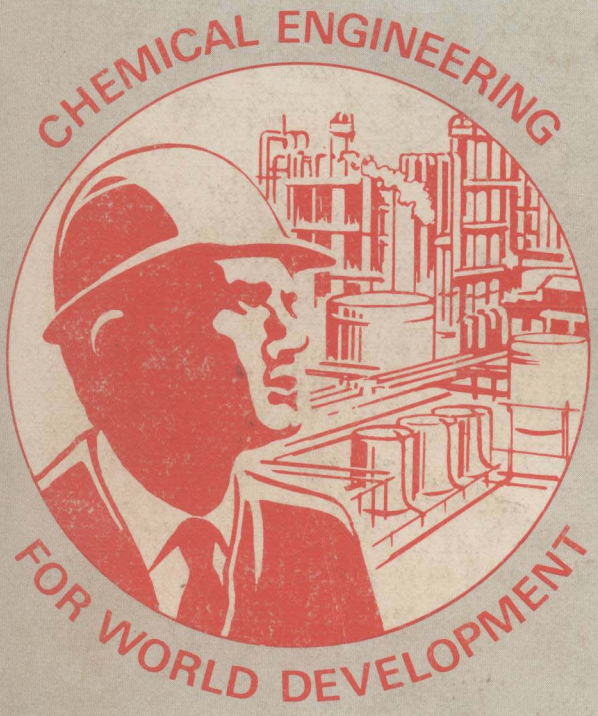
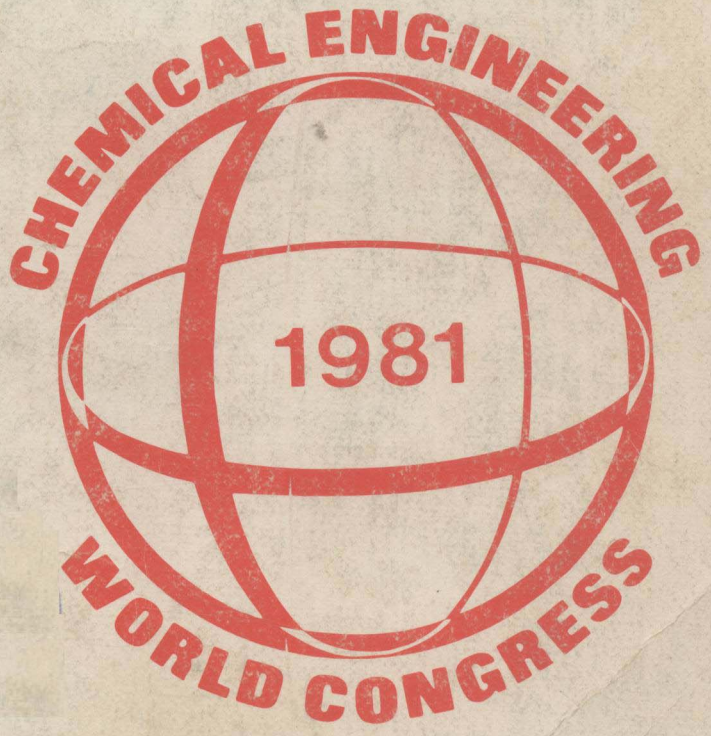



# PROCEEDINGS

## 2nd World Congress of Chemical Engineering




**VOLUME III**

- Reaction Engineering
- Biomedical Engineering
- Fluidization

## Montréal, Canada 1981 October 4-9

IX Interamerican Congress of Chemical Engineering

31st Canadian Chemical Engineering Conference

"Chemical Engineering
for World Development"


# 2nd World Congress of Chemical Engineering

## IX Interamerican Congress of Chemical Engineering

## 31st Canadian Chemical Engineering Conference

## Montreal, Canada
## October 4-9, 1981

# PROCEEDINGS
# Volume III

## PROGRAM COMMITTEE

**Program Chairman**
Professor Musa R. Kamal
McGill University

**Communications**
Dr. R.H. Crotogino
Pulp and Paper Research Institute of Canada

**Proceedings**
Professor Martin E. Weber
McGill University

**Poster Sessions**
Professeur Claude Chavarie
Ecole Polytechnique de Montréal

Mr. R. Burnside
Pulp and Paper Research Institute of Canada

**Student Program**
Dr. W. Ian Patterson
Ecole Polytechnique de Montréal

**Secretary**
Mrs. Karen W. Brown
McGill University

## CONTENTS OF PROCEEDINGS BY THEME

| | |
|---|---|
| Volume I: | Economic & Technological Outlook<br>International Cooperation<br>Canadian Industry and Energy<br>Sesiones de la Confederación Interamericana<br>Biochemical Engineering<br>Education |
| Volume II: | Fossil Resource Development – Energy & Petrochemicals<br>Energy Development and Utilization<br>Nuclear Engineering |
| Volume III: | Reaction Engineering<br>Biomedical Engineering<br>Fluidization |
| Volume IV: | Unit Operations (excluding fluidization) |
| Volume V: | Fundamentals<br>Control |
| Volume VI: | Environmental Chemical Engineering<br>Primary Industries<br>Polymer Engineering |

To order individual volumes, contact the Congress Secretariat:

2nd World Congress of Chemical Engineering
c/o Canadian Society for Chemical Engineering
151 Slater Street, Suite 906
Ottawa, Ontario, Canada. K1P 5H3
Tel.: (613) 233-5623
Telex: 053-4929 – CHEM ENG OTT

## CONGRESS COMMITTEE

**President, 2nd World Congress**
Professeur Pierre Carreau
Ecole Polytechnique de Montréal

**President, Interamerican Confederation of Chemical Engineering**
Dr. William H. Gauvin
Noranda Research Centre

**Program Chairman**
Professor Musa R. Kamal
McGill University

**Vice-President, International**
Professor W.J. Murray Douglas
McGill University

**Vice-President, Operations**
Dr. George R. Kubanek
Noranda Research Centre

**Vice-President, Finance**
Mr. Eric Jones
Noranda Research Centre

**Treasurer**
M. Georges L. Bata
Institut de Génie des Matériaux

**Exposition Chairman**
**Continuing Education, Chairman**
Dr. Michael M. Avedesian
Noranda Research Centre

**Publicity Chairman**
Dr. Keith M. Thompson
Pulp and Paper Research Institute of Canada

**Secretary**
Professeur Frank Ajersch
Ecole Polytechnique de Montréal

**Congress Secretariat**
Mr. Barry Bockus
Canadian Society for Chemical Engineering

## REGIONAL COORDINATORS

Dr. James Buckham
American Institute of Chemical Engineers

Dr. Trevor Evans
European Federation of Chemical Engineering

Ing. Rafael Kohanoff
Interamerican Confederation of Chemical Engineering

Professor Tokuro Mizushina
Asian Pacific Confederation of Chemical Engineering

## THEME COORDINATORS

1. **Economic and Technological Outlooks**
   Dr. J.F.C. Dixon
   C-I-L Inc.
2. **International Cooperation**
   Mr. M. Livingood
   E.I. DuPont de Nemours & Company, Inc.
3. **Canadian Industry and Energy**
   Professor Musa R. Kamal
   McGill University
4. **Sesiones de la Confederación Interamericana**
   Ing. Rafael Kohanoff
   Secretary General
   Confederación Interamericana de Ingeniería Química
5. **Fossil Resource Development – Energy and Petrochemicals**
   Dr. C.W. Selvidge
   Koch Industries, Inc.
6. **Energy Development and Utilization**
   Dr. I. Farag
   University of New Hampshire
7. **Nuclear Engineering**
   Dr. H.K. Rae
   Atomic Energy of Canada Limited
8. **Fundamentals**
   Professor T.W. Hoffman
   McMaster University
9. **Unit Operations and Separation Processes**
   Professor J.R. Grace
   University of British Columbia
10. **Control**
    Professor D.G. Fisher
    University of Alberta
11. **Reaction Engineering**
    Dr. M.J. Phillips
    University of Toronto
12. **Safety in Ammonia Plants and Related Facilities**
    Mr. J.W. Gearinger
    E.I. DuPont de Nemours & Company, Inc.
13. **Environmental Chemical Engineering**
    Dr. A. Benedek
    McMaster University
14. **Primary Industries**
    Professor M.E. Weber
    McGill University
15. **Polymer Engineering**
    Professor J.L. White
    University of Tennessee
16. **Biochemical Engineering**
    Professor M. Moo-Young
    University of Waterloo
17. **Biomedical Engineering**
    Professor M. Moo-Young
    University of Waterloo
18. **Education and Student Program**
    Dr. W. Ian Patterson
    Ecole Polytechnique de Montréal

## PREFACE

This volume contains the text of manuscripts received from authors prior to the printing deadline of July 27, 1981. The papers were printed directly from the best copy submitted. Since some of the manuscripts were not received by the Program Committee before the deadline, the Proceedings include only a partial collection of the presentations made at the 2nd World Congress of Chemical Engineering.

The Technical Program of the 2nd World Congress of Chemical Engineering and these Proceedings were the result of considerable effort by volunteers who do not appear on any list of committee members. We would like to thank the following students at McGill University for many hours of help: D. Abu-Fara, E. Chu, P. Higgins, A. Kallos, K. Kant, P. Lafleur, A. Menon, S. Sabade, M. Sahto and S. Soong. Secretarial services were cheerfully provided by Mrs. K. Brown and Mrs. K. Braginetz.

The Program Committee

VOLUME III

Table of Contents

# LIQUID PHASE DISPERSION IN THREE PHASE FLUIDIZED BEDS

Chang Ho Kim and Sang Done Kim
Department of Chemical Engineering
Korea Advanced Institute of Science and Technology
Seoul, 131, Korea

## Abstract

The axial dispersion characteristics of liquid phase in two (gas-liquid, liquid-solid) and three (gas-liquid-solid) phase fluidized beds have been studied in a 14.5 cm-I.D. column.

The effects of liquid velocity (2-13 cm/sec), gas velocity (0-12 cm/sec), liquid viscosity (1-27 cp), surface tension (38.5-76 dyne/cm) and particle size (1.6-6.0 mm) on axial dispersion of liquid phase have been examined.

Liquid phase axial dispersion in terms of Peclet numbers were correlated empirically by equations involving liquid and gas phase Froude, Reynolds and Weber numbers. The dispersion coefficients increased with gas flow rate, liquid surface tension, and viscosity. However, liquid viscosity generally reduced the coefficient in the beds of smaller particles at higher gas rates.

## Introduction

In three phase fluidization, the particles are fluidized by the cocurrent flow of liquid and gas. The gas forms a discrete bubble phase and the liquid a contineous phase containing solid particles.

Three phase fluidized beds can be used in reaction systems in which the liquid is not readily vaporized, the gas is not easily liquefied, and a catalyst is required to enhance the rate of reaction. Present industrial applications include the catalytic hydrogenation and desulphurization of petroleum products, production of calcium bisulfite and coal liquefaction ( H-coal) process. To date, studies on bed expansion, liquid and gas holdups, gas bubble characteristics and fluid mixing have been reported. The recent literature has been reviewed by Østergaard/1,2/ and Kim and Kim /3/.

Most of the studies on fluid mixing have been carried out using water as the liquid phase and air as the gas phase in small diameter beds. The present work was undertaken to obtain information of the effect of liquid properties on liquid dispersion or mixing in three phase fluidized beds since no other such information has so far been published. In the present study, the effects of liquid and gas velocity, particle size and the properties of liquids on axial liquid mixing have been determined.

## Experimental

Experiments were carried out in a relatively large plexiglass column of 250 cm high and 14.5 cm in diameter as shown schematically in Figure 1. The main section of the column was constructed from two pieces of 14.5 cm-diameter x 125 cm-high x 0.5 cm-thick plexiglass cylinder were flanged together. An approximately constant dynamic liquid level was maintained in the column by means of a concentrically mouted outlet header which is acted as a liquid weir. A stainless steel screen was attached in the top of the column to prevent the losses of particles.

The solid particles were supported on a perforated plate grid which contained 237 evenly spaced holes with diameter of 3 mm and served as the liquid distributor. The grid was situated between the main column section and a 35.5 cm high x 14.5 cm diameter stainless steel distributor box into which liquid was introduced through a 2.54 cm pipe. The liquid was pumped from a 600 liters reservoir through a 2.54 cm pipe. Its flow rate was measured with one of two calibrated rotameters and regulated by means of globe valves on the feed and bypass lines.

Oil free compressor air was fed to the column through a pressure regulator, filter and calibrated rotameter. It was admitted to the bed through four 6.35 mm perforated feed pipes drilled horizontally in the grid. The pipes were evenly spaced across the distributor plate.

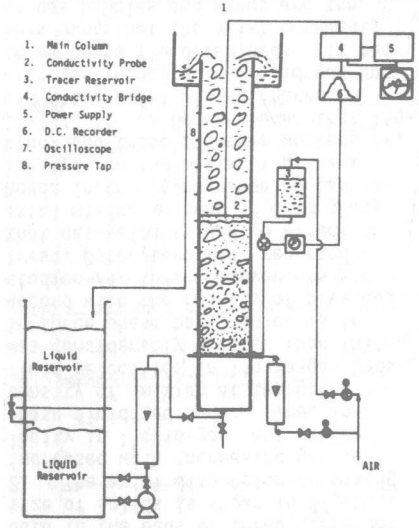



FIGURE 1. APPARATUS

Ten pressure taps were mounted flush with the wall of the column at 180 mm height intervals. The static pressure at each of these points was measured with a liquid manometer.

The solids used were either 1.63 mm, 3.0 and 6.0 mm glass beads with density of 2.5 g/cm$^3$. The unfluidized bed height in the liquid-solid and three phase experiments was 270 mm (6.0 kg).

Details of the fluidizing liquid employed are given in Table 1. In order to determine the effect of liquid viscosity on the liquid phase dispersion, solutions of commercial grade glycerol and of carboxymethyl cellulose (CMC) in tap water were employed. Technical grade methanol-water and triton X-100-water solutions were used to examine the influence of surface tension on axial dispertion.

The viscosity of glycerol solution was measured with a Ostwald capillary viscometer. A Brookfield Synchrolectric rotational viscometer was used to characterize the Pseudoplastic CMC solutions. Within the range of shear rates studied (7.5-75 sec$^{-1}$), power law behaviour was observed. The parameters n and K in the power law equation are also given in Table 1. A capillary rise method was used to determine the surface tension of all the solutions.

## Liquid holdup and Bed expansion measurements

Air and liquid were introduced into the bed of solid at the desired superficial velocities. When steady-state was reached, the pressure profile up the entire height of the column was measured using the liquid manometers. The bed height, He, was taken as the point at which a change in the slope of the plot was observed/4,5/. Values so obtained agree well with those determined by visual observation. The liquid and gas holdups were calculated from the relations /4/:

$$E_\ell + E_g + E_s = 1.0 \qquad (1)$$

$$P_b = H_e (E_\ell \rho_\ell + E_g \rho_g + E_s \rho_s)\ g/g_c \qquad (2)$$

in which $E_\ell$ and $E_g$ are the only unknown quantities since $E_s$ can be calculated from a knowledge of the weight and density of the solids in the bed.

## Tracer response Measurements Technique

Sodium chloride solution (1.0 N), the tracer, was contained in a reservoir pres-

surized by air. This reservior was connected by way of a solenoid valve controlled by an automatic timer to a feed distributor located inside the column at 1.5 cm above the liquid distributor. In each experiment, a half second pulse of tracer was injected into the column. Its volume was measured by means of a level gauge attached to the tracer reservoir. The concentration of tracer was monitored by a conductivity probe which is connected to a conductivity bridge. The probe was made of 0.5 mm diameter platinum wires. Seven probes were installed horizontally in a stainless steel tube of 14 cm-long and 5.0 mm diameter. The probes are 2 cm aprat each other and each pair of the electrode was connected parallely with the high and low lines of the bridge. The supporting pipe of the probes can be fixed at the top of the rack so that the height of the measuring points were varied with experimental conditions. The obtained conductivity gain from the response curve can be converted into the concentration from the previously calibrated relationship between conductivity gain and concentration of NaCl.

Table 1. Properties of the liquids (at 19.5°C)

| Liquids | density (gr/ml) | viscosity($mNs/m^2$) or consistency index($mNs^n/m^2$) | behaviour index (n) | surface tension (dynes/cm) |
|---|---|---|---|---|
| water | 1.00 | 1.00 | 1.00 | 73.0 |
| water-CMC (0.2% wt.%) | 1.001 | 7.85* | 0.946 | 73.6 |
| water-CMC (0.4 wt.%) | 1.002 | 27.12* | 0.836 | 76.01 |
| water-glycerol (6.38 vol.%) | 1.012 | 3.042 | 1.00 | 71.85 |
| water-methanol (18.9 vol.%) | 0.971 | 1.770 | 1.00 | 56.71 |
| water-tritonX-100 (0.045 vol.%) | 1.003 | 1.069 | 1.00 | 38.50 |

CMC : Carboxy Methyl Cellulose
triton X-100 : alkyl polyester surfonate, water soluble
* : consistency index

The dispersion data was interpreted using the axially dispersed plug flow model /4,6-10/. This model has been found to adequately describe axial mixing in liquid-solid /11/, liquid-gas /11,12/ and three phase fluidized beds /4, 11, 13,14/.

The second moment, $\sigma^2$, about the mean, $\bar{t}$, for the tracer response curves were computed using the following relationships:

$$\bar{t} = \int_0^\infty t\, C(t)dt \;/\; \int_0^\infty C(t)dt \qquad (3)$$

$$\sigma^2 = \frac{\int_0^\infty (t-t)^2\, C(t)dt}{\int_0^\infty C(t)dt} - \bar{t}^2 \qquad (4)$$

To circumvent the difficulties of perfect pulse injection and tailing problem, the numerical Laplace transform method was employed /4/. Peclet numbers, computed from the second moment of the corrected tracer response curves with the open vessel assumption /8/, were used to calculate the axial dispersion coefficient.

$$D_z = \frac{U_\ell H_e}{E_\ell \, Pe} \qquad (5)$$

in which liquid holdup, $E_\ell$ has been determined from pressure drop measurement, (Equations 1-2) and mean residence time from tracer response curve. The mean deviation of $E_\ell$ values from two different methods was in the range of 15%. The axial dispersion coefficient values quoted below was obtained by averaging the results of more than five tracer response experiments. The deviation of the individual values from the mean was around 10%.

## Results and Discussion

The axial mixing parameters have been presented /4, 13, 14/ previously in two ways namely, axial dispersion coefficient, $D_z$, and the height of mixing unit (HMU). Since the two terms contain same experimental variables, the effects of fluid velocities and the properties of liquids and solids on axial dispersion coefficient, $D_z$ are discussed in the present report.

### Effect of gas Phase Velocity

The liquid phase axial mixing data in the beds of three different size of solids is shown in Figure 2. The axial dispersion or mixing increased with increasing gas velocity in liquid-gas and three phase fluidized beds. The intensity of mixing at the given fluid velocities in liquid-gas beds was considerably greater than that in three phase beds, which is in accord with the results of previous studies /4, 13/. However, in contrast, Østergaard /14/ reported that gas velocity had no effect on axial mixing in beds of 6 mm glass beads in the lower range of gas velocity. On the basis of present study and those of other workers /4, 13-17/, it can be concluded that liquid phase axial mixing increased with gas velocity in liquid-gas and three phase fluidized beds. It has been known that the axial movements of gas bubbles and wakes are the main cause of axial mixing in the direction of flow in liquid-gas and three phase fluidized beds /4, 13, 19/. With this regard, an increase in gas velocity would under all conditions lead to an increase in axial mixing parameters since bubble size and rising velocity increased with gas velocity in liquid-gas and three

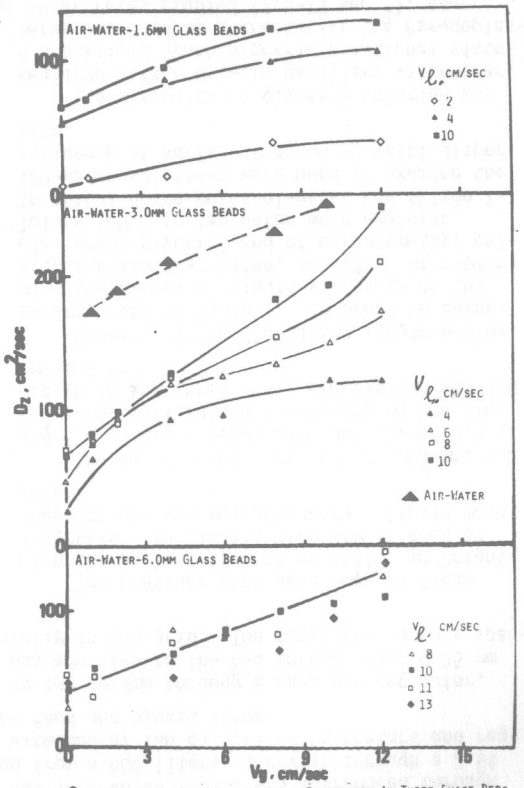



FIGURE 2. EFFECT OF GAS VELOCITY ON AXIAL DISPERSION IN THREE PHASE BEDS.

phase fluidized beds /4, 18/. In addition, previous studies /4, 18/ showed that bubble size and its rising velocity decreased with increasing particle size and that the bubbles were generally smaller and slower moving in three phase beds than in liquid-gas beds. This findings may explain the intensity of axial mixing in liquid-gas beds is significantly higher than that in three phase beds in the present study.

Effect of Liquid Phase Velocity

The flow rate of the liquid phase had positive effect on the axial dispersion coefficient in the beds of 1.6 and 3.0 mm glass beads in liquid-solid and three phase systems. However, the axial mixing in beds of 6 mm particles is nearly independent of the liquid velocity in the range of 8-13 cm/sec. As may be seen in the figure 3 that axial mixing increased with liquid velocity until the bed porosity reaches about 0.62-0.65 in liquid-solid beds and three phase beds at low gas rates. However, reverse trend was observed /13, 14/ in the beds in which bed porosity exceeding 0.65. In contract, axial mixing increased with liquid velocity at high gas rate in both systems. This behaviour is not clearly exhibited for the beds of 6 mm particles. In addition, the rate of increase in $D_z$ in the beds of 3 mm particles was higher than that in the beds of 1.6 mm particles.

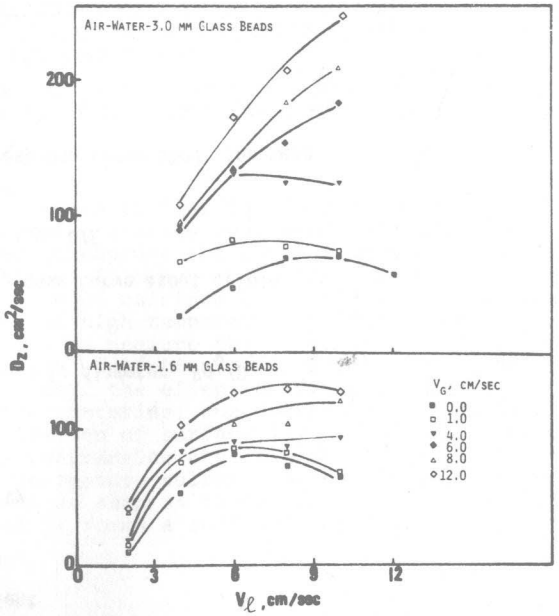



FIGURE 3. EFFECT OF LIQUID VELOCITY ON AXIAL DISPERSION IN THREE PHASE BEDS

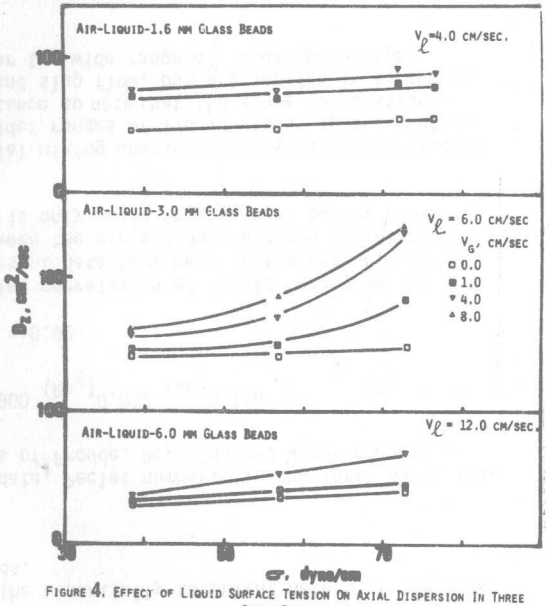



FIGURE 4. EFFECT OF LIQUID SURFACE TENSION ON AXIAL DISPERSION IN THREE PHASE BEDS.

An increase in liquid flow rate will result in higher bed porosity or lower particle concentration, finer bubble dispersion at lower gas rates and increase particle oscillation in vertical direction /13/. The former two consequences contribute to decreasing the intensity of axial mixing, the third acts to enhance the axial dispersion coefficient. In the beds of 1.6 mm particles, the axial dispersion increased sharply with liquid velocity up to 6 cm/sec. However, the rate of increase is marginal at the liquid velocities above 6.0 cm/sec in which case the solid concentration is relatively low that may led to decrease of axial mixing. Same trend was also exhibited in the beds of 3 mm particles at lower gas rates. The bed of 3 mm particles has been characterized by bubble breakup regime at low liquid and gas velocities and bubble coalescence regime at high gas rates/5,14/. This characterization is well represented by the present findings, i.e., axial mixing is relatively low in the bubble breakup regime and is high in the bubble coalescence regime as shown in the figure 3.

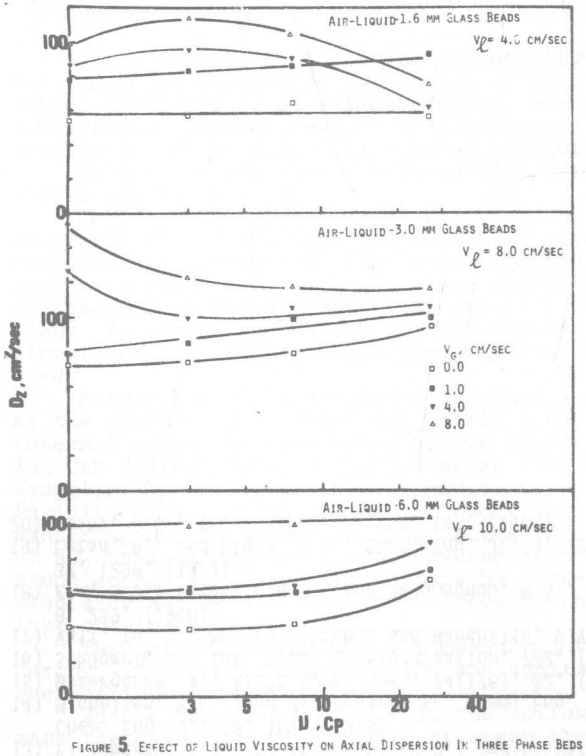



FIGURE 5. EFFECT OF LIQUID VISCOSITY ON AXIAL DISPERSION IN THREE PHASE BEDS

Effect of Liquid Phase Surface Tension

Typical plots of liquid phase axial mixing coefficient against surface tension are shown in Figure 4. The effect of surcafe tension on axial mixing in liquid-solid beds was minimal. However, there did appear to be a small though significant increase in $D_z$ with increasing surface tension in the beds of 3 mm glass beads at high gas rates.

A change in the surface tension of the liquid can be expected to have a less dramatic effect on $D_z$ since the increase of bubble size and rising velocity with surface tension found to be small in liquid-gas and three phase fluidized beds/18/. However, in general, the liquid axial mixing increased somewhat with surface tension in three phase fluidized beds. The effect is more pronounced in the beds of 3 mm particles in the bubble coalescence regime. These findings, however, are somewhat inconclusive because of the rather narrow range of surface tensions studied and the possible presence of surface active contaminants.

Effect of Liquid Phase Viscosity

As noted previously/4,5/, liquid holdup increased with liquid velocity and viscosity in liquid-solid and three phase beds. However, the effect of viscosity on axial dispersion is mainly dependent on the flow rates of gas phase at given liquid velocity as shown in Figure 5. The axial mixing increased with liquid viscosity in liquid-solid beds, three phase beds of 6 mm particles, and the beds of 1.6 and 3.0 mm glass beads at lower gas rate. In contrast, the axial mixing decreased with viscosity in the beds of 1.6 and 3.0 mm particles at higher gas rates.

Momentum transfer from the gas bubbles to the liquid phase presumably increases with bubble size and velocity and leads to more vigorous mixing. Since the bubble rising velocity would decrease with increasing viscosity, it is logical that

axial mixing decreased with liquid viscosity in bubble coalescence regime. However, the smaller bubble size and rising velocity in highly viscouse solutions did not play an significant role on the axial mixing in bubble disintegrating regime. In general, twentyseven fold increase in viscosity increased or decreased $D_z$ by only 20%, confirming the essentially turbulent nature of the flow regimes in three phase fluidized beds.

## Correlation of the Data

The liquid phase axial mixing data, Peclet numbers, in the three phase fluidized beds were correlated in terms of Froude, Reynolds and Weber numbers as shown below:

$$Pe = 0.010(Fr_\ell)^{0.048} (Fr_g)^{-0.900} (Re_\ell)^{0.022} (We)^{0.760} \qquad (6)$$

Correlation coefficient = 0.90

Recently, Joshi/20/ proposed a unified correlation of liquid mixing in two and three phase fluidized beds. The present data have been tested with his correlation. However, the agreement between the present data and his correlation was very poor since his correlation is only valid in the ideal bubbly flow regime.

In this study, liquid phase axial mixing characteristics have been studied at higher gas velocities and over wider ranges of liquid viscosity and surface tension. It is of particular importance to note that the above correlations are not restricted to ideal bubble and slug flow, but are applicable to the industrially realistic flow regime over the wide range of liquid properties.

## Nomenclature

C : Concentration
$D_z$ : axial Dispersion coefficient
$d_p$ : particle diameter
Fr : Froude number, $U^2/gd_p$
g : acceleration due to gravity
$g_c$ : dimensional constant
He : expanded bed height
K : fluid consistency Index
n : fluid behaviour index
Pe : Peclet number based on particle diameter, $Vd_p/D_z$
Pb : bed pressure drop
Re : Reynolds number, $U\, d_p/\mu$
$\bar{t}$ : first moment of tracer response curve about origin
U : superficial fluid velocity
V : average linear fluid velocity, U/E
We : Weber number, $\rho U_g d_p/\sigma$
E : holdup of individual phase
$\sigma^2$ : second moment of tracer response curve about the mean
$\rho$ : density
$\mu$ : viscosity

### Subscripts

g : gas phase
$\ell$ : liquid phase
s : solid phase

## References


1) Østergaard, K., Adv. Chem. Eng., Vol. 7, 71, (1968)
2) Østergaard, K., "Fluidization",(Davidson and Harrison Ed.,), Academic press, 753, (1971)
3) Kim, S.D., and Kim, C.H., J. KIChE., 18, 313, (1980)
4) Kim, S.D., Baker, C.G.J., and Bergougnou, M.A., Can. J. Chem. Eng., 50, 695, (1972)
5) Kim, S.D., Baker, C.G.J., and Bergougnou, M.A., Can. J. Chem. Eng., 53, 134, (1975)
6) Bishoff, K.B., and Levenspiel, O., Chem. Eng. Sci., 17, 257, (1962)
7) Levenspiel, O., and Bishoff, K.B., Adv. Chem. Eng., 4, 95, (1963)
8) Van der Laan, E.T., Chem. Eng. Sci., 7, 187, (1957)
9) Savinsky, J., Hunek, J., and Podmaniczky, L., Int. Chem. Eng., 20, 681, (1980)
10) Østergaard, K., and Michelsen, M.L., Symp. Fund. Appl. Fluidization, Tampa, Florida, May, (1968)
11) Eissa, S.H., and Schügerl, K., Chem. Eng. Sci., 30, 1251, (1975)
12) Oki, Y., and Inoue, H., Chem. Eng. Sci., 25, 1, (1970)
13) El-Temtamy, S.A., El-Sharnoubi, Y.D., and El-Halwagi, M.M., Chem. Eng. J., 18, 151, (1979)
14) Michelsen, M.L., and Østergaard, K., Chem. Eng. J., 1, 37, (1970)
15) Østergaard, K., AIChE Symp. Ser., 74(176), 82, (1978)
16) Schügerl, K., Int. Symp. On Fluidization, 782, (1967)
17) Vail, Yu. K., Manakov, N.Kh., and Manshilin, V.V., Int. Chem. Eng., 8, 239, (1968)
18) Kim, S.D., Baker, C.G.J., and Bergougnou, M.A., Chem. Eng. Sci., 32, 1299, (1977)
19) Letan, R., and Elgin, J.C., Chem. Eng. J., 3, 136, (1972)
20) Joshi, J.B., Trans IChem. E., 58, 155, (1980)

# HETEROGENEOUS GAS-SOLID REACTION STUDIES IN A HIGH TEMPERATURE DIFFUSION CELL: THE EFFECT OF SODIUM CHLORIDE ON SULFUR CAPTURE IN FLUIDIZED BED COMBUSTION

*Tevfik Bardakci, The Catholic Univ. of America, Wash. D.C.
Larry L. Gasner, University of Maryland, Maryland

SUMMARY

Greer limestone has been used in fluidized bed combustion to capture potentially harmful sulfur dioxide generated by combustion of fossil fuels.It is desired to capture the maximum amount of $SO_2$ with a given amount of limestone. In order to better understand the reaction mechanism of sulfation of calcined Greer limestone with $SO_2/O_2$ mixture a single pellet high temperature diffusion cell reactor is constructed and used to measure the effective diffusivities of gases during calcination, sulfation, salt addition and additional sulfation. It is found that the effective diffusivities are increased with calcination and sintering, and decreased with sulfation. Even after complete sulfation of surface layer, NaCl vapors were able to open up the pores by rearranging crystals and increase the capacity of Greer limestone to capture sulfur dioxide. It is found that the sulfur dioxide reacts as soon as it can diffuse into the calcined Greer limestone, and it forms a sulfated layer at the surface of the pellet.

## INTRODUCTION

It is important to control potentially harmful sulfur dioxide emitted to atmosphere by combustion of fossil fuels. One of the developing technologies of sulfur dioxide removal is its reaction with limestone or another sorbent in a fluidized bed combustor. Incomplete utilization of limestone is a major problem.

Sulfur dioxide reacts with calcium oxide and oxygen to give stable calcium sulfate.

$$CaO(s) + SO_2(g) + \tfrac{1}{2}O_2 \rightleftharpoons CaSO_4(s) \qquad (1)$$

Borgwardt (1), found that the sulfation reaction is a first order reaction with respect to $SO_2$ concentration and zero order with respect to oxygen concentration. Kito and Wen(2) reported that the rate of reaction is first order with respect to $SO_2$ at low $SO_2$ concentrations. Borgwardt and Harvey (3) calculated the average first order kinetic rate constants which were depended on the type of stone they used.

Harrington et al.(4) concluded that a product shell is formed at the surface of the reacting particle. Borgwardt(1) showed that the internal diffusion resistance become limiting after conversion of 20% CaO for particles with an average size of 0.0096 cm.. Hartman and Coughlin(5) and Pigford and Sliger(6) considered that effective diffusivity of $SO_2$ changes at the product shell. Salt addition causes sintering of the limestone thus increasing the effective diffusivity of $SO_2$ Shelton Ehrlich (7) discovered that the salt addition to limestone enchances the sulfur capture by limestone. Shearer et al. (8) also studied the salt addition effect on the sulfation of different type of limestone sample.

The effective diffusivity measurements during calcination, sintering, sulfation, salt addition and additional sulfation have not been performed before.

In our previous work(9,10), the following equation found to estimate the effective diffusivity of argon through calcined Greer limestone as a function of temperature (750 to 1000°C) and calcination time.

$$D_{Ar} = 62.3\, e^{-14600/RT} + 113.6\, \theta\, e^{-29400/RT} \qquad (2)$$

Where $D_{Ar}$ is the effective diffusivity of argon in $cm^2/sec$, $\theta$ is the calcination time in hr, R is ideal gas constant and T is the calcination temperature in °K.