for contactor scale-up, see Sect. 7), then the 5.76 Ci of ^{14}C per day in 7×10^6 rld of KALC off-gas would be reduced to 0.00019 Ci/day. Other contacting sequence options are available, including

Table 1. Fixation of pure CO₂ in the gas-lime slurry contactor, n = 1700 rpm

Influent CO ₂		CO ₂ effluent pressure (atm)	Effluent CO ₂ , F _O (g-moles/min)	Mass transfer rate, constant period, N _{CD} (g-moles/liter-min)	(F _I -F _O)/F _I (% conversion)	Decontamination factor (F _I /F _O)	Impeller speed n (rpm)	Impeller diam/blades
Q _{CD} (rlm)	F _I (g-moles/min)							
3.760	0.1568	1.0	ND ^a	0.0231	>99 ^b	ND	1700	3-4
6.880	0.2870	1.0	ND	0.0431	>99	ND	1700	3-4
10.610	0.4432	1.0	ND	0.0660	>99	ND	1700	3-4
10.930	0.4557	1.0	0.000887	0.0680	99.80	514	1700	4-6
12.025	0.5020	1.0	0.001238	0.0747	99.75	405	1700	4-6
15.716	0.6550	1.0	0.001781	0.0980	99.72	360	1700	4-6
18.722	0.7807	1.0	ND	0.1172	>99	ND	1700	3-4
19.683	0.8207	1.0	ND	0.1221	>99	ND	1700	3-4
20.903	0.8716	1.0	ND	0.1300	>99	ND	1700	3-4
20.304 ^c	0.8468	1.0	0.00353	0.1259	99.58	240	1700	4-6
24.946	1.0404	1.0	0.01400	0.1530	98.60	74	1700	3-4
33.535 ^c	1.399	1.0	0.01300	0.2070	99.07	107	1700	4-6
37.789	1.5760	1.0	0.08600	0.2300	94.50	18	1700	3-4
4.745 ^d	0.1979	0.011	0.00032	0.0295	99.84	619	1700	4-6

^a Not determined.

^b >99 indicates runs where F_O was not precisely determined.

^c commercial lime.

^d CO₂-O₂ mixture, 87.5% CO₂-12.5% O₂.

Table 2. Fixation of pure CO₂ in the gas-liquid slurry contactor, n = 800 rpm

Influent CO ₂		CO ₂ effluent pressure (atm)	Effluent CO ₂ , F ₀ (g-moles/min)	Mass transfer rate, constant period, N _{CD} (g-moles/liter-min)	(F _I -F ₀)/F _I (% conversion)	Decontamination factor (F _I /F ₀)	Impeller speed n (rpm)	Impeller diam/blades
Q _{CD} (rlm)	F _I (g-moles/min)							
3.76 ^a	0.157	1.0	0.000183	0.023	99.38	834	800	4-6
7.18	0.299	1.0	ND ^b	0.045	>99 ^c	ND	800	4-6
7.23	0.301	1.0	0.000830	0.045	99.71	36C	800	4-6
10.94	0.456	1.0	ND	0.068	>99	ND	800	4-6
10.98	0.458	1.0	0.002073	0.068	99.54	22C	800	4-6
15.03	0.627	1.0	ND	0.094	>99	ND	800	4-6
18.95	0.790	1.0	0.013800	0.116	98.20	57	800	4-6
20.58 ^a	0.858	1.0	0.020200	0.125	97.70	43	800	4-6
22.25	0.928	1.0	0.012700	0.137	98.60	73	800	4-6
33.40	1.403	1.0	0.179000	0.183	37.20	8	800	4-6
38.45	1.603	1.0	0.230000	0.210	37.50	7	800	4-6
44.30	1.848	1.0	0.255000	0.240	36.20	7	800	4-6

^a Commercial lime.

^b ND - not determined.

^c >99 indicates runs where F₀ was not precisely determined.

Table 3. Fixation of CO₂ from an 87.5 CO₂-12.5% O₂ stream, using the gas-lime slurry contactor

Q _{CD} (rln)	Influent gas		Superficial gas velocity, total gas (cm/min)	CO ₂ effluent pressure (atm)	Effluent CO ₂ , F _O (g-moles/min)	Mass transfer rate, constant period, N _{CD} (g-moles/liter-min)	(F _I -F _O)/F _I (% conversion)	Decontamination factor (F _I /F _O)	Impeller speed n (rpm)	Impeller diam/blades
	Q _G (rlm)	F _I (g-moles/min)								
2.64 ^a	3.02	0.110	10.03	0.0019	0.000031	0.0164	99.97	3548	800	4-6
2.97	3.40	0.124	11.29	0.0019	0.000034	0.0185	99.97	3600	800	4-6
3.53	4.04	0.147	13.42	0.0170	0.000370	0.0219	99.75	398	800	4-6
3.60	4.11	0.150	13.66	0.0220	0.000480	0.0223	99.70	313	800	4-6
4.63	5.30	0.193	17.61	0.0040	0.000110	0.0288	99.94	1753	800	4-6
6.21	7.10	0.259	23.60	0.0210	0.000794	0.0385	99.70	326	800	4-6
10.26	11.74	0.428	39.00	0.0700	0.004600	0.0620	96.60	93	800	4-6
14.72	16.84	0.614	55.94	0.0304	0.002800	0.0912	99.50	215	800	4-6
15.40	17.61	0.642	58.52	0.0960	0.009740	0.0940	98.48	66	800	4-6
15.40	17.61	0.642	58.52	0.0700	0.006460	0.0950	98.98	99	800	4-6

^a All runs with commercial lime.

Table 4. Fixation of CO₂ from a 33.6 CO₂-66.4% O₂ stream, using the gas-lime slurry contactor

Q _{CD} (rlm)	Influent gas		Superficial gas velocity, total gas (cm/min)	CO ₂ effluent pressure (atm)	Effluent CO ₂ , F ₀ (g-moles/min)	Mass transfer rate, constant period, N _{CD} (g-moles/liter-min)	(F _I -F ₀)/F ₀ (% conversion)	Decontamination factor (F _I /F ₀)	Impeller speed n (rpm)	Impeller diam/blades
	Q _G (rlm)	F _I (g-moles/min)								
0.857 ^a	2.600	0.0358	8.64	0.00032	0.000037	0.0053	99.90	969	800	4-6
1.102	3.345	0.0459	11.11	0.00030	0.000071	0.0068	99.84	645	800	4-6
1.300	3.948	0.0542	13.12	0.00126	0.000131	0.0081	99.76	414	800	4-6
1.489	4.522	0.0621	15.02	0.00126	0.000150	0.0093	99.76	414	800	4-6
1.807	5.483	0.0754	18.23	0.00126	0.000132	0.0112	99.76	413	800	4-6
2.521	7.629	0.1048	25.25	0.00251	0.000438	0.0156	99.53	208	800	4-6
4.219	12.810	0.1760	42.56	0.00639	0.002270	0.0260	98.71	77	800	4-6
6.135	18.740	0.2574	62.26	0.03140	0.023020	0.0350	91.06	11	800	4-6
8.460	25.690	0.3528	85.25	0.02919	0.018164	0.0483	94.85	20	800	4-6

^a All runs with commercial lime.

Table 5. Fixation of CO₂ from a 4.74% CO₂-95.26% O₂ stream, using the gas-lime slurry contactor

C _{CD} (rlm)	Influent gas		Superficial gas velocity, total gas (cm/min)	CO ₂ effluent pressure (atm)	Effluent CO ₂ , F _O (g-moles/min)	Mass transfer rate, constant period, N _{CD} (g-moles/liter-min)	(F _I -F _O)/F _I (% conversion)	Decontamination factor (F _I /F _O)	Impeller speed n (rpm)	Impeller diam/blades
	Q _G (rlm)	F _I (g-moles/min)								
C.040	0.849	0.00167	2.81	0.000125	0.0000042	0.000248	99.75	398	800	4-6
C.042 ^a	0.896	0.00176	2.97	0.00012	0.0000044	0.000260	99.75	400	800	4-6
C.044 ^a	0.932	0.00183	3.09	0.00012	0.0000044	0.00027	99.76	415	800	4-6
C.044	0.932	0.00183	3.09	0.00009	0.0000034	0.00027	99.81	541	800	4-6
C.065 ^a	1.363	0.00270	4.51	0.00013	0.0000069	0.00040	99.74	391	800	4-6
C.126	2.674	0.00525	8.85	0.00019	0.000020	0.00078	99.62	263	800	4-6
C.151	3.220	0.00633	10.66	0.00027	0.000024	0.00094	99.46	265	800	4-6
C.177 ^a	3.763	0.00740	12.46	0.00028	0.000040	0.00110	99.46	185	800	4-6
C.304 ^a	6.453	0.01268	21.37	0.00038	0.000096	0.00188	99.24	132	800	4-6
C.323 ^a	6.872	0.01350	22.75	0.00049	0.000133	0.00200	99.01	103	800	4-6
C.378	8.352	0.01580	26.66	0.00059	0.000187	0.00233	98.80	85	800	4-6
C.031	21.951	0.04300	72.69	0.00248	0.002156	0.00600	94.90	20	800	4-6
C.390 ^b	24.490	0.058	81.09	4.603	ND ^c	0.00870	>98.00	ND	1700	3-4
3.750 ^b	10.650	0.157	35.26	12.417	ND	0.00230	>98.00	ND	1700	3-4
7.530 ^b	30.03	0.314	99.43	24.934	ND	0.04700	>98.00	ND	1700	3-4
13.935 ^b	14.765	0.498	48.89	39.520	ND	0.07400	>98.00	ND	1700	3-4

^a Commercial lime.

^b CO₂-O₂ mixtures other than 4.74%-95.26%.

^c ND - not determined.

either continuous flow of the lime slurry or semibatch operation of a single large contactor designed according to the capability of the bench-scale contactor to deliver a DF of >3000 (Table 3) for 3.4 rlm of KALC off-gas. This latter case would obviously require a larger full-scale gas-slurry contactor than that needed for scaling up from a 15-rlm CO_2 flow.

5.4 Dependence of Conversion on Impeller Speed

In Fig. 5 (and Table 6), the importance of proper mixing is shown by the strong dependence of the mass transfer rate on the impeller speed during the fixation of pure CO_2 . For the fixed CO_2 flow rate of 17.8 rlm, it is evident that for impeller speeds <1200 rpm, the 4-in., six flat-blade turbine provided considerably better mass transfer than that obtained from the 3-in. turbine. However, at impeller speeds >1200 , both impellers gave $>99\%$ CO_2 removal, although higher DFs were always obtained with the 4-in. turbine. When the gas flow rate was decreased, the narrow range of impeller speeds for which conversion markedly decreased simply moved to lower speeds. Conversely, if the total gas flow rate was increased, the critical impeller speed at which $>95\%$ removal of CO_2 was achieved was increased (unpublished results).

Although the rate of CO_2 absorption without mechanical agitation was not determined, extrapolation of the data indicates that a finite, albeit very small, conversion would be observed. The low conversion for the bench-scale operation of the contactor as a short bubble column effectively eliminates the use of a large-scale bubble column for processing of the large quantity of KALC off-gas that would be available in a full-sized plant.

Fig. 5. Percent conversion of pure CO_2 as a function of agitator speed at a fixed gas flow rate.

Table 6. Fixation rate as a function of impeller speed; pure CO₂ at a constant flow rate in the gas-liquid slurry contactor

Influent CO ₂		Superficial gas velocity, U _G (cm/min)	Effluent CO ₂ , F _O (g-moles/min)	Mass transfer rate, constant period, NCD (g-moles/liter-min)	(F _I -F _O)/F _I (% conversion)	Decontamination factor (F _I /F _O)	Impeller speed n (rpm)	Impeller diam/blades
Q _{CD} (liters/min)	F _I (mcles/min)							
17.80	0.74	59.1	0.020	0.110	98	37.0	1200 ^a	3-4
17.80	0.74	59.1	0.179	0.082	76	4.0	1000	3-4
17.80	0.74	59.1	0.357	0.057	52	2.1	800	3-4
18.00	0.75	59.3	0.169	0.087	78	4.4	520	4-6
17.85	0.75	55.0	0.223	0.078	70	3.4	440	4-6
18.00	0.76	59.8	0.293	0.069	61	2.6	400	4-6
16.39	0.68	50.6	0.383	0.045	44	1.8	300	4-6
17.95	0.75	59.7	0.455	0.044	39	1.6	200	4-6
18.90	0.79	62.8	0.634	0.024	20	1.2	100	4-6

^aSome of the data for various impeller speeds and impeller designs, used to construct Fig. 5, are found in Tables 1 and 2.

5.5 Experimental Mass Transfer Coefficients

5.5.1 Overall mass transfer coefficients

The overall gas-side mass transfer coefficients were calculated for mass transfer in the agitated contactor, using Eq. (17), for feed gases with compositions of 100, 87.5, 33.6, and 4.74% CO_2 (the balance as O_2). The $K_G a$ values from these calculations are tabulated in Table 7 and shown in Fig. 6. Due to uncertainty in the CO_2 effluent pressure, there was concern about the $K_G a$ values at low flow rates for all feed compositions. For flow rates of pure CO_2 less than ~ 10 rlm, the pressure above the slurry actually reached values slightly less than atmospheric, since air was observed to flow in a reverse direction through the effluent lines into the contactor. However, in general the gage pressure at the slurry surface varied from 1 to 10 in. H_2O , depending on flow rate and downstream fittings, so that assuming the pressure above the slurry was near atmospheric was reasonable.

Based on inspection of the data of Table 7, several important trends are noteworthy: (1) the most useful $K_G a$ values were calculated utilizing backmix and plug flow assumptions; (2) $K_G a$ values were smallest for pure CO_2 and rich CO_2 feed gases; (3) for a particular feed gas, $K_G a$ varied directly as the total gas velocity; (4) a values were smallest for pure and rich CO_2 feed gases. Each of these particular experimental trends requires separate discussion.

5.5.2 Backmixing vs plug flow

The $K_G a$ values were calculated for three different assumptions of pressure driving force, as tabulated in Table 7. The two most useful

Table 7. Mass transfer coefficients and interfacial areas for CO_2 - $\text{Ca}(\text{OH})_2$ reaction in a stirred tank

Q_G	N_{CD}	P_0	K_{Ga} back- mixed	$k_{L,Ra}$ back- mixed	k_{Ga} log mean	$k_{L,Ra}$ log mean	K_{Ga} average p	$k_{L,Ra}$ average p	a back- mixed	a log mean
Feed gas contained pure CO_2 at $n = 1700$ rpm										
3.76	0.0231	1	large	large			large	large		
6.88	0.0431	1	0.63×10^{-6}	0.017			0.63×10^{-6}	0.017	0.270	0.24 ^a
10.61	0.0660	1	0.97×10^{-6}	0.026			0.97×10^{-6}	0.026	0.414	0.37
10.93	0.0680	1	1.00×10^{-6}	0.026			1.00×10^{-6}	0.026	0.427	0.38
12.03	0.0747	1	1.10×10^{-6}	0.029			1.10×10^{-6}	0.029	0.469	0.42
15.72	0.0980	1	1.44×10^{-6}	0.038			1.44×10^{-6}	0.038	0.615	0.55
18.72	0.1172	1	1.72×10^{-6}	0.045			1.72×10^{-6}	0.045	0.735	0.65
19.68	0.1221	1	1.79×10^{-6}	0.047			1.79×10^{-6}	0.047	0.766	0.68
20.90	0.1300	1	1.97×10^{-6}	0.052			1.97×10^{-6}	0.052	0.816	0.73
20.30	0.1259	1	1.85×10^{-6}	0.049			1.85×10^{-6}	0.049	0.790	0.70
24.95	0.1530	1	2.25×10^{-6}	0.059			2.25×10^{-6}	0.059	0.960	0.85
33.54	0.2070	1	3.04×10^{-6}	0.080			3.04×10^{-6}	0.080	1.299	1.16
37.79	0.2300	1	3.38×10^{-6}	0.089			3.38×10^{-6}	0.089	1.443	1.28
Feed gas contained pure CO_2 , at $n = 800$ rpm										
3.76	0.023	1	large	large			large			
7.18	0.045	1	0.65×10^{-6}	0.017			0.65×10^{-6}	0.017	0.218	
7.23	0.045	1	0.99×10^{-6}	0.026			0.99×10^{-6}	0.026	0.218	
10.94	0.068	1	0.99×10^{-6}	0.026			0.99×10^{-6}	0.026	0.424	
10.98	0.068	1	0.99×10^{-6}	0.026			0.99×10^{-6}	0.026	0.424	
15.03	0.094	1	1.36×10^{-6}	0.036			0.99×10^{-6}	0.036	0.590	
18.95	0.116	1	1.68×10^{-6}	0.044			1.68×10^{-6}	0.044	0.728	
20.58	0.125	1	1.81×10^{-6}	0.048			1.81×10^{-6}	0.048	0.784	
22.25	0.137	1	1.98×10^{-6}	0.052			1.98×10^{-6}	0.052	0.859	
33.40	0.183	1	2.65×10^{-6}	0.070			2.65×10^{-6}	0.070	1.148	
38.45	0.210	1	3.03×10^{-6}	0.080			3.03×10^{-6}	0.080	1.317	
44.30	0.240	1	3.57×10^{-6}	0.094			3.57×10^{-6}	0.094	1.505	
Feed gas contained 87.5% CO_2 -12.5% O_2 , at $n = 800$ rpm										
3.02	0.0164	0.0019	12.73×10^{-5}	3.350	1.7×10^{-6}	0.045	0.55×10^{-6}	0.014	54.15	0.72
3.40	0.0185	0.0019	13.96×10^{-5}	3.674	1.9×10^{-6}	0.050	0.62×10^{-6}	0.016	61.08	0.82
4.04	0.0219	0.0170	1.87×10^{-5}	0.492	1.5×10^{-6}	0.039	0.72×10^{-6}	0.019	8.08	0.63
4.11	0.0223	0.0220	1.47×10^{-5}	0.387	1.4×10^{-6}	0.037	0.73×10^{-6}	0.019	6.36	0.60
5.30	0.0288	0.0040	10.51×10^{-5}	2.766	2.6×10^{-6}	0.068	0.96×10^{-6}	0.025	45.17	1.12
7.10	0.0385	0.0210	2.66×10^{-5}	0.700	2.4×10^{-6}	0.063	1.26×10^{-6}	0.033	11.50	1.03
11.74	0.0620	0.0700	1.28×10^{-5}	0.337	2.6×10^{-6}	0.070	1.93×10^{-6}	0.051	5.56	1.13
16.84	0.0912	0.0304	4.33×10^{-5}	1.145	5.2×10^{-6}	0.137	2.96×10^{-6}	0.078	18.80	2.21
17.61	0.0940	0.0960	1.43×10^{-5}	0.376	3.9×10^{-6}	0.103	3.84×10^{-6}	0.075	6.14	1.68
17.61	0.0950	0.0700	2.09×10^{-5}	0.550	4.0×10^{-6}	0.105	2.96×10^{-6}	0.078	8.51	1.77
Feed gas contained 33.6% CO_2 -66.4% O_2 at $n = 800$ rpm										
2.600	0.0053	0.00052	14.02×10^{-5}	3.90	1.50×10^{-6}	0.039	0.46×10^{-6}	0.012	63.94	0.64
3.345	0.0068	0.00080	12.41×10^{-5}	3.27	1.78×10^{-6}	0.047	0.59×10^{-6}	0.016	53.32	0.76
3.948	0.0081	0.00126	9.36×10^{-5}	2.46	1.98×10^{-6}	0.052	0.71×10^{-6}	0.019	40.33	0.85
4.522	0.0093	0.00126	10.69×10^{-5}	2.81	2.28×10^{-6}	0.060	0.81×10^{-6}	0.021	46.30	0.97
5.488	0.0112	0.00126	12.96×10^{-5}	3.41	2.74×10^{-6}	0.072	0.98×10^{-6}	0.026	55.76	1.17
7.629	0.0156	0.00251	8.98×10^{-5}	2.36	3.37×10^{-6}	0.089	1.36×10^{-6}	0.036	38.99	1.44
12.810	0.0260	0.00689	5.46×10^{-5}	1.44	4.49×10^{-6}	0.118	2.23×10^{-6}	0.059	23.67	1.92
18.740	0.0350	0.03140	1.62×10^{-5}	0.43	3.99×10^{-6}	0.108	3.81×10^{-6}	0.074	6.99	1.70
25.690	0.0483	0.02919	2.40×10^{-5}	0.63	5.68×10^{-6}	0.149	3.88×10^{-6}	0.102	10.38	2.42
Feed gas contained 4.74% CO_2 -95.26% O_2 , at $n = 800$ rpm										
0.849	0.00024	0.00012	2.88×10^{-5}	0.758	0.46×10^{-6}	0.012	0.15×10^{-6}	0.004	12.45	0.19
0.896	0.00026	0.00012	3.06×10^{-5}	0.805	0.48×10^{-6}	0.012	0.16×10^{-6}	0.004	13.59	0.20
0.932	0.00027	0.00012	3.30×10^{-5}	0.868	0.48×10^{-6}	0.012	0.17×10^{-6}	0.004	14.12	0.21
0.931	0.00027	0.00009	4.29×10^{-5}	1.129	0.52×10^{-6}	0.014	0.17×10^{-6}	0.004	18.82	0.22
1.363	0.00040	0.00013	4.55×10^{-5}	1.197	0.73×10^{-6}	0.019	0.25×10^{-6}	0.007	19.30	0.31
2.674	0.00078	0.00019	5.96×10^{-5}	1.568	1.33×10^{-6}	0.035	0.48×10^{-6}	0.013	25.75	0.57
3.220	0.00094	0.00027	5.05×10^{-5}	1.329	1.52×10^{-6}	0.040	0.58×10^{-6}	0.015	21.84	0.65
3.763	0.00110	0.00028	5.69×10^{-5}	1.497	1.76×10^{-6}	0.046	0.68×10^{-6}	0.018	24.65	0.75
6.453	0.00188	0.00038	8.28×10^{-5}	2.179	3.07×10^{-6}	0.081	1.16×10^{-6}	0.031	31.04	1.31
6.872	0.00200	0.00049	5.90×10^{-5}	1.552	2.85×10^{-6}	0.075	1.23×10^{-6}	0.032	25.61	1.22
8.052	0.00233	0.00059	5.73×10^{-5}	1.508	3.20×10^{-6}	0.084	1.43×10^{-6}	0.038	24.77	1.37
21.951	0.00600	0.00248	3.50×10^{-5}	0.921	5.76×10^{-6}	0.152	3.54×10^{-6}	0.093	15.18	2.46

^aThese a values are based on Eq. (18).

Fig. 6. Values of the overall mass transfer coefficients for the CO_2 - $\text{Ca}(\text{OH})_2$ slurry reaction in the stirred tank.

groups of mass transfer coefficients were found for the backmix model and the plug flow model, in which the effluent CO_2 partial pressure p_o and the log-mean CO_2 partial pressure term were utilized, respectively. Although the mass transfer coefficients (and a values) obtained with the average pressure assumption were well behaved, they are of no utility in providing a basis for future scale-up calculations or extrapolations to other operating conditions, since they do not provide a method of accurately estimating the effluent gas partial pressure and, hence, the DF for the operation. On the other hand, the mass transfer coefficients and interfacial areas obtained from backmix and plug flow models would be useful for equipment scale-up, as can be seen from Eq. (22). If N_{CD} , V_D , k_L , and $[\text{OH}]$ are established for the contactor and alkaline slurry being used, then the physicochemical properties H , D , and k_{OH} can be calculated. With experimental knowledge of effective interfacial area, the effluent partial pressure of CO_2 and, thus, the DF can also be accurately estimated.

5.5.3 Relative mass transfer resistance

The larger mass transfer resistances ($1/K_G a = 1/Hk_{\text{LR}} a$ for liquid-phase control) observed for richer CO_2 gas mixtures appear to be primarily due to the smaller net interfacial areas obtained for the richer CO_2 gas feeds. This observation seems reasonable from both theoretical and strictly operational considerations. It has previously been noted that for lower flow rates, pure CO_2 can actually be dead-ended into the slaked lime slurry contactor. Thus, at the upper regions of the slurry, the operative interfacial area would tend to approach zero due to diminishing

CO₂ near the slurry surface. For example, $K_G a$ (based on $p_o = 1$ atm) for sorption of pure CO₂ at $n = 800$ rpm for $Q_G \approx 15$ rlm was 1.36×10^{-6} moles/(cm³-sec-atm), whereas $K_G a$ (based on log-mean p) for sorption of CO₂ from 87.5% CO₂ at $n = 800$ rpm for $Q_G \approx 15$ rlm was 3.0×10^{-6} units. However, the effluent gas for the pure CO₂ feed was 0.00026 liters/min, while the effluent gas from the 87.5% feed was 1.875 liters/min. Based on these differences in effluent gas rates, it would follow that there would be accompanying differences in the average interfacial area. That is, the pure CO₂ stream with the smaller interfacial area would encounter the larger mass transfer resistance (smaller $K_G a$).

This example seems to indicate that perhaps the appropriate interpretation of the overall gas-side mass transfer coefficients for the various feed compositions can be made by comparing the $K_G a$ values of pure CO₂ based on average partial pressure (or effluent partial pressure, since they are the same), with those calculated from other feeds based on the log-mean pressure driving force. This method is attractive since not only are the $K_G a$ values based on the average partial pressure for pure CO₂ the same order of magnitude as $K_G a$ values based on log-mean pressure for other feed compositions, but, more logically, as will be seen below in a discussion of effective interfacial area, the most reasonable values for a (from a physical standpoint) are predicted for these driving force assumptions.

5.5.4 Functionality of the overall gas-side mass transfer coefficient

For each feed gas composition, the $K_G a$ profiles appear to have the same shape. This functional similarity is most apparent for coefficients

calculated on the basis of log-mean pressure or average pressure driving force. The scatter obtained for mass transfer coefficients based on effluent pressure introduced difficulty in ascertaining the trend of that data.

The log-mean $K_G a$ values varied directly with superficial gas velocity, indicating that higher gas flow rates were accompanied by decreasing mass transfer resistance (this would be attributed to the effect of increasing interfacial area).

The trend for the overall mass transfer coefficient at very low flow rates would appear to be towards asymptotically increasing values. This may be seen by analysis of Eq. (20) as $p_{DF} \rightarrow 0$:

$$N_{CD} = K_G a V_D p_{DF} \quad (20)$$

It has already been noted that p_o can be driven essentially to zero for a pure CO_2 feed by operation at a flow rate of less than 10 rlm at $n = 1700$ rpm (see Fig. 4). Thus, for the backmixed model with N_{CD} , V_D , and a having finite values and $p_o \rightarrow 0$, $K_G a$ must approach an infinite value. For the same dead-ended operating conditions, it can also be argued that as $p_o \rightarrow 0$, p_{DF} also approaches 0 provided the plug-flow assumption is made [i.e., $p_{DF} = (p_I - p_o) / (\ln p_I / p_o)$]. Again as $p_{DF} \rightarrow 0$, $K_G a \rightarrow \infty$.

The interpretation of the variation in $K_G a$ as the flow rate, Q_G , was decreased for feed gases containing any amount of O_2 is more complicated. In order to achieve very high DFs, and thus very low effluent CO_2 partial pressures, for these feeds it was necessary to operate at reduced Q_G conditions. Thus, N_{CD} was reduced both by the lower total gas rate and further by the percentage of feed gas that was CO_2 . The result was that

no operating conditions were obtained at which the $K_G a$ values, based on the plug-flow model, were calculated to increase as Q_G decreased. For a few cases of low Q_G values, the calculated $K_G a$ values, based on the backmix model, were observed to increase as Q_G decreased (Table 7).

More importantly, however, it can be argued that, at least theoretically, a range of low Q_G values could be reached at which all the CO_2 was removed from the CO_2 - O_2 feed gas; thus p_{DF} based on either the backmix or plug flow model would approach 0, and by previous arguments concerning p_{DF} in Eq. (20), $K_G a$ would begin to increase asymptotically.

5.5.5 Interfacial area calculated from chemical reaction model

The effective interfacial areas were calculated (see Table 7 and Fig. 7) from the theory of gas absorption accompanied by fast pseudo-first-order reaction, as stated by Eq. (22):

$$N_{\text{CD}} = \alpha H V_D p_{\text{DF}} (Dk_{\text{OH}}[\text{OH}] + k_L^2)^{0.5} \quad (22)$$

According to the assumptions outlined previously, for the CO_2 - $\text{Ca}(\text{OH})_2$ system the term describing the chemical reaction mass transfer coefficient, $Dk_{\text{OH}}[\text{OH}] + k_L^2$, was essentially constant during the constant rate period. Thus, the interfacial area would vary primarily according to the impeller speed n and the gas flow rate Q_G . The effective interfacial areas calculated from the perfectly backmixed assumption would appear to be physically too large; that is, they do not agree with interfacial areas that have been measured for agitated tanks by means other than a chemical reaction method (Morris's¹⁸ values were $\sim 1.3 \text{ cm}^2/\text{cm}^3$, as obtained by physical techniques). The effective interfacial areas calculated from a plug-flow assumption agreed favorably with those obtained by physical techniques.

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Fig. 7. Values of the interfacial areas calculated from the fast pseudo-first-order reaction model, Eq. (22), compared with those calculated from physical data, Eq. (29), at $n = 800$ rpm.

Interfacial area values predicted by the standard literature correlations (Miller³⁴) for our operating conditions were calculated from Eq. (29) and are also shown in Fig. 7. It is of considerable interest to compare the values predicted by these correlations, which were derived from physically measured areas, with those calculated from our system based on a chemical reaction model. From Eq. (29), for $n = 800$ rpm, the interfacial area was predicted to increase from 1.7 to $3.0 \text{ cm}^2/\text{cm}^3$ as the gas flow rate increased from 5 to 20 rlm (approximate values). From Table 7, it can be seen that for 87.5, 33.6, and 4.74% CO_2 feed gases, the interfacial area based on a log-mean pressure driving force was calculated to vary from 1.0 to $2.5 \text{ cm}^2/\text{cm}^3$. This is surprisingly good agreement between two independent methods of determining a reaction parameter. Because the log-mean driving force could not be satisfactorily calculated for the cases of pure CO_2 feeds, it was necessary to utilize the average pressure (influent and effluent $p = 1 \text{ atm}$) to determine the interfacial area. Overall, interfacial areas for the pure CO_2 feeds were smaller than those for the other feeds, a trend which has previously been discussed as reflecting the shrinkage of the gas stream which occurred for pure CO_2 feeds.

It should be noted that a number of investigators (Reith,²⁹ Mehta,²³ Westerterp²⁵) have reported values of interfacial area in aerated, agitated tanks, based on assumptions for backmixed systems, which ranged from 2 to $30 \text{ cm}^2/\text{cm}^3$. However, the backmixed model appears to fail drastically at the low flow rates of this study. This effect is readily apparent from the data of Table 7. For any feed gas containing O_2 , the

backmix model predicted an increase in a as Q_G decreased in the low Q_G regime. Such an increase would appear to contradict the physical conditions.

The log-mean estimates for interfacial areas for our data do not increase by the same factor as that predicted by the Miller correlation, Eq. (29), which predicts interfacial area as a function of impeller speed (and other parameters). This disagreement may arise because the log-mean estimate is based on a chemical reaction model while Miller's correlation is based on physically determined interfacial areas.

Because of their averaging characteristics, it would appear that the effective interfacial area values calculated for the log-mean pressure term are the most representative of the actual physical operation of CO_2 - $\text{Ca}(\text{OH})_2$ reaction in agitated tanks. According to Fig. 7, the log-mean interfacial areas were found to increase directly with an increase in gas velocity. Also, comparison of the sorption rates of pure CO_2 at equal gas flow rates but at impeller speeds of 800 and 1700 rpm indicates that a varies directly with n . And of particular interest is the observation that for feed gas compositions varying from 87.5 to 4.74% CO_2 , the log-mean interfacial areas were predicted to be about the same at equal total gas flow rates (Fig. 7).

The significance of this trend can be appreciated from inspection of Eq. (22). If an empirical relationship for a range of feed compositions could be derived for interfacial area as a function of total gas velocity (or for scale-up, more appropriately, a nominal holding time, V_D/Q_G), then as previously noted, given a rate of N_{CD} to be removed from a large gas

stream per second, utilizing standard methods for estimation of H , D , k_{OH} , and k_L , and knowing the alkaline reactant to be used (OH), the p_{DF} and, thus, the overall DF could be predicted in a scale-up operation.

5.5.6 Final conclusions about the overall gas-side mass transfer coefficient and the effective interfacial area

In the previous study most similar to ours, Morris chose to consider the sorption of CO_2 by $Ca(OH)_2$ in an agitated contactor on a micro basis; that is, rather than considering the overall mass transfer coefficients, he analyzed the mass transfer during the life of a gas bubble as it passed through the contactor. Thus, it was concluded that the constant rate period was governed by the gas phase diffusion and that the removal of CO_2 from the bubble could best be described as a first-order process with respect to CO_2 concentration. This first-order decay of CO_2 in the bubble was described by:

$$\frac{C_I}{C_0} = e^{-K_1 \theta} \quad (32)$$

The gas-side mass transfer coefficient was calculated from Eq. (32). However, the values obtained by this technique are not readily comparable to the overall mass transfer coefficient obtained by our Eq. (17). Further, since the DF curves in our Fig. 4 appear to approximate an exponential function, efforts were made to fit the data of Fig. 4 by Eq. (32). However, the exponential function will not adequately describe the DF vs Q_G curve over the entire Q_G range, failing at both high and low Q_G values.

The other literature study that is most related to our experiments is the work of Mehta and Sharma,²³ which has been extensively utilized in

previous arguments. That work proposes that CO_2 absorption into alkaline solutions in agitated tanks can be adequately described by the fast pseudo-first-order reaction theory. In particular, Mehta proposed that CO_2 sorption into alkaline solutions over a wide range of conditions was almost totally liquid-phase-controlled.

There is general agreement among Mehta and Sharma and the other very limited, relevant literature reports that the gas flow, for high impeller speeds ($n > n_0$), has no effect on the interfacial area and the true liquid-side mass transfer coefficient. However, in the experiments of Mehta and Sharma, virtually all of the data on interfacial area and the true liquid-side mass transfer coefficient were obtained for gas superficial velocities >2 cm/sec. Most of our data was obtained for superficial velocities <1 cm/sec (20 rlm). Inspection of Figs. 6 and 7 indicates that for superficial velocities >2 cm/sec, the trend is toward reduced dependency of the interfacial area and the overall gas-side mass transfer coefficient on gas velocity. Furthermore, it should be remembered that the presence of two different solids, Ca(OH)_2 and CaCO_3 in our gas-slurry reaction system was likely to complicate agreement between the relationships obtained in our experiments and those of other studies without slurries, when a is expressed as a function of n and Q_G .

In one experiment of particular interest to our ongoing efforts, Mehta investigated the sorption of CO_2 from lean mixtures into 0.1 M Ba(OH)_2 solutions (below the limit of solubility at 21°C). It was concluded that this system could be described by the fast pseudo-first-order theory which was utilized to study the effect of solid BaCO_3 , as a product of the CO_2 - Ba(OH)_2 reaction, upon the interfacial area. In

scoping studies using $\text{Ba}(\text{OH})_2$ slurries to sorb CO_2 from lean mixtures, we have obtained DFs for $\text{Ba}(\text{OH})_2$ at a given gas flow rate which were three to five times greater than those obtained with $\text{Ca}(\text{OH})_2$. According to Eq. (22), the increased DFs with the $\text{Ba}(\text{OH})_2$ - CO_2 system would have been predicted because $\text{Ba}(\text{OH})_2$ was 20 times more soluble than $\text{Ca}(\text{OH})_2$ at standard operating conditions. Further studies are underway to determine whether the plug flow or backmixed assumption best describes the CO_2 - $\text{Ba}(\text{OH})_2$ reaction in a stirred tank.

It would be easy to question our statement (as confirmed by Mehta and Sharma²³) that overall the mass transfer control is in the liquid-phase coefficient, $k_{\text{LR}}a$ (particularly in the interfacial area portion), as compared to Morris's conclusion that the control is in gas diffusion in the bubble and not in the resistance to transfer across the bubble-liquid interface. Without attempting to reconcile Morris's micro bubble-to-liquid mass transfer analysis with our macro overall-mass-balance analytical approach, it is worthwhile to point out that there are a number of striking similarities in the data and conclusions of our work and Morris's work.

First, both analysis methods indicated that for the CO_2 - $\text{Ca}(\text{OH})_2$ reaction in an agitated tank, the flow pattern was best described by plug flow. Also, the conversion for similar gas compositions, impeller speeds, and hydrodynamic conditions agreed very well. Hence, our calculated overall gas-side mass transfer coefficients for similar conditions are also in good agreement with those calculated from Morris's data.

The real test of any model that is proposed to describe the absorption of CO_2 from gas mixtures into alkaline slurries in agitated tanks will

occur when there are changes in operating conditions, such as temperature, impeller speed, hydroxide species, etc. It is believed, based on all prior discussions and the literature, that the pseudo-first-order chemical reaction-gas absorption theory has the flexibility to be applied to a wide range of parametric variations.

5.6 Fixation of Carbon Dioxide with Continuous Flow of Both Gas and Slurry

The results of Fig. 8 (and Table 8) were obtained for a commercial lime that had undergone aging and clumping due to exposure to air. Hence, the effective molarity (in the absence of milling for particle reduction) of the slurry, which was assumed to be 1.0 *m*, was actually only 0.6 to 0.7 *m*. Thus, the results must be carefully interpreted according to the effective slurry concentration because, for CO₂ flow rates where 99.9% of the CO₂ was removed, the conversion curve for the slurry would obviously be shifted downward for a nearly pure Ca(OH)₂ slurry. For example, at $Q_{CD} = 7.0$ rlm, the mass transfer rate was $N_{CD} = 0.29$ g-moles/min. Then $Q_{SL} (C_{SL,I} - C_{SL,O}) = 0.29$ and for a fixed Q_{SL} , a considerably lower conversion would be observed for a 1.0 *m* slurry than that for a 0.6 *m* slurry.

The results of Fig. 8 do serve to indicate that the gas-lime slurry contactor can be easily operated with continuous flow of both gas and slurry. In the limited studies conducted for continuous flow of the lime slurry (along with normal continuous gas flow), there was evidence, although not conclusive, that for the continuous flow mode the contactor could be operated to achieve as much as 99% conversion of the Ca(OH)₂.

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Fig. 8. Sorption and fixation of CO_2 with both the feed gas and the $Ca(OH)_2$ slurry in continuous flow.

Table 8. Fixation of pure CO₂ with a 0.6 M slurry feed, using the gas-lime slurry contactor with both gas and slurry in continuous flow

Influent CO ₂ flow rate, Q _{CD} (liters/min)	$\frac{F_I - F_O}{F_T}$ (% conversion)	Slurry flow rate, Q _{SL} (liters/min)	$\frac{C_{SL,I} - C_{SL,O}}{C_{SL,I}}$ (% slurry conversion)	Impeller speed n (rpm)
2.97	>99.9	0.84	33	800
6.92	>99.9	0.80	62	800
7.00	>99.9	0.80	62	800
11.18	99.6	0.80	80	800
13.35	99.5	0.80	98	800

This can be compared with the batch reaction in which only ~90% conversion was feasible before the gas absorptive rate began to decrease significantly. However, taking into consideration the uncertainties in the quality of lime and also possible discrepancies in the slurry assays, judgment will be reserved on the observation that superior slurry conversion occurs in the continuous slurry flow mode. Future studies into CO₂ fixation with lime slurries should entail further in-depth experimentation and analysis of continuous slurry flow. It would be particularly intriguing to fix the gas flow rate for a condition of 0.50 conversion and then study the effect of varying the slurry composition and flow rate on this conversion. Such experiments would elucidate the effect of increased slurry flow rate on the interfacial area for mass transfer.

5.7 Lime Quality and Assay

As noted previously in Sect. 4.2, in addition to Fisher reagent-grade lime, commercial slaked limes from three different sources were also studied. Comparison of the commercial supplies was complicated by recent changes (fortunately favorable) in the quality control of the bulk slaked lime. In 1976, a Tennessee state law was enacted requiring that all commercial manufacturers of hydrated lime retailing in Tennessee include with their product (usually by bag labeling) both accurate chemical analyses and particulate classification. According to a personal communication with production control personnel at Williams Lime Co., Knoxville, the contents of any bag not bearing these guaranteed analyses was either likely to be too old to maintain its quality (1 year or more) or may not initially have been a guaranteed grade.

Our inquiries into the question of quality control were precipitated by analyses of commercial limes, such as those shown in Table 9. The quality of these stocks are obviously inferior. Supplies A-1, A-2, and B-1 assayed ~50% carbonate. Only supply A-3 evidenced any significant amount of Ca(OH)_2 . It was not clear what compounds comprised the bulk of the commercial limes of Table 9, but it was obvious that none of those commercial grades would have been suitable for CO_2 fixation. Due to the recent imposition of the stringent controls on the bagged commercial limes, the lime stocks obtained during the past year which bear the guarantee that at least 90% of the weight is Ca(OH)_2 have been found to meet the required standards.

Table 9. Analysis of commercially available slaked limes prior to initiation of guaranteed labeling

Source	Weight percent					
	HCO_3^-	OH^-	CO_3^-	Mg	Ca	SO_4
Company A-1 ^a		13.3	47.9	0.23	48.4	0.17
Company A-2 ^a	15.9		49.9	0.27	42.6	0.28
Company A-3 ^b		42.0			53.0	
Company B-1 ^a		4.0	55.0	0.19	48.0	0.16

^a Nonguaranteed.

^b Guaranteed analysis.

It was observed that prolonged exposure of even 90% pure slaked limes to air and water vapor resulted in clumping and aggregation of the hydrated

lime powder. Apparently, the Ca(OH)_2 reacted with CO_2 in the room air to initiate the formation of CaCO_3 , which then impeded suspension of the lime slurry. A reasonable hypothesis is that the CaCO_3 forms as a slight film on the surface of the Ca(OH)_2 particles. When this partially carbonated lime is slurried, the CaCO_3 acts as a deterrent to the dissolution of the Ca(OH)_2 particles during agitation in the contactor. Data indicated that the extent of CaCO_3 precoating of Ca(OH)_2 particles effected a proportional reduction in the quantity of Ca(OH)_2 available for dissolution and reaction with CO_2 . That is, an exposed lime, which would assay 80% Ca(OH)_2 after grinding, would react without grinding as if it were only 60% Ca(OH)_2 due to the interference of the CaCO_3 coating. Hence, a considerable amount of the Ca(OH)_2 , not yet converted to CaCO_3 , would be lost if the lime slurry were discarded when it appeared that the rate of reaction was decreasing due to insufficient Ca(OH)_2 . Thus, a premium is placed on maintaining fresh slaked lime. The best quality slurries (those which assayed to be equal to reagent-grade Ca(OH)_2) were formed from freshly opened bags of hydrated lime. The unused lime was then stored in plastic bags to prevent excessive exposure to air. The effect of the exposure to air could be considerably negated by ball-milling lime, which had been exposed to air for several days, and sieving the resultant powder through No. 10 Tyler standard sieve screens, thus producing a hydrated lime powder that formed an acceptable milk of lime slurry.

Bulk quantities of hydrated lime of an acceptably high quality could be obtained from the local vendor, Williams Lime Co. Their product is now guaranteed to contain at least 90% Ca(OH)_2 , with 90% of the particles passing through a 300 mesh screen. This lime gave CO_2 absorption rates

(see Sect. 5.8.2) that were indistinguishable from those observed for reagent grades of Ca(OH)_2 . However, because the Ca(OH)_2 content of the commercial limes was only 90 to 95% that of the reagent-grade lime, the fixation reaction with the commercial limes normally lasted some 5 to 10% less total time than that observed for an equal weight of pure Ca(OH)_2 .

5.7.1 Effect of lime quality on fixation rates

Several runs were made to ascertain the effects on the CO_2 fixation rate of such parameters as lime purity, slurry temperature, and lime concentration in the slurry. The effect of lime purity on fixation rates, which was mentioned in the preceding section, is indicated in Tables 5 and 10. In the first four runs of Table 5 for a total gas flow rate of ~ 0.9 rlm, there is little difference in the mass transfer rates [~ 0.00027 g-moles/(liter-min)] observed for either commercial- or reagent-grade lime slurries.

5.8 Effect of Temperature on Fixation Rate

The fixation rate of pure CO_2 into the agitated lime slurry was essentially unaffected by the variation in slurry temperature, as shown by a comparison of runs 2 and 3 of Table 10. The rate for 8.65 rlm at a slurry temperature of 21°C was 0.0540 g-moles/(liter-min), whereas the rate for the same flow rate at 46°C was 0.0535.

It is informative to determine whether the theoretical model utilized in Sect. 2.5.2 to describe the CO_2 - Ca(OH)_2 reaction adequately described the effect of temperature change on the net mass transfer rate. The model was given by Eq. (22):

Table 10. Fixation of pure CO₂ as a function of such parameters as lime quality and slurry temperature

Influent CO ₂		Superficial gas velocity:	Effluent CO ₂ ,	Mass transfer rate, constant	(F _I -F ₀)/F _I (% conversion)	Decontamination factor	Impeller speed	Impeller
Q _{CD} (liters/min)	F _I (moles/min)	U _G (cm/min)	F ₀ (g-moles/min)	period, N _{CD} (g-moles/liter-min)		(F _I /F ₀)	n (rpm)	diam/blades
7.23	0.301	24.0	0.1400	0.0240	54.00	2	500	3-4
8.65 ^a	0.361	28.7	0.0016	0.0540	99.56	226	800	4-6
8.65 ^b	0.361	28.7	0.0023	0.0535	99.36	157	800	4-6
13.21 ^c	0.550	43.9	ND ^d	0.0820	>99 ^e	ND	1750	3-4
17.41 ^f	0.726	57.8	ND	0.1084	>99	ND	1750	3-4
5.46 ^{f,g}	0.227	18.1	ND	0.0338	>99	ND	800	4-6
12.45 ^{f,g}	0.519	41.4	ND	0.0774	>99	ND	800	4-6
12.45 ^{f,g,h}	0.519	41.4	ND	0.0774	>99	ND	800	4-6
12.45 ^{f,g}	0.519	41.4	ND	0.0774	>99	ND	1500	4-6
5.45 ^{f,g,i}	0.227	18.1	ND	0.0338	>99	ND	800	4-6

^a slurry temperature of 21°C.

^b slurry temperature of 46°C.

^c 2 m initial slurry.

^d ND - not determined.

^e >99 indicates runs in which F₀ was not precisely determined.

^f Commercial lime, Williams Lime Co., Knoxville.

^g Settling rate studies.

^h Slurry temperature of 46°C.

ⁱ Reduced flow rate, slurry temperature at 46°C.

$$N = aHV_D P_{DF} (Dk_{OH}[OH] + k_L^2)^{0.5} . \quad (22)$$

The temperature was increased from 21 to 46°C over the reaction time; thus, it was necessary to use an average $T = 34^\circ\text{C}$ for the slurry during the reaction. For a temperature increase from 21 to 34°C, the hydroxyl ion concentration, due to the decreasing solubility of $\text{Ca}(\text{OH})_2$, was found (by pH measurement) to decrease from 0.032 M to ~ 0.01 M. However, for the same temperature change, the rate constant k_{OH} was calculated to increase from 6000 to $\sim 18,000$.

Apparently, the change in solubility was offset by the rate constant change, and any changes in the solubility constant H was compensated by other parameter adjustments (e.g., by a); hence, the net mass transfer rate was not significantly affected by the temperature change. Inspection of Eq. (22) indicates that the expression does accurately predict these compensating variable changes.

5.9 Effect of Slurry Concentration on Fixation Rate

Under the appropriate operating conditions, slurries containing as much as 1.5 *m* $\text{Ca}(\text{OH})_2$ could probably be used without a significant detrimental effect on the average mass transfer rate. The constraints on operating at slurry concentrations >1.5 *m* arose due to a phase phenomenon observed during routine runs with streams containing $>90\%$ CO_2 and flowing at >15 rlm into the slurry agitated at speeds <1000 rpm. During the constant rate period, the slurry passed through a bulking phase marked by a pasty appearance, and it seemed that much of the slurry water had become incorporated into the solid phase. One result of this variation

in the density and viscosity of the slurry, and thus disruption of mixing, was a slight transient increase in effluent CO_2 concentration. The reduction in slurry mixing could be counteracted by a short-term increase in impeller speed. Since the bulky phase lasted for only about one-third of the total reaction time and the CO_2 loss was relatively small, the overall effect on the CO_2 removal rate was minimal with a 1.0 *m* concentration. However, the mass transfer rate was considerably more affected when the initial slurry concentration was 2.0 *m*. Finally, it should be stressed that this bulky, pasty phase was insignificant for gas streams that contained <90% CO_2 at any flow rate or for pure CO_2 at flow rates <15 rlm.

5.10 Calcium Carbonate Product Settling Rates

Several runs were made to determine which parameters have the greater effect on the settling characteristics of the CaCO_3 product (see the last five runs of Table 10). All these runs were made with the same commercial lime. For the parameter ranges studied in the five runs, the minimum settling rate of 0.083 cm/min was found for the control study (indicated by curve 1 of Fig. 9), for operating conditions of 12.5 rlm pure CO_2 , $n = 800$, and slurry temperature = 22°C in the standard 6.7-liter, 7.1/2-in.-ID stirred contactor. When the gas flow rate was decreased, with the other parameters held constant, the settling rate always increased. This behavior is shown by curve 2, Fig. 9, in which a settling rate of 0.508 cm/min is indicated for a product produced by the fixation of a 5.5-rlm gas flow rate. The settling rate for the CaCO_3 produced by the fixation of a 5.5-rlm stream is, thus, approximately six times as fast as the rate observed for the product produced from the 12.5-rlm stream. When the only

Fig. 9. Effects of such operating parameters as gas feed rate, temperature, and agitation speed on the product (CaCO_3)-slurry settling rate.

variable changed was temperature, the settling rate for the CaCO_3 produced by the fixation of a 12.5-rlm stream at 46°C was 0.140 cm/min (curve 3). Thus, an increase in slurry temperature of 24°C resulted in a 170% increase in settling rate. An increase in the impeller speed to 1500 rpm, as compared with the control speed of 800 rpm, resulted in an increase in settling rate to 0.192 cm/min (curve 4). The settling rate was thus increased by a factor of ~ 2.3 . Finally, a run was made with both reduced gas flow rate, 5.5 rlm, and increased slurry temperature, 46°C (no change in agitation). The settling curve for these conditions is shown as curve 5 in Fig. 9 and is found to have the maximum slope, 0.83 cm/min, of all the operating curves produced.

The products from runs 2 and 5 of the settling studies (these were the control run and the run for reduced flow rate and increased temperature, respectively) were treated and observed by scanning electron microscopy at a magnification of 2300X. The results of these microscopic examinations were somewhat difficult to interpret. The ambiguities could well have been the result of the manner in which the samples were treated in preparation for examination. In any case, the particle size range was similar for each sample, with the slower settling control showing a size range of 0.2 to 6μ and the faster settling sample showing a size range of 0.2 to 4μ , with a smaller maximum limit. Although extensive statistical studies would likely be necessary to thoroughly characterize the particulate differences for the two samples, it was superficially noted that the particles of the control were less spherical and more heterogeneous than the particles of the faster settling sample.

If the results of the settling studies are considered in a simplistic macroquality manner, thereby circumventing the extensive studies required to explain the intricacies and complexities of particle nucleation and growth, the data shown in Fig. 9 apparently are not surprising. That is, the production of regular, homogeneous, and more dense particles seems to be logically enhanced by increased agitation, increased temperature, and reduced gas flow rate. Of course, the choice of a particular set of operating conditions that would yield a product of maximum settling rate would always have to be balanced by considering the necessity of achieving maximum gas mass transfer rates in the fixation process.

5.11 A Question of Carbonate Scale Buildup

In actual plant operation, the contactor would be maintained essentially in continuous use, either with continuous lime slurry flow or with semi-batch operation, so that there would be no routine cleanup of scale deposits after each batch operation, as practiced in the bench-scale studies. A limited study was conducted into the effect of prolonged carbonate scale accumulation on the fixation rate. The operating conditions consisted of pure CO_2 at a flow rate of 11 rlm, an impeller speed of 800, a slurry temperature of 22°C , and a slurry concentration of 1.0 m. After ten consecutive runs over a period of 2 days, there was observable scale buildup on the inner walls of the contactor and on the cooling coil. However, all runs showed essentially the same CO_2 fixation rate, indicating no interference by the scale deposits with the mass transfer process. Although there would be scale accumulation on the inner surfaces of the contactor during continuous use, it is probable that the violent fluid

shearing action produced by the impeller, and the continued exposure of the carbonate scale to CO_2 gas [a reaction which produces more soluble $\text{Ca}(\text{HCO}_3)_2$], would allow for long operating times before this accumulation would significantly interfere with CO_2 fixation.

6. SCALING-UP THE PROCESS

6.1 Background Scale-up Criteria

Recently in Chemical Engineering,³⁶ a series of 11 papers was published describing the procedure for scaling-up mixing and mass transfer processes in mechanically agitated tanks. That review of design considerations included all basic operational criteria and parameters, such as impeller design (geometry and material), drive-train selection, design of shafts and seals, power input, etc.

Geometric similarity is the most familiar and important similarity concept applied in agitation problems. When geometric similarity is applied to the scale-up operation, the design of full-scale process equipment is based on directly proportional linearity to the bench-scale model. It is necessary that each component of the contactor be related by the same ratio regardless of the equipment scale; for example, the ratios of impeller diameter to tank diameter, impeller blade dimensions to the impeller diameter, and height of the impeller to the height of the liquid must all be the same regardless of tank size. Consequently, if the tank is five times the diameter of the bench-scale model, then a turbine is required that is also five times the diameter of the original turbine.

Kinematic and dynamic similarity are the two most common forms of mechanical similarity that can be maintained in agitated contactor scale-up operations. In order to ensure kinematic similarity, ratios of corresponding times or velocities are held constant for each increase in equipment size. Dynamic similarity is obtained by requiring fixed ratios of corresponding forces, such as inertial, viscous, or gravitational forces. In scale-up calculations, it is often not possible to maintain both kinematic and dynamic similarity. This inability sometimes leads to confusion concerning the application of similarity scaling concepts. It should be noted, however, that neither kinematic nor dynamic similarity is essential since the objective of scale-up is to duplicate process results.

One example of maintaining two types of similarity for the same scale-up operation is in the provision of turbulent agitation. For turbulent agitation, it can be shown by fundamental and experimental analysis that the dimensionless-velocity distribution becomes constant; thus, it follows that fixed ratios exist between correspondence velocities. As a result of such mechanisms, geometric similarity can be accompanied by kinematic similarity.

6.2 Geometric and Kinematic Similarity

According to Valentin,³⁰ scale-up can be based on maintenance for any size contactor of (1) constant superficial velocity, (2) constant volumetric flow rate per unit contactor volume, or (3) constant power input per contactor volume. The first two criteria are basically combinations of geometric and kinematic similarity, and thus provide information based

on the bench model, which suggests the dimensions of the scaled-up contactor. From the third criterion, information is obtained concerning the specifications for large-scale impeller speed, impeller size, and power and drive train. There are various other criteria that can be utilized to scale-up the standard stirred-tank operation; for example, provision of constant "tip speed," equal solids suspension, equal liquid motion, etc. The scale-up technique that is discussed below was based on the combination of geometric similarity with each of the two candidate kinematic similarity concepts — constant superficial velocity or constant volumetric flow rate per contactor volume. The ranges of contactor sizes bracketed by the two different velocity similarity concepts should allow for sufficient design flexibility. Power equipment size for all cases was based on equal power input per contactor volume.

Now, for geometric similarity and equal power inputs per volume, it can be shown that the larger-scale impeller speed is simply related to the geometric scale-up factor and the bench-scale impeller speed.³⁶ For geometric similarity, the relative magnitudes of all linear dimensions between large and small scale are defined by a simple scale ratio, S_c ;

$$S_c = \frac{d_{T2}}{d_{T1}} = \frac{W_{B2}}{W_{B1}} = \frac{h_{T2}}{h_{T1}} \quad (33)$$

Also, it follows that

$$S_c = \left(\frac{V_{R2}}{V_{R1}} \right)^{1/3} \quad (34)$$

From Eq. (26), the power input can be described as:

$$P_A \propto n^3 d_I^5 \quad (35)$$

Because length ratios are constant in geometric similarity, tank dimensions are a fixed multiple of impeller diameter, or

$$V_R \propto d_I^3. \quad (36)$$

When Eqs. (35) and (36) are combined, the expression for equal power per volume is:

$$\frac{P_A}{V_R} \propto n^3 d_I^2, \quad (37)$$

or

$$n_1^3 d_{I1}^2 = n_2^3 d_{I2}^2.$$

Finally,

$$n_2 = n_1 \left(\frac{d_{I1}}{d_{I2}} \right)^{2/3}. \quad (38)$$

6.3 Scale-Up for this Study

In Table 11 are shown the results of scale-up calculations for the fixation process, based on the bench-scale fixation of CO_2 in the agitated gas-lime slurry contactor. The bench-scale data that are shown were chosen to represent the extremes of high and low gas flow rates which were studied, so that the extremes of DFs would be presented. The calculations shown for scale-up are based on equalizing both the superficial velocities, Q_G/S , and the volumetric flow rates per unit volume, Q_G/V_R . Total off-gas flow for the large-scale process was taken to be 5.7×10^3 liters/min, or ~ 200 g-moles CO_2 /min, which is approximately equal to the KALC off-gas stream for a HTGR fuel reprocessing plant handling 108 MTHM/day.

Table 11. Calculations for scale-up of the bench-scale gas-liquid slurry contactor

Case	Gas flow Q_G (liters/min)	Bench-scale CO_2 molar effluent, F_0 (g-moles/min)	Bench-scale CO_2 effluent mole fraction Y_{CD}	Decontamination factor (F_I/F_0)	Scale factor S_c (r_2/r_1)	Scaled-up radius r_2 (cm)	Scaled-up volume V_R (liters)	Scaled-up impeller speed n (rpm)	Scaled-up power required P_{MS} (hp)	Electrical power costs per 250 day-year (thousands of dollars)
Scale-up based on constant residence time and equal power/volume; 87.5% CO_2 -12.5% O_2 gas										
1	3.02	0.000031	0.0019	3548	12.21	120	12,200	150	300	33.6
2	5.30	0.00011	0.0040	1753	10.11	99	6,943	171	120	13.4
3	17.61 ^a	0.00646	0.0700	99	6.8	66	2,087	223	47	5.3
4	17.61	0.00646	0.0700	100	9.2	90	4,578	182	24	2.7
Scale-up based on constant superficial velocity and equal power/volume; 87.5% CO_2 -12.5% O_2 gas										
5	3.02	0.000031	0.0019	3548	43.6	427	489,000	64	14,000	1500.0
6	5.30	0.00011	0.0040	1753	32.7	320	206,000	78	5,916	689.0
7	17.61	0.00646	0.0700	100	18.0	176	34,200	117	888	99.0
Scale-up based on constant residence time and equal power/volume; 4.74% CO_2 -95.26% O_2 gas										
8	0.85	0.000042	0.000125	398	9.8	96	5,600	174	150	16.8
9	3.22	0.000240	0.00027	265	6.3	62	1,480	235	35	3.9
10	8.05	0.000187	0.00059	85	4.6	45	590	290	12	1.3
11	21.95 ^b	0.002160	0.00248	20	3.3	33	216	359	3	0.3
Scale-up based on constant superficial velocity and equal power/volume; 4.74% CO_2 -95.26% O_2 gas										
12	0.85	0.000042	0.000125	398	28.9	283	140,000	85	4,277	478.0
13	3.22	0.00024	0.00027	265	14.9	146	19,400	132	567	63.0
14	8.05	0.000187	0.00059	85	9.4	92	4,890	180	134	15.0
15	21.95	0.00216	0.00248	20	5.7	56	1,102	251	26	3.0
Scale-up for 100-scfm air containing 0.000315 m.f. CO_2 comparable residence time and equal power/volume										
	15.00	2.1×10^{-6}	0.00000315	100	7.1	70	2,154	215	40	4.5

^aFlooding of impeller.^bNear flooding.

Note: Large-scale flow rate for the 87.5% CO_2 gas was taken to be 200 scfm (representative of typical fuel reprocessing). The large-scale flow rate for the 4.74% CO_2 gas was then set at 25 scfm to represent essentially the oxygen stream that would result from 90% removal of CO_2 from initial stream.

The differences in the sizes of contactor predicted by each type of velocity scaling are explained as follows. According to the concept of equal superficial velocities,

$$\frac{Q_{G1}}{S_1} = \frac{Q_{G2}}{S_2} . \quad (39)$$

However, if equal volumetric flow rates per contactor volume are maintained,

$$\frac{Q_{G1}}{S_1 h_{T1}} = \frac{Q_{G2}}{S_2 h_{T2}} . \quad (40)$$

Thus, the quantities are equal only if the height of the second contactor is equal to that of the first. But such a restriction would result in an unrealistic tank geometry for the large contactor and would violate geometric similarity for both the impeller design and liquid height relative to tank diameter. On the other hand, if the h_{T2}/d_{T2} ratio is made equal to the h_{T1}/d_{T1} ratio, geometric similarity is maintained, but the volume of the second tank becomes obviously too large. That is, the holding time for the larger tank is greater than that of the first by the ratio h_{T2}/h_{T1} .

One method of resolving this contradiction is simply to equate the Q_G/V_R values for both contactor sizes and then to provide geometric similarity by allowing part of the volume increase for the larger tank to be contributed by the greater height necessary to maintain this similarity. For example, if the higher flow rate for scale-up is 100 times that of Q_{G1} , then V_{R2} must be 100 V_{R1} . If only the superficial velocities are held constant, then $d_{T2} = 10d_{T1}$ and $h_{T2} = h_{T1}$. However, if $V_{R2} = 100V_{R1}$

where $V_{R2} = \frac{\pi d_{T2}^2}{4} (d_{T2})$ (for liquid height about equal to tank diameter), then $d_{T2} = 4.64 d_{T1}$ and $h_{T2} = 4.64 h_{T1}$. The criterion of scale-up with equal superficial velocities and liquid height equal to tank diameter would probably lead to overcapacity for the large-size tank. The criterion of scale-up with equal Q_G/V_R values could lead to insufficient true residence times, since there is little evidence to indicate that such scaling predicts the residence time accurately for a perfectly backmixed tank. It is likely, however, that the correct tank size would be somewhere between the values predicted by the two velocity ratio equalization guidelines.

The gas compositions presented in Table 11 were selected as those most representative of the KALC off-gas process; that is, the initial off-gas composition of ~90% CO_2 -10% O_2 is represented by 87.5% CO_2 , whereas a product stream that could result from a first treatment of the initial 90% CO_2 stream is represented by the 4.74% CO_2 -95.26% O_2 gas. This 4.74% CO_2 stream could then serve as feed to a second stage of contacting in the event that staging was determined to be necessary to achieve very high cumulative DFs ($>10^4$).

For cases 1 through 4, projected equipment size was calculated for delivery of DFs ranging from 3500 to 100. It should be noted here that for a total flow rate of 200 g-moles CO_2 /min, the 12,000-liter tank of case 1, if operated in a semibatch mode, could only be utilized for ~50 to 60 min, at which time the 1.0 m slurry would be depleted. This factor should be remembered when batch operation is under consideration, since such operation would obviously necessitate that two or three of these tanks be utilized in a sequence of reacting, unloading, refilling

with fresh slurry, etc. However, the alternate and more practical mode of continuous slurry flow has already been discussed and has been shown to be very reasonable.

When the scale-up of the contactor for fixation of 90% CO_2 -10% O_2 gas was based on maintaining Q_G/S ratios, obviously much larger full-scale tanks were calculated; for example, to deliver a DF of 100, a tank of 4578 liters was calculated for equal Q_G/V_R ratios, whereas a tank of 34,200 liters was calculated for equal Q_G/S values. The two major disadvantages of very large gas-lime slurry contactors are: (1) space requirements in a reprocessing plant, and (2) power costs to operate the impeller. The power costs for operating the various size contactors at the appropriate impeller speeds were calculated assuming 24-hr operation for 250 operating days per year, at a cost of \$0.025/kWhr.

The likelihood of flooding (short-circuiting or plug flow of gas without sufficient stirring) the impeller was greater when the cross-sectional area was restricted by maintaining equal Q_G/V_R values during scale-up from high bench-scale flow rates (and low DFs). When scale-up for both feed gases of 87.5 and 4.74% CO_2 was based on providing equal Q_G/S ratios, the tank size predicted for DFs of $\sim 10^3$ or greater was obviously prohibitive. Again, for the feed gas of 4.74% CO_2 -95.26% O_2 , the scale-up criterion of equal Q_G/V_R ratios resulted in the most reasonable and tractable contactor volumes.

Any number of contacting sequences, and thus cumulative DFs, can be deduced from the data of Table 11. For example, as shown in case 4, a 5000-liter tank was indicated to be capable of delivering a DF of 100 for a flow rate of 200 g-moles of 87.5% CO_2 feed gas per minute. The

product stream of $\sim 7\%$ CO_2 , balance as O_2 , could then be processed in a second tank of ~ 1500 liters to yield a DF of 265. The overall DF for the two-stage process would then be $\sim 25,000$. Or, the product stream from case 4 could be processed through a second tank of ~ 600 liters (case 10) to yield a DF of 85. The cumulative DF for the processing sequences of cases 4 and 10 would then be ~ 8500 .

7. FIXATION OF CO_2 IN SOLID SORBENT BEDS

The first study was conducted with ~ 1000 g of commercial quick lime (CaO) packed into a 5.08- by 60-cm glass column. Operation was conducted at room temperature. Pure CO_2 was first humidified by passing it through water as it was being thoroughly mixed in the stirred contactor. Humidification was supplied in order to provide water, if required, to the CaO - CO_2 reaction. For an influent flow rate of ~ 0.205 g-moles CO_2/min (4.92 rlm), virtually no decrease in the flow rate (and thus no CO_2 sorption) was observed for a single pass through the solid CaO bed. No studies were conducted to determine the solid-particulate characteristics of the CaO .

Although the reaction between CaO and CO_2 is thermodynamically favorable, apparently there is a severe rate limitation operating at the gas-solid interface. In a Mitsubishi patent application of 1974,³⁷ a process was described for removing H_2O and CO_2 from the recycle gas in the iron-producing industries. Air at a temperature of 600°C and a pressure of 8 atm containing 10% CO_2 was passed through a column of solid CaO at a superficial velocity of 0.1 m/sec. The CO_2 content in the exit air stream was 0.5 to 1.0% (DF of 10 to 20). The spent CaO was regenerated

in situ in a calcining reaction by passing air through the loaded bed (CaCO_3) at 1 atm and 900°C so that the CaCO_3 was reconverted to CaO . Thus, it is apparent that a very high operating temperature is necessary to obtain quantitative reaction between gaseous CO_2 and solid CaO .

The second study was conducted with ~ 1000 g of analytical-grade slaked lime, Ca(OH)_2 , in the glass column (5.08 by 60 cm). For pure, humidified CO_2 at a feed rate of 7.00 rlm, an apparent removal rate of 0.032 g-moles of CO_2 per minute was observed for only ~ 10 minutes. The presence of heat at the column walls contributed further evidence that the solid slaked lime reacted with the CO_2 . However, the extent of the reaction was too low to suggest that the CO_2 -solid Ca(OH)_2 reaction was a practical operation.

Finally, the glass column was packed with 4 to 8 mesh soda lime. At a pure CO_2 flow rate of 7 rlm (0.293 g-moles/min), a DF of at least 100 was observed for the first 5 min of the process. However, after 10 min of operation, the DF had decreased significantly to a value of ~ 2 . Although a very practical DF was delivered for the initial 5 min, the operating volume of a column necessary to process a large flow rate of 90 to 100% CO_2 would appear to be prohibitively large. Further, the composition of the product produced from the CO_2 -soda lime reaction is uncertain. Soda lime has a composition as follows: CaO , 62 to 89%; NaOH , 5 to 20%; H_2O , 6 to 18%. The most desirable reaction, in terms of producing a stable product, would be an interaction between the CO_2 , CaO , and H_2O to yield CaCO_3 . However, the reaction between CO_2 , H_2O , and NaOH to yield Na_2CO_3 is most likely and would produce the unstable (for long-term storage) product Na_2CO_3 .

Of the three solid sorbents studied, soda lime was found to show the most promising reaction with pure CO_2 . However, a relatively large amount of soda lime [as compared to a Ca(OH)_2 slurry] was needed to react with the pure CO_2 , and the effect of the product composition on the long-term storage capabilities was uncertain.

8. CONCLUSIONS

1. The fixation of CO_2 by a slaked-lime slurry in a mechanically-agitated contactor is a feasible process. The CO_2 - Ca(OH)_2 reaction appears to compare well with other standard CO_2 removal techniques because the rate of reaction is fast, the agitated tank operation is simple, and the product CaCO_3 is a good candidate for long-term storage of $^{14}\text{CO}_3^{-2}$.

2. In general, the DFs (decontamination factor) for the CO_2 - Ca(OH)_2 reaction were observed to vary inversely with the gas flow rate (Q_G) and directly with impeller speed (n) and CO_2 concentration in the feed. For example, the DFs for the removal of CO_2 from a 87.5% CO_2 feed gas were found to decrease from very large values to 100 as the gas flow rate was increased from 3.0 to 17.6 rlm. Also for a 87.5% CO_2 feed gas, the DFs increased by a factor of ~ 2.0 when the impeller speed was increased from 800 to 1700 rpm. Finally, for a constant total gas velocity, the DFs were found to increase directly with CO_2 mole fraction in the feed for $Q_G = 10$ rlm and $n = 800$ rpm as follows: 4.74% CO_2 , DF = 50; 87.5% CO_2 , DF = 175; 100% CO_2 , DF = 250.

3. It was determined that the general mass transfer reaction between CO_2 and Ca(OH)_2 followed the same pattern. For any gas composition, the

mass transfer rate N_{CD} , the DF, and the pH were found to remain constant until ~90% of the total Ca(OH)_2 in the slurry was reacted. After 90% of the Ca(OH)_2 was reacted, the "constant rate" period was followed by a "falling rate" period in which the DF and pH were both observed to decrease rapidly. Hence, the final equilibrium solution contained CaCO_3 and $\text{Ca(HCO}_3)_2$ at $\text{pH} \approx 6.0$.

4. Based on an overall gas-side mass transfer of 1.2×10^{-2} g-moles/ $(\text{cm}^3\text{-sec-atm})$, which was accepted as the definitive value delineating gas-phase control, the great majority of our $K_G a$ values were definitiely not in the gas-phase control range. However, if the CO_2 flow pattern in the contactor is best described by some form of a plug flow model rather than by a perfectly backmixed assumption, it would seem reasonable to predict that for very high DF operations, there is considerable gas-phase resistance to the mass transfer in the gas bubbles which leave the contactor with CO_2 partial pressures of less than 0.0001 atm.

Alternatively, for all the bubbles in the tank at one time, the mass transfer mechanism could be fairly well described by invoking the classic model for gas absorption accompanied by fast pseudo-first-order irreversible reaction, with an assumption of overwhelming liquid-phase control for the majority of the gas bubbles in the contactor.

Overall gas-side mass transfer coefficients were calculated for our data for both a plug-flow and a perfectly backmixed model. The best behaved and most easily compared $K_G a$ values were obtained for the plug-flow model. For most of the gas flow rates studied, the following ranges for log-mean $K_G a$ were found: 87.5% CO_2 , $K_G a = 1.0 - 5.0 \times 10^{-6}$; 33.6% CO_2 , $K_G a = 1.0 - 6.0 \times 10^{-6}$; 4.74% CO_2 , $K_G a = 0.40 - 6.0 \times 10^{-6}$ g-moles/ $(\text{cm}^3\text{-sec-atm})$.

The $K_G a$ values based on an average pressure driving force for fixation of CO_2 from 100% pure CO_2 feed gas were calculated to be in the range 0.6×10^{-6} to 3.0×10^{-6} g-moles/(cm³-sec-atm).

For a particular feed gas, $K_G a$ was determined to vary directly as the gas velocity. This prediction was consistent with the observed direct variation in mass transfer rate with increasing gas flow rates, because increasing $K_G a$ indicates decreasing mass transfer resistance.

5. If overall liquid-phase control is assumed, the following equality is obtained from the fast pseudo-first-order mass transfer model:

$$N_{\text{CD}} = a H V_{\text{D}} p_{\text{DF}} (D k_{\text{OH}} (\text{OH}) + k_{\text{L}}^2)^{0.5} . \quad (22)$$

The interfacial areas were calculated from Eq. (29) to be smaller for the rich CO_2 feed gases (100%, 87.5% CO_2) than those for the more dilute feeds at comparable gas flow rates. This model prediction appeared to accurately represent the extensive stream shrinkage that occurred for 100% CO_2 feeds.

The more logical functionality was obtained for the log-mean interfacial areas computed from the plug-flow model. These log-mean values of a were calculated to vary directly with Q_G . The increases in net mass transfer rate observed when Q_G increased could be explained by the direct dependence of interfacial area on Q_G . The determination of interfacial area for the backmix model was complicated by experimental scatter. Further, unrealistically high interfacial areas were predicted at low gas flow rates. It did not seem logical that interfacial area would increase as Q_G decreased. It is possible that these unrealistically large values

are evidence of either incipient failure of the liquid-side control mass transfer model, or the inaccuracy of the assumption of a perfectly back-mixed system in the low Q_G -high DF region.

Log mean a values were calculated to be in the ranges indicated for the various feed gases: 87.5% CO_2 , $a = 0.70 - 2.0 \text{ cm}^2/\text{cm}^3$; 33.6% CO_2 , $a = 0.6 - 2.5 \text{ cm}^2/\text{cm}^3$; 4.74% CO_2 , $a = 0.2 - 2.5 \text{ cm}^2/\text{cm}^3$.

Backmix a values were calculated to be in the ranges indicated for the various feed gases; 87.5% CO_2 , $a = 6.0 - 55 \text{ cm}^2/\text{cm}^3$; 33.6% CO_2 , $a = 6.0 - 60 \text{ cm}^2/\text{cm}^3$; 4.74% CO_2 , $a = 12 - 25 \text{ cm}^2/\text{cm}^3$.

6. The mass transfer fixation rate of CO_2 in $\text{Ca}(\text{OH})_2$, for a fixed gas flow rate, was determined to be affected only slightly by $\text{Ca}(\text{OH})_2$ concentrations varying from 0.50 to 1.5 m . When higher $\text{Ca}(\text{OH})_2$ concentrations were used, the process was somewhat impeded by slurry bulking for high flow rates of very rich CO_2 feeds. The mass transfer rates (and DFs) were not affected by poor quality slaked lime which contained as much as 50% impurities, such as CaCO_3 . However, as would be expected, the extent to which the slaked lime could react was affected by clumping, impurities, and prolonged exposure to the atmosphere.

Only a limited range of temperatures (21 to 46°C) were utilized to study the effect of slurry temperature on the CO_2 fixation rate. Only slight reductions in mass transfer rate and DF were observed for the small increase in slurry temperature.

7. The settling rate of the CaCO_3 product was determined to vary directly with impeller speed and temperature and inversely with gas flow rate. When the gas flow rate of the control study was halved and the

slurry temperature was increased from 22°C to 46°C, the CaCO_3 settling rate increased by an order of magnitude.

8. Calculations were made for designing large-scale contactors to produce, for a reference reprocessing plant gas flow of 200 scfm, DFs comparable to those achieved in the experimental bench-scale contactor. The scale-up was based on the criteria of geometric similarity, kinematic similarity, and equal power dissipated per cubic foot of slurry volume. In the laboratory, DFs of as much as 3600 were obtained for removal of CO_2 from 87.5% CO_2 feed gas at flow rates of 3 to 4 rlm. When the feed gas was reduced to 4.74% CO_2 , DFs of only 250 to 300 were obtained for the 3- to 4-rlm flow rate range. However, utilizing the laboratory results for the 87.5% CO_2 feed gas to scale-up the first-stage contactor and the laboratory results for the 4.74% CO_2 feed to scale-up the second-stage contactor, DFs $>10^4$ were considered to be feasible for series CO_2 - $\text{Ca}(\text{OH})_2$ agitated contactor operation. The calculated full-scale size of the contactor was of course dependent on whether equal mass transfer conditions could be provided for the bench-scale and full-scale contactors by scaling for either equal superficial velocities or equal residence times.

9. Finally, it was noted that the gas absorption with pseudo-first-order reaction mass transfer model, Eq. (22), could be utilized to serve as a basis for scale-up. The applicability of this model would be dependent on establishing the same values of a , $[\text{OH}]$, and k_L for the large tank that were operative in the bench-scale tank (the physicochemical properties H , D , and k_{OH} would remain constant).

9. NOMENCLATURE

For the following, L is length, M is mass or moles, θ is time, and F is force.

A_c	Constant for calculating minimum impeller speed, Eq. (31); 1.22 for six-blade turbine.
a	Effective interfacial area for mass transfer, L^2/L^3 .
B_c	Constant for calculating minimum impeller speed, Eq. (31); 1.25 for six-blade turbine.
[B]	Molar concentration of anion reacting with gas, M/L^3 .
B_h	Concentration of B at a position in a tower.
C_1	Constant in Eq. (28).
C^*	Concentration of dissolved CO_2 at the liquid-gas interface which is in equilibrium with the gas, M/L^3 .
C^o	Concentration of a gas component absorbed into the bulk of the liquid, M/L^3 .
C_o	Concentration of a gas component in the contactor effluent, M/L^3 .
C_{SL}	Molar concentration of $Ca(OH)_2$ in the slurry, M/L^3 .
D	Diffusivity of the reacting gas component in the liquid, L^2/θ .
d_I	Diameter of impeller, L.
DF	Decontamination factor $(\text{moles } CO_2/\text{time})_{in}/(\text{moles } CO_2/\text{time})_{out}$.
D_{OH}	Diffusivity of hydroxyl ion in liquid, L^2/θ .
d_T	Contactor diameter, L.

e	Constant in Eq. (23).
E	Mass transfer enhancement factor, $E = \frac{R}{k_L C^*}$.
F_I	Molar flow rate of CO_2 in influent stream, M/ θ .
F_O	Molar flow rate of CO_2 in effluent stream, M/ θ .
F_{IN}	Molar flow rate of insoluble gas, M/ θ .
F_T	Molar flow rate of total gases, M/ θ .
g	Acceleration due to gravity, L/ θ^2 .
g_c	Conversion constant ML/ $F(\theta)^2$.
h	Fractional gas holdup.
h_I	Height of impeller above contactor bottom, L.
h_T	Liquid height in contactor, L.
H	Gas solubility in a multicomponent solution, M/(L ³ -atm).
H_w	Gas solubility in a multicomponent solution, M/(L ³ -atm).
I	Ionic strength (= one-half the sum of the quantity obtained by multiplying the concentration of each species by the square of its electric charge, M/L ³).
i_+ , i_- , i_G	Contributions to K_s , Eq. (9), representing cation, anion, and gas, respectively.
k_1	First-order reaction rate constant, θ^{-1} .
k_2	Second-order reaction rate constant, L ³ /(M- θ).
k_G	True gas-side mass transfer coefficient, M/(L ² - θ -atm).
k_L	True liquid-side mass transfer coefficient, L/ θ .
k_{OH}	Rate constant for reaction between carbon dioxide and hydroxyl ion, L ³ /(M- θ).
k_{LR}	Mass transfer coefficient with chemical reaction, L/ θ .
K	Constant in Eq. (23).

K_1	First-order decay constant in Eq. (32), θ^{-1} .
K_G	Overall gas-side mass transfer coefficient, $M/(L^2-\theta\text{-atm})$.
K_S	Quantity in Eq. (9), L^3/M .
m	General order of reaction, not necessarily an integer.
M	Defined by Dk_1/k_L^2 .
n	Impeller speed, rpm.
n_1	Impeller speed for contactor 1, rpm.
n_2	Impeller speed for scaled-up contactor 2, rpm.
n_o	Minimum impeller speed in Eq. (8), rpm.
n_p	Power number for Rushton agitator power characteristics.
N_{CD}	Mass transfer rate of CO_2 , M/θ .
N_G	Mass transfer rate of gas G, M/θ .
N_{Re}	Impeller Reynolds number = $d_I^2 n \rho / \mu$.
$[OH]$	Soluble hydroxyl ion concentration, M/L^3 .
p	Partial pressure, atm.
P_{DF}	Pressure driving force, atm.
P_E	Total effluent stream pressure, atm.
P_I	Inlet gas partial pressure, atm.
P_O	Effluent gas partial pressure, atm.
P_T	Total influent stream pressure, atm.
P_A	Impeller power input, with mechanical agitation only, hp or $(M - L^2)/\theta^3$.
P_E	Effective power input by both mechanical agitation and gas sparging, hp or $(M - L^2)/\theta^3$.
P_{MS}	Aerated power input by mechanical agitation, hp or $(M - L^2)/\theta^3$.

P_s	Power dissipated by sparged gas, hp or $(M - L^2)/\theta^3$.
Q_{CD}	Carbon dioxide volumetric flow rate, L^3/θ .
Q_G	Total volumetric gas flow rate, L^3/θ .
Q_L	Liquid phase volumetric flow rate, L^3/θ .
Q_{SL}	Slurry flow rate, L^3/θ or M/θ .
R	Mass transfer rate per unit interfacial area, $M(L^2 - \theta)$.
RTP	Reference temperature and pressure, which for all our data were 70°F and 1 atm.
S	Contactor cross-sectional area, L^2 .
S_c	Scale factor.
T	Temperature
T_H	Packed tower height, L .
U_G	Gas superficial velocity, L/θ .
U_L	Liquid superficial velocity, L/θ .
U_T	Terminal bubble rise velocity, L/θ .
V_D	Volume of dispersion, L^3 .
V_R	Volume of agitated liquid, L^3 .
W_B	Impeller blade width, L .
Y_{CD}	CO_2 effluent m.f.
Z	Moles of anion [B] reacting per gas mole

Greek letters

ρ	density, M/L^3 .
σ	surface tension, F/L .
μ	viscosity, $M/(L-\theta)$.

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