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**Advanced Technology Section
Semiannual Progress Report for
the Period October 1, 1977, to
March 31, 1978 Volume 2:
Engineering Science Programs**

J. S. Watson
S.D. Clinton

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CHEMICAL TECHNOLOGY DIVISION

ADVANCED TECHNOLOGY SECTION SEMIANNUAL PROGRESS REPORT

FOR THE PERIOD OCTOBER 1, 1977, TO MARCH 31, 1978

VOLUME 2: ENGINEERING SCIENCE PROGRAMS

Compiled by:

J. S. Watson
S. D. Clinton

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SUMMARY

Chemical Engineering Research

Continuous chromatographic separation of nickel, cobalt, and copper was demonstrated. New in-line instrumentation permitted accurate measurements of the resolution between peaks.

The effects of fluid viscosity and flow rate on pressure drop and overall efficiencies (gross efficiency and centrifugal efficiency) for removal of kaolin particles (0.3 to 3 μm diam) by a hydraulic cyclone were measured using a 10-mm Dorr-Oliver hydroclone and slurries containing approximately 5 wt % kaolin in water-glycerin solutions. Increasing viscosity affects the ratio of the underflow rate to the overflow rate as well as decreases the particle removal efficiency. Initial measurements of kaolin particle distributions in the underflow and overflow streams (point efficiencies) are also reported.

Studies of agglomeration processes in heavy organic liquids focused on the effects of various components of coal-derived liquids on physical properties important to slurry stability and agglomeration processes. Viscosity, density, and electrical conductivity are affected most strongly by the presence of asphaltenes; they increase with asphaltene addition.

A new study of the removal of small particles ($\sim 1 \mu\text{m}$) from process streams with deep granular beds has been initiated. Initial results for removal of titania particles from mineral oil by a bed of 0.30-cm glass spheres demonstrate that these very small particles can be removed by beds of rather coarse materials in the presence of high electric potential fields. Evidently, the electric fields polarize the bed granules (and perhaps the slurry particles) so that the particles can be attracted to the bed material.

Studies of three-phase fluid beds included measurements of minimum fluidization velocities and phase holdup in 7.62- and 15.2-cm-ID columns. Dimensionless correlations were developed for predicting these parameters. An attempt was made to determine axial dispersion in the liquid phase by measuring residence-time distributions in the column, but response of the measuring apparatus was not rapid enough for accurate results.

Fusion Energy

Studies of cryosorption pumping of hydrogen with molecular sieves at temperatures between 16 and 35 K indicate that type Na-Y sieve gives significantly higher average pumping speeds than the more conventional type 5A sieve. Apparently, pump speeds are affected by diffusion rates into the crystallite particles, and the larger pore openings in the Na-Y sieve permit higher diffusion rates.

Measurements of the rate of tritium sorption from liquid lithium by yttrium coupons gave encouragingly high values despite the stagnant lithium in the contact device.

Resource Recovery

Investigations of processes for recovering aluminum and other metals from fly ash focused on sinter-leach processes where the ash is first sintered with a low melting salt mixture and then leached with acid. The most interesting of these processes are the salt-soda process which uses a sinter mixture of NaCl and Na₂CO₃ in a ratio of 2:1 and the Calsinter process which uses a CaSO₄ and CaCO₃ mixture. Both processes can give aluminum yields of better than 90%. The Calsinter process can use flue gas desulfurization (FGD) sludge as a source of CaSO₄. This both reduces reagent costs and utilizes another troublesome waste material from coal combustion, FGD sludge.

1. INTRODUCTION

The Engineering Science Program in the Advanced Technology Section consists of three parts: (1) Chemical Engineering Research, (2) Fusion Energy, and (3) Resource Recovery. The Chemical Engineering Research studies and the Resource Recovery studies are supported by the U.S. Department of Energy (DOE)/Office of Basic Energy Sciences. The Fusion Energy studies are supported in part by the DOE/Office of Basic Energy Sciences and in part by the DOE/Office of Fusion Energy.

2. CHEMICAL ENGINEERING RESEARCH

The Chemical Engineering Research Program includes several fundamental studies of chemical engineering problems that are important to energy development. These studies are funded by the DOE/Office of Basic Energy Sciences. Current activities are concerned with new equipment for chromatographic and absorption processes and with physical and chemical methods for separating solids from viscous liquids. These studies are important in coal conversion, nuclear fuel reprocessing, and a variety of separation processes.

2.1 Continuous Chromatography

R. M. Canon

Investigations during this period have centered on the cobalt-nickel-copper carbonate amine system. Copper has been added to the system to simulate its presence in the commercial leach liquor from lateritic ores. Use of the Perkin-Elmer spectrophotometer as an in-line instrument has produced better measurement of the various bands. Data that demonstrate the effectiveness of a typical separation can be recorded directly from the spectrophotometer. Thus, a typical separation is observed (Fig. 2.1) to elute copper first, followed by nickel, cobalt 1, and cobalt 2. Copper and nickel bands were measured at 644 nm, whereas Co-1 and Co-2 were measured at the absorption maxima of 523 and 510 nm respectively. Figure 2.2 shows the effect of column length on this separation, which was performed with 1 M $(\text{NH}_4)_2\text{CO}_3$ at pH 7.8.

Use of in-line instruments has also made accurate determinations of the resolution possible. Resolution (R) is defined as

Fig. 2.1. Chromatogram of the separation of Cu, Ni, Co-1, and Co-2 with 1 M $(\text{NH}_4)_2\text{CO}_3$ on the continuous chromatograph. Rotation rate was $50^\circ/\text{hr}$.

Fig. 2.2. Location of the bands of the various species for a typical continuous separation.

$$R = \frac{\theta_2 - \theta_1}{2(W_1 + W_2)},$$

where θ_1 and θ_2 are the angular displacements (from the feed point) of the maximum concentrations of constituents 1 and 2 and W is the constituent bandwidth. A resolution value of unity indicates no dead volume between peaks but virtually no overlapping. A series of experiments was conducted to determine the effect of feed rate on resolution for a given feed concentration. Data for copper, nickel, Co-1, and Co-2 are shown in Fig. 2.3. These data show that resolutions greater than unity could be maintained at feed rates as high as 2.5% of the total eluent flow for all but the copper-nickel separation. Since the Perkin-Elmer spectrophotometer is intended for large-scale preparative chromatography, operating near the maximum feed rates is desirable. Loss of resolving power is the limiting factor for feed rate and determines this maximum.

Another inducement to operate near maximum is the reduction in constituent dilution at high feed rates. While it is not possible to separate the constituents with no dilution, it is possible to approach this ideal condition. Figure 2.4, for example, shows the reduction in dilution which occurs with an increase in feed rate. At 2.5% of the eluent flow, dilution is a factor of 6 for Co-2 and of <4 for the other components.

In a preparative device, the feed rate could be easily manipulated to achieve the desired separation with the maximum throughput. Changing the feed concentration if there were sufficient benefit to be gained might also be possible. Consequently, the effect of feed concentration on resolution and dilution for the same carbonate system has been

Fig. 2.3. Resolution as a function of feed rate for the carbonate system. Feed concentration was 3 g Ni, 0.75 g Cu, 0.75 g Co-1, and 0.75 g Co-2 per liter of solution. The eluent was 1 M $(\text{NH}_4)_2\text{CO}_3$ at pH 7.8 with a superficial velocity of 2.52 cm/min.

Fig. 2.4. Effect of feed rate on dilution for 1 M $(\text{NH}_4)_2\text{CO}_3$ at pH 7.8. Superficial eluent velocity was 2.52 cm/min, and the feed concentration was 3 g Ni, 0.75 g Cu, 0.75 g Co-1, and 0.75 g Co-2 per liter of solution.

investigated. The ratios of constituent concentrations in the feed were held constant, as would be the case if evaporation or dilution were used. As Fig. 2.5 indicates, results of these experiments did not show a drastic reduction in resolution with an increase in feed concentration. In general, resolution was reduced by only about 20% for a sixfold increase in the total metal concentration of the feed. The dilution factor unexpectedly showed a slight increase (20 to 40%) over the same concentration range (Fig. 2.6). These results demonstrate that it is possible to operate at high feed concentrations and at the maximum flow rate and still maintain the desired resolution.

A new chromatograph, CAC-II, has been fabricated and installed during this period. It is about 20% longer than the previous device and incorporates improvements made over the past 18 months. It was fabricated with close tolerances; both pipes were machined to within 0.005 in. of true round before assembly. No spacers are used in the annulus, and all flange seals are made with O-rings. The seals have eliminated all leaking problems previously experienced at the bottom of the chromatograph when flat gaskets were used. All surfaces of the CAC-II were polished transparent to make better observation of the resin bed possible.

The new chromatograph was designed to operate in either the isocratic or gradient elution modes without modification. Each of the four pumps that are not used for the eluents supplies one manifold (Fig. 2.7) occupying one quarter of the annulus. The pumps are calibrated to give equal flows, and the gas overpressure is varied to maintain the proper liquid level (i.e., just at the top of the glass beads). The optical level detector used previously¹ has been replaced with a differential

Fig. 2.5. Variation of resolution with feed concentration in 1 $\underline{M}$ $(\text{NH}_4)_2\text{CO}_3$ at pH 7.8. The ratio of Ni, Cu, Co-1, and Co-2 was 4:1:1:1.

Fig. 2.6. Effect of feed concentration on dilution in 1 M $(\text{NH}_4)_2\text{CO}_3$ at pH 7.8. The ratio of Ni, Cu, Co-1, and Co-2 was 4:1:1:1.

Fig. 2.7. Eluent manifold system for the CAC-II. Each supplies one-fourth of the chromatograph through six matched capillary tubes.

pressure transducer, which gives a full-scale deflection at 0.05 psid. The high-pressure side of the transducer is attached to the head space in the column, and the low-pressure leg is about 0.75 in. below the surface of the glass beads. The transducer output is conditioned and fed to a p-i-d* controller which operates a valve in the discharge from the chromatograph head space. Regulated air is constantly fed to this space and discharged to maintain a constant liquid level. Pressure fluctuations (and, therefore, flow variations in the column) can be held to less than 1% while the liquid level is held to within $\pm 1/32$ in. of set point. With this system, gradient elution operation is no more difficult and requires no more operator attention than operation with a single eluent. Experiments with the Cu-Ni-Co system have shown very little mixing between eluents (Fig. 2.8). The boundary (indicated in the photo by the change in slope of the copper and nickel bands) is very sharp, and its position is stable.

Investigations with continuous chromatography are continuing and will emphasize gradient elution techniques with other systems, including an Al-Fe-Ti system which is of interest in resource recovery from power plant fly ash.

2.2 Hydraulic Cyclone Studies

J. B. Talbot

Experiments designed to evaluate the performance of a 10-mm-diam hydroclone were completed during this reporting period. Hydroclones are

*Proportional-integral-derivative controller.

Fig. 2.8. Gradient elution separation of Cu, Ni, and Co with 1 M $(\text{NH}_4)_2\text{CO}_3$. The left side is at pH 9.4, and the right side is at pH 7.8.

potentially useful devices for the removal of solids from coal liquids; therefore, their ability to separate micron-sized particles from relatively viscous liquids was examined. Performance criteria are usually defined by pressure drop, the ratio of the underflow rate to the overflow rate, and hydroclone efficiency, which depends on the physical properties of the solids and liquid medium.

2.2.1 Experimental procedures

The apparatus and procedures used to study hydroclone performance have been described previously.² Slurry from a stirred tank is recirculated by a pump through a 10-mm Dorr-Oliver hydroclone. The inlet, overflow, and underflow streams are sampled at each pressure drop, and particle size distributions are determined by a photolometer method performed by the Analytical Chemistry Division. Samples of the overflow and underflow are dried and weighed to measure the solids concentration. During this reporting period, experiments have been conducted using slurries containing about 5 wt % kaolin in water-glycerol solutions with average viscosities of 4.3, 10.7, 11.8, and 12.8 cP. The kaolin particles (sp gr, 2.40 g/cc) are less than 10 μm in diameter (about 70 wt % of the particles are less than 5 μm in diameter).

2.2.2 Results

Experiments designed to determine the effects of flow rates and viscosity (1 to 15 cP) on both pressure drop and hydroclone efficiency were continued. Figure 2.9 shows the feed-to-overflow pressure drop as a function of feed rate at 1.0, 3.8, 4.3, 7.0, 10.7, 11.8, and 12.8 cP. The data for each viscosity were fit to an equation of the form

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Fig. 2.9. Feed-to-overflow pressure drop vs feed rate for kaolin-glycerol solutions.

$$\Delta P = aQ^b, \quad (1)$$

where

ΔP = feed-to-overflow pressure drop (psi),

Q = feed rate (l/min),

a, b = constant coefficients selected by the regression analysis (Table 2.1).

Table 2.1. Regression coefficients for Eq. (1)
for a kaolin-glycerol solution^a

Viscosity (cP)	a	b	Coefficient of determination, r^2
1.0	5.94	1.95	0.9929
3.8	3.84	2.12	0.9962
4.3	3.88	2.12	0.9973
7.0	4.69	1.90	0.9967
10.7	3.69	2.08	0.9704
11.8	4.37	1.95	0.9972
12.8	4.27	1.98	0.9899

^aAverage values of a and b are 4.38 ± 0.77 and 2.01 ± 0.09 respectively.

Figure 2.9 also shows a least-squares fit of 60 data points for all the kaolin-glycerol runs (except those at 1 cP) that can be described by the following equation:

$$\Delta P = 4.25Q^{2.00} \quad (2)$$

The coefficient of determination, r^2 , is 0.9919. This equation and the data at 1 cP agree with a relationship in the literature³ which states that the pressure drop is proportional to the square of the feed rate. Viscosity does not seem to affect this exponent; however, some of our previous data indicated that the slope decreased with increasing viscosity and approached a value of unity.⁴

The viscosity of the feed, which affects hydroclone efficiency, was measured for each run. Gross efficiency, the ratio of the solids discharge rate at the underflow to the total solids feed rate, increases with increasing feed flow rate. But, as Fig. 2.10 shows, the gross efficiency increase effected by an increasing feed rate is diminished as the liquid viscosity increases. For kaolin-glycerol solutions with a feed rate of 2.5 l/min, Fig. 2.11 shows that gross efficiency (interpolated from Fig. 2.10) decreases at higher viscosities. Previous data,³ using solid particles of fly ash and AC Test Dust, indicated that the fraction of solids and the fraction of liquid that go to the underflow were essentially equal (gross efficiency = 0.5) for a comparable flow rate at viscosities of >30 cP. Figure 2.11 indicates that a gross efficiency of 0.5 occurs at an even lower viscosity (11 cP).

Overall centrifugal efficiencies were calculated for the various flow rates of each kaolin run. Centrifugal efficiency, E , is defined as follows:

$$E = \left(\frac{G - R_f}{1 - R_f} \right), \quad (3)$$

where

Fig. 2.10. Effect of feed capacity on gross efficiency.

Fig. 2.11. Effect of viscosity on efficiency for a feed rate of 2.5 l/min.

G = gross efficiency (ratio of solids discharge rate at underflow to solids feed rate),

R_f = ratio of underflow to feed flow rate.

As is displayed in Fig. 2.12, overall centrifugal efficiency increases with increasing feed flow rate. Figure 2.11 also shows centrifugal efficiency (interpolated from Fig. 2.12 at a feed rate of 2.5 l/min) as a function of viscosity. Centrifugal efficiency, like gross efficiency, decreases with increasing viscosity until the least-squares fit of the points actually becomes negative at 12 cP. Negative centrifugal efficiency does occur if R_f is greater than G ; in this case, more liquid than solid material is discharged to the underflow port of the hydroclone. However, this is an unusual method for operating a hydroclone.

Another phenomenon that occurs during the kaolin runs with viscosities of 7 cP and greater is that the ratio of underflow rate to overflow rate falls below unity at lower inlet-to-overflow pressure drops. At 7 cP, the ratio of underflow rate to overflow rate is below unity for runs with pressure drops of ≤ 26.0 psi. This occurrence is consistent with the low centrifugal efficiency values. Underflow-to-overflow rate values below unity were also observed previously at higher viscosities and comparable pressure drops with other solid particles.⁴

Particle size distributions in all streams have been measured for the kaolin runs to evaluate the hydroclone efficiency at various particle sizes. Figure 2.13 shows typical size distributions for the slurry feed, overflow, and underflow streams of a kaolin-aqueous solution with a viscosity of 1 cP. At higher viscosities the size distribution curves for the overflow stream become less steep, the hydroclone becomes less efficient for the removal of the small-diameter particles, and different size

Fig. 2.12. Effect of feed rate on centrifugal efficiency.

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Fig. 2.13. Typical size distribution curves for slurry feed, overflow, and underflow streams.

distributions are observed in the feed, overflow, and underflow streams. For example, at an average pressure drop of 66 psig for slurry viscosities of 1.0, 4.2, and 12.0 cP, the weight-near-particle diameters (50 wt % less than that diameter) in the overflow are 1.39, 2.28, and 2.90 μm respectively. Thus the hydroclone efficiency for small particles decreases more rapidly with increased viscosity.

Point efficiencies were calculated from the data for the particle size analyses, solids concentration, and flow rates of both the overflow and underflow streams. Point efficiency is the fraction of particles of a given size that goes to the underflow. Several methods may be used to determine point efficiency from particle size distributions.^{5,6} Bradley⁵ uses differential relationships for the feed, overflow, and underflow analyses calculated for the small particle size interval. The equation for this point efficiency is as follows:

$$E = \frac{1}{1 + \frac{\Delta O}{\Delta U} \left(\frac{1 - G}{G} \right)}, \quad (4)$$

where

E = point efficiency at a specific particle size,

O = wt % less than a specific size in the overflow,

U = wt % less than a specific size in the underflow.

Chaplin⁶ uses the cumulative particle size distribution data, rather than a difference technique. Thus, point efficiency is determined using the following relationship:

$$E = \frac{U \cdot SIU \cdot QU}{F \cdot SIF \cdot Q}, \quad (5)$$

where

F = wt % less than a specific size in the feed,

SIU = solids concentration in the underflow (g/ml),

SIF = solids concentration in the feed (g/ml),

QU = underflow rate (l/min).

The point efficiency using this equation for a kaolin-aqueous solution with a viscosity of 1 cP is shown in Fig. 2.14. Although the data show the expected S-shaped curve, further data analysis is required to ascertain the effect of flow rate and viscosity on point efficiency. Suitable correlations are being developed for predicting hydroclone performance over the wide range of physical properties studies. When the data analysis is completed, the particle diameter that gives a 50% point efficiency, d_{50} , can be determined from known parameters. As shown in a previous report,⁷ performance variables such as liquid viscosity, feed rate, particle density, and liquid density are usually correlated with the d_{50} value.

Since operation of a hydroclone involves a large number of variables, the experimental results of some investigations have been expressed in terms of dimensionless groups. The influence of the Reynolds number (N_{Re}) on hydroclone performance has also been examined⁸; this number is defined as

$$N_{Re} = \frac{(\text{main diameter of cyclone}) (\text{average feed velocity})}{\text{kinematic viscosity of liquid}}$$

The conclusions in the literature⁷ are that the centrifugal efficiency (or separation number) for a given hydroclone and particle size is dependent on the Reynolds number only and increases with increasing N_{Re} .

Figure 2.15 shows that centrifugal efficiency does increase with an

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Fig. 2.14. Point efficiency for kaolin-glycerol solution (viscosity, 1 cP).

Fig. 2.15. Effect of Reynolds number on centrifugal efficiency.

increasing Reynolds number for the kaolin data, but other variables also appear to be involved.

2.3 Fundamental Agglomeration Studies in Heavy Organic Media

B. R. Rodgers and J. D. Hewitt

2.3.1 Introduction

The tendency for particles to agglomerate and precipitate, or to disperse and stabilize, is characterized by a number of physical parameters,⁹⁻¹¹ the most obvious of which are size and density relative to the suspending matrix. Generally, colloidal dispersions are defined as those dispersed particles with diameters $<1\text{ }\mu\text{m}$, an artificial limit corresponding roughly to the maximum size particle that will stay in suspension for a reasonable time. In heavy organic systems, such as coal liquefaction products, unconverted coal and mineral matter may be present both as a suspension (particles $>1\text{ }\mu\text{m}$) and as a colloidal dispersion (particles $<1\text{ }\mu\text{m}$). The former particles are not difficult to remove by conventional techniques, but the remaining dispersed particles often constitute up to 50 vol % of the total particle mass¹² and must be removed to meet stringent Environmental Protection Agency specifications. Agglomeration followed by sedimentation is an effective separation technique for coal-derived materials,¹³ but little is known about the mechanism of agglomeration.

The properties of colloidal dispersions may be altered by effecting a change in particle size distribution, and hence superficial interfacial area, or by changing the nature of the interfacial forces with electrolytes or surface-active agents. Even though the agglomerated condition

represents the lowest thermodynamic energy state, an energy barrier exists, which prevents particle adhesion. Thus the rate of agglomeration depends on the collision frequency of colloidal particles and the surface energy relative to the energy barrier. Because colloidal particles undergo Brownian motion, the collision frequency can be increased by raising the solution temperature. However, the energy barrier, which prevents close approach of particles, must also be lowered, or little agglomeration will occur. Verwey and Overbeek⁹ have shown that energy barriers can be caused by overlapping double layers, which interact to increase the free energy of the system, thus leading to a potential energy of repulsion. The stability of an electrolyte suspension is determined by the balance between these repulsive forces and the attractive Van der Waals forces. The zeta potential, a measure of the repulsive strength of the outer electrical double layer, often can be related to the agglomerating tendency of the dispersion.

Kitahara,^{10,14} among others, has applied the above theory to non-aqueous (low-electrolyte) systems. This project has applied the theory to coal-derived liquids and has shown that significant zeta potentials do exist for particles in the liquefaction product. Further experimentation is necessary to relate this parameter to agglomeration, and thus separation, of solids from coal liquids.

2.3.2 Theory

The principal theory for electric double layers was formulated independently by Derjaguin and Landau¹⁵ and Verwey and Overbeek⁹ during the forties and is generally referred to as the DLVO theory. According to this theory, which is generally accepted as the basic theory for

stability of lyophobic colloids, the interaction between colloidal particles is controlled by electrostatic repulsion due to the double layer and attraction due to Van der Waals forces. However, the theory is not adequate for describing the stability of polymer and polyelectrolyte dispersions or the effect of very weak electrolyte solutions on lyophilic systems. Nevertheless, significant zeta potentials have been measured for weak electrolyte solutions such as carbon black in benzene,¹⁶ heptane,¹⁷ and toluene,¹⁸ iron oxide and alumina in xylene,¹⁹ etc. Some conductivity was imparted to these solutions by the addition of organic-soluble dissolution compounds, such as calcium oleate, aerosol OT, and calcium diisopropyl salicylate; no zeta potential was measured in the absence of electrolyte.

In the last report in this series, the basic equations of electrokinetics were developed from the arbitrary element balance shown in Fig. 2.16. The general double-layer equation was shown to be

$$\nabla \tau = \rho_c \underline{E} , \quad (1)$$

where

τ = viscous tensor (kg/m·s),

ρ_c = charge density (C/m³),

$\underline{E}$ = electric field (V/m).

With the use of Poisson's equation,

$$\nabla^2 V_{12} = - \frac{\rho_c}{\epsilon} , \quad (2)$$

where

V_{12} = potential (V),

ϵ = permittivity (sec²/m³),

ARBITRARY VOLUME FORCE BALANCE OF A PARTICLE MOVING THROUGH A STATIONARY
DIELECTRIC MEDIUM UNDER THE INFLUENCE OF AN ELECTRIC FIELD

Fig. 2.16. The electric double layer for a particle with a radius much greater than double-layer thickness.

the charge density was eliminated to give

$$\frac{\mu}{E} d^2 v_x = \epsilon d^2 V_{12} , \quad (3)$$

where

ϵ = viscosity (P),

v_x = velocity in x direction.

Integration of this equation gives the standard zeta potential equation for electrophoresis,

$$V_{12} = \frac{\mu V_4}{\epsilon E} \equiv \zeta \text{ (zeta potential)}, \quad (4)$$

where the boundary conditions,

$$\left. \frac{dv_x}{dy} \right|_{\infty} = \left. \frac{dV_{12}}{dy} \right|_{\infty} = v_x \big|_{\infty} = V_{12} \big|_{\infty} = 0 , \quad (5)$$

were used to evaluate the integration constants.

2.3.3 Experiments

In the last report, asphaltenes, unconverted coal particles, and inorganic particles were shown to have a significant zeta potential in liquefied coal solutions. A limited number of physical properties were measured for use in the zeta potential calculations. Asphaltenes had an unexpectedly significant effect on these physical properties and resembled a colloidal suspension rather than a solution. Subsequent experiments have quantified this effect at different temperatures for three physical properties: viscosity, conductivity, and density. The viscosity results have been used to test the applicability of various colloidal models to the asphaltene system.

The coal liquid was fractionated into four components by use of a procedure similar to that reported by Mima et al.²⁰ The basics of the procedure are given in Table 2.2.

Table 2.2. Fractionation of unfiltered SRC coal liquid

Component	Method of removal	Weight percent of component
1. Solids	Precoat filtration at 530°F	6.8
2. Carbenes and carboids	Soxhlet extraction with benzene (insoluble portion)	3.4
3. Asphaltenes	Soxhlet extraction of recovered extract from step 2 with pentane (insoluble portion)	5.7
4. Oils and resins	Recovered portion (solvent free) from step 3	64.1

Figure 2.17 shows the results of viscosity measurements made at 37.8, 65.6, and 98.9°C with a Cannon-Fenske reverse-flow capillary viscometer. The carbenes and carboids curve was determined using the filtrate from the precoat filtration, the asphaltene curve was determined from the solvent-free extract from the benzene extraction, and the oils and resins curve was determined from the extract from the pentane extraction. The asphaltenes had a much greater effect on viscosity than did the carbenes and carboids. As Fig. 2.18 shows, asphaltenes also had a much greater effect on conductivity, which was evaluated by the "Precise Conductivity

ORNL DWG 77-2185R3

Fig. 2.17. The effect of carbenes-carboids and asphaltenes on viscosity.

ORNL-DWG 77-2191R

Fig. 2.18. The effect of carbenes-carboids and asphaltenes on conductivity.

Method" given in ASTM D 3114-72. Figure 2.19 shows that asphaltenes significantly increase the solution density, whereas carbenes and carboids have little effect.

2.3.4 Interpretation of results

Dispersion of a particle in a liquid disturbs the flow of the liquid; consequently, the internal friction of the system is higher than that of the pure liquid. The effect of spherical particles on viscosity has been calculated by Einstein²¹ to be

$$\mu_s = \mu_o (1 + k\phi) , \quad (6)$$

where

μ_s = viscosity of the dispersed system,

μ_o = viscosity of the medium,

ϕ = volume fraction of the dispersed particle.

In this equation, k is a constant which for spherical, rigid, uncharged particles at low concentrations is equal to 2.5. This equation has been tested many times²² and is often used to identify colloids that meet the above requirements. Rearranging Eq. (6) and substituting values from Fig. 2.17 allows the prediction that for spherical particles

$$\frac{\mu_s - \mu_o}{\mu_o \phi} = 2.5 .$$

Experiments with asphaltenes showed that at 37.8°C, $8.86 - 4.46 / [(0.0464)(4.46)] = 21.3$. Stated another way, the predicted solution viscosity was 4.92 compared to the measured values of 8.86. This indicates that the above assumptions for spherical colloidal particles were incorrect.

Fig. 2.19. The effect of carbenes-carboids and asphaltenes on density.

Various corrections to Eq. (6) are listed by Kruyt.²² For more concentrated solutions,

$$\frac{\mu_s - \mu_o}{\mu_o} = 2.50 + 7.350^2 = 2.5(0.0464) + 7.35(0.0464)^2 = 49 . \quad (7)$$

This indicates that concentration effects are minimal in the current system.

For charged particles, Smoluchowski's equation gives the correction as follows:

$$\frac{\mu_s - \mu_o}{\mu_o \phi} = 2.5 + \frac{2.5}{\lambda \mu_o a^2} \left(\frac{\epsilon \zeta}{2\pi} \right)^2$$

where

λ = conductivity (mhos/m),

a = particle radius (m).

Substituting values of μ_o from Fig. 2.17 and values of ϵ , ζ , and λ from the last report and assuming a 1- μ m particle, the second term is 0.011, which is negligible compared to the first term. For a 0.01- μ m (100-Å) particle, the second term is 1.08, which is significant. These results show that the charge on the particles has a significant effect on viscosity only for particles of considerably less than 1 μ m.

For nonspherical particles, Kuhn gives the following corrected equation for a dilute suspension of very long prolate ellipsoids:

$$\frac{N_s - N_o}{N_o \phi} = 1.6 + \frac{P^2}{5} \left(\frac{1}{3 \ln 2P - 1.5} + \frac{1}{\ln 2P - 0.5} \right), \quad (8)$$

where P is the axial ratio. In light of the failure of concentration and charge corrections to account for the increased viscosity, the most likely explanation would be deviation of particles from the assumed spherical shape. About 90% of the asphaltene particles could be observed microscopically to have a linear, chainlike structure yielding a significant axial ratio. Using Eq. (8), the asphaltene axial ratio is estimated to be 15, which is not inconsistent with visual observations.

2.3.5 Conclusions

Over broad temperature ranges, asphaltenes significantly affect viscosity, conductivity, and density and do so to a greater extent than do carbenes and carboids. The effect of viscosity cannot be accounted for by the Einstein viscosity model or the corrections for concentration and charge applied herein. However, a reasonable fit to the viscosity data is obtained by application of the Kuhn equation for prolate ellipsoids.

2.4 Deep-Bed Filtration

R. F. Barker

The removal of small particles ($\sim 1 \mu\text{m}$) from process and waste streams is both expensive and difficult. Such separations often must be performed in energy-related processes, such as coal conversion and nuclear fuel reprocessing. Deep-bed filtration (DBF) has long been used to remove small particles from water and wastewater streams. It has also been found useful for removing small particles from gas streams.²³ The importance of electrical forces in filtration of gas-solid suspensions has been known since about 1930;²⁴ however, similar effects in the filtration of liquid-solid systems were not discovered until 20 years later.²⁵ Exploitation of these electrical forces makes high filtration efficiencies possible

at pressure drops which are low compared to those of mechanical separation devices (e.g., cyclones and baghouse filters).

A study of the fundamentals of DBF has been initiated. An extensive literature search has been completed, and potential applications and research needs have been identified.

The use of strong (on the order of kilovolts per centimeter) electric fields shows promise for improving the particle removal efficiency of DBF. For example, strong electric fields have been applied to fibrous filters being used for air filtration with significant improvement of filter performance.²⁶⁻²⁹ Though this scheme does not rely on charged particles, as do other electrical filtering devices,^{30,31} it is effective for uncharged particles as well as particles carrying a discrete charge. Figure 2.20 illustrates the mechanism used to improve collection efficiency. Part A of the figure shows a homogeneous electric field with straight, parallel electric lines of force. As Part B shows, if a polarizable object (representing a grain of the DBF media) is placed in the homogeneous field, the object is polarized, thus distorting the electric lines of force. In this case, the object in the field has no net force exerted on it. Part C of Fig. 2.20 shows two small particles (representing the suspended material to be filtered) being attracted to the polarized object. The particle on the left has no net electrical charge but is attracted to the polarized object because the particle itself is polarized. This phenomenon is known as "dielectrophoresis" and is explained more thoroughly in the literature.^{32,33} The particle on the right carries a discrete negative charge and is therefore attracted to the positive end of the polarized object. The consideration of an

A. HOMOGENEOUS ELECTRIC FIELD

B. FIELD DISTORTED BY POLARIZABLE OBJECT

C. ATTRACTION OF CHARGED (RIGHT) AND UNCHARGED (LEFT) PARTICLES TO A POLARIZED OBJECT

Fig. 2.20. Illustration of the interaction of an electric field and polarizable objects.

isolated sphere as an element of DBF is an oversimplification, but it illustrates the principles that must be applied to the more rigorous case.

A small test apparatus has been assembled to obtain some preliminary data on DBF enhanced by a strong electric field. The system, shown in Fig. 2.21, consists of two parallel filtering beds, one with and one without an applied electric field. The beds are fed from a common feed tank at equal flow rates by a duplex peristaltic pump. An electric field is imposed on one bed by coaxially placing an electrode supplied by 0-5 kV of DC power in the bed and connecting the outside of the pipe to ground.

Some preliminary data, shown in Fig. 2.22, were taken using beds of 3-in. (7.62-cm) ID that were packed with 1 kg of 0.30-cm glass spheres. Each column was fed a suspension of micron-sized TiO_2 particles in mineral oil at a flow rate of ~ 80 ml/min. The improvement seen in Fig. 2.22 can be better appreciated when one considers that the data were taken with a relatively shallow bed of large particles, and that for a longer bed, the improvement in effluent quality would be an exponential function of the bed depth. Experiments are being initiated to study these phenomena systematically.

2.5 Three-Phase Fluidized-Bed Reacting Systems

J. M. Begovich

The study of three-phase (gas-liquid-solid) fluidized beds continued during this report period. Various packings in 7.62- and 15.2-cm-ID columns were used, and the minimum gas and liquid velocities necessary to fluidize a bed were determined for two additional sizes of glass beads. Dimensionless correlations were developed to predict the minimum

Fig. 2.21. Schematic of apparatus used for testing deep-bed filtration in an electric field.

ORNL DWG 78-9896R

Fig. 2.22. Preliminary results for deep-bed filtration in an electric field.

fluidization (MF) velocity and the five parameters which can be used to completely describe the holdup profiles for the gas, liquid, and solid phases in a column. In addition, overall gas and solid holdups were combined with similar data from the literature to yield dimensional correlations for each of the overall volume fractions.

Residence-time-distribution (RTD) and liquid-phase mass transfer experiments were performed in the 7.62-cm-ID column using three sizes of glass beads and one size of plexiglass beads. The amount of axial dispersion present in the liquid phase was very difficult to characterize. Apparently, the measuring devices used did not have response times short enough to measure the fast-moving tracer pulses. Since axial dispersion coefficients were not available, the liquid-phase mass transfer data were analyzed using both the plug-flow (PF) and continuously stirred tank reactor (CSTR) models. The overall volumetric mass transfer coefficient increased with both increasing gas and liquid velocities and increasing particle size and density.

2.5.1 Experimental procedures

The experimental apparatus and procedures used to obtain MF velocities, overall phase holdups, local phase holdups, and axial dispersion coefficients have been described previously.^{1,2,7} Mass transfer experiments were performed by continuously measuring the dissolved oxygen content of water entering the 7.62-cm-ID column and of water at various heights in the bed after cocurrent contact with nitrogen.

Tables 2.3 and 2.4 present the physical characteristics of the solids and the range of experimental conditions used in these experiments. Experiments designed to measure MF velocities used each of the solids

Table 2.3. Physical characteristics of solid beads used in three-phase fluidization studies

Solid	Diameter (mm)	Density (g/cm ³)
Glass ^a	3.2	2.24
Glass	4.6	2.24
Glass ^a	6.2	2.20
Plexiglass	6.3	1.17
Alumina	6.2	1.99
Alumino-silicate ^a	1.9	1.72

^aUsed only in MF experiments.

Table 2.4. Experimental conditions used in three-phase fluidization studies

Superficial gas velocity (U_G), cm/sec	0-17.3
Superficial liquid velocity (U_L), cm/sec	0-12.0
Column diameter (D_c), cm	7.62 and 15.2
Initial bed height (H_0), cm	22-45

listed in Table 2.3 whereas the phase holdup experiments did not use either the 1.9-mm-diam alumino-silicate or the 6.2- and 3.2-mm-diam glass beads. The mass transfer experiments used only the nonporous glass and plexiglass beads.

2.5.2 Results

Minimum fluidization. Figure 2.23 shows MF velocities for each of the systems studied. As the gas velocity was increased, the minimum liquid velocity required to achieve fluidization decreased in all of these systems. The plexiglass beads, which have the same diameter as the alumina beads and one set of the glass beads, also have a much smaller solid-liquid density difference; thus, they fluidized at lower velocities. All three sizes of glass beads have about the same density. As their diameters increased, the MF velocity also increased.

Note the interaction of particle size and density. At zero gas velocity, the curves of the 6.2-mm-diam glass beads and the alumina beads start at essentially the same point (i.e., they fluidize at the same liquid velocity). However, as the gas velocity is increased, the two curves rapidly diverge. Furthermore, at gas velocities greater than 8 cm/sec, the 6.2-mm-diam alumina beads behave much like the 4.6-mm-diam beads. As the gas velocity is increased, the nonporous beads yield MF curves of similar shape, although the curves do not cross each other.

Liquid-phase axial dispersion. The amount of axial dispersion present in the liquid phase was determined by analyzing the spread of a tracer injected into the liquid phase.³⁴ The tracer was monitored over the column increment of electrode spacing. Three sizes of glass beads and various mass loadings were tested in the 7.62-cm-ID column and yielded

Fig. 2.23. Effect of particle size and density on MF velocities.

the results presented in Tables 2.5-2.11.³⁵ The holdups were determined in two ways: from the RTD curve and from the pressure gradient.⁷

Monitoring the conductivity of the liquid in the column at two points generates two curves of conductivity vs time each time a tracer pulse is injected. The first moment of each curve is referred to as its mean and is calculated as follows:

$$\mu_i = \frac{\int_0^{\infty} ct \, dt}{\int_0^{\infty} c \, dt} \approx \frac{\sum c_j t_j \Delta t}{\sum c_j \Delta t}, \quad (1)$$

where

μ_i = mean of curve,

c = concentration,

t = time,

and subscript j refers to time j .

The difference in means of the two curves is equal to the mean residence time, τ , of the liquid between the two measurement points:

$$\tau = \mu_2 - \mu_1, \quad (2)$$

where subscripts 1 and 2 refer to the first and second measurement points respectively.

The liquid holdup is the volume fraction of the bed made up of liquid and is found from the following:

$$\epsilon_L = \tau U_L / L, \quad (3)$$

Table 2.5. RTD measurements using 1500 g of 4.6-mm-diam glass beads

Run No.	Electrode spacing, L (cm)	Superficial gas velocity, U_G (cm/sec)	Superficial liquid velocity, U_L (cm/sec)	From pressure gradient		From RTD curve		Peclet number, Pe	Axial dispersion coefficient, D_L (cm ² /sec)
				Gas holdup, ϵ_G	Liquid holdup, ϵ_L	Gas holdup, ϵ_G	Liquid holdup, ϵ_L		
1	8.3	0	4.18	0.057	0.344	0.055	0.348	a	b
2	8.3	4.39	4.18	0.108	0.338	0.099	0.354	44.6	2.19
3	8.3	7.91	4.18	0.145	0.254	0.115	0.354	0.354	850
4	8.3	11.9	4.18	0.185	0.271	0.155	0.326	1.41	75.2
5	8.3	15.9	4.18	0.214	0.280	0.247	0.220	3.61	43.6
6	8.3	0	5.96	-0.007	0.517	0.090	0.343	a	b
7	8.3	4.03	5.96	0.050	0.426	0.396	c	a	d
8	8.3	7.90	5.96	0.131	0.362	0.373	c	a	d
9	8.3	11.9	5.96	0.136	0.391	0.251	0.183	0.484	560
10	8.3	15.9	5.96	0.149	0.405	0.095	0.504	1.88	52.2
11	12.7	0	7.99	-0.013	0.539	0	0.516	a	b
13	12.7	7.86	7.99	0.116	0.440	0.009	0.632	0.869	185
14	12.7	11.9	7.99	0.154	0.469	0.162	0.455	0.599	373
15	12.7	15.9	7.99	0.169	0.455	0.189	0.408	0.556	448
16	16.0	0	10.0	-0.003	0.589	-0.028	0.635	16.5	15.3
17	16.0	4.01	10.0	0.082	0.541	0.107	0.496	1.24	260
18	16.0	7.85	10.0	0.104	0.551	0.344	0.118	6.16	220
19	16.0	11.8	10.0	0.146	0.520	0.399	0.065	a	b
20	16.0	15.8	10.0	0.194	0.469	0.315	0.250	2.14	300
21	20.5	0	11.9	-0.002	0.635	-0.015	0.658	24.6	15.1
22	20.5	4.02	11.9	0.098	0.589	-0.094	0.936	1.94	135
23	20.5	7.87	11.9	0.131	0.569	0.172	0.496	3.53	140
24	20.5	11.9	11.9	0.162	0.556	0.214	0.462	6.16	85.9
25	20.5	15.8	11.9	0.175	0.554	0.329	0.275	a	b

^a $Pe < 0$.^b D_L is very small.^c $\epsilon_L < 0$.^d D_L is very large.

Table 2.6. RTD measurements using 2250 g of 4.6-mm-diam glass beads

Run No.	Electrode spacing, L (cm)	Superficial gas velocity, U_G (cm/sec)	Superficial liquid velocity, U_L (cm/sec)	From pressure gradient		From RTD curve		Peclet number, Pe	Axial dispersion coefficient, D_L (cm ² /sec)
				Gas holdup, ϵ_G	Liquid holdup, ϵ_L	Gas holdup, ϵ_G	Liquid holdup, ϵ_L		
26	19.5	0	4.18	0.115	0.290	0.034	0.436	26.4	7.07
27	19.5	4.02	4.18	0.091	0.330	0.102	0.309	12.1	21.8
28	19.5	7.87	4.18	0.136	0.307	0.120	0.336	6.20	39.1
29	19.5	11.9	4.18	0.124	0.358	0.143	0.323	1.90	132
30	19.5	15.9	4.18	0.120	0.360	0.089	0.414	1.58	124
31	22.5	0	5.96	0.028	0.435	-0.014	0.511	126	2.08
32	22.5	4.02	5.96	0.066	0.403	0.382	c	a	b
33	22.5	7.87	5.96	0.115	0.373	0.105	0.372	2.66	129
34	22.5	11.9	5.96	0.145	0.381	0.198	0.287	1.45	323
35	22.5	15.8	5.96	0.176	0.318	0.103	0.443	1.52	197
36	27.0	0	7.99	-0.003	0.530	-0.020	0.561	36.0	10.7
37	27.0	4.02	7.99	0.074	0.467	0.017	0.57	2.64	143
38	27.0	7.86	7.99	0.114	0.441	0.229	0.235	a	b
39	27.0	11.9	7.99	0.150	0.434	0.079	0.562	1.49	258
40	27.0	15.8	7.99	-0.023	0.622	-0.003	0.587	1.00	368
41	32.0	0	10.0	-0.001	0.581	0.014	0.555	a	b
42	32.0	4.02	10.0	0.061	0.559	0.214	0.284	a	b
43	32.0	7.86	10.0	0.125	0.520	0.227	0.336	2.30	415
44	32.0	11.8	10.0	0.154	0.499	0.185	0.444	2.38	304
45	32.0	15.8	10.0	0.186	0.476	0.241	0.376	6.99	122
46	32.0	0	11.9	0.004	0.632	0.032	0.582	a	b
47	32.0	4.02	11.9	0.094	0.608	0.396	0.064	0.049	d
48	32.0	7.87	11.9	0.133	0.575	0.192	0.469	1.92	425
49	32.0	11.9	11.9	0.177	0.533	0.312	0.290	0.934	1410
50	32.0	15.8	11.9	0.192	0.537	0.144	0.624	2.49	246

^a $Pe < 0$.^b D_L is very small.^c $\epsilon_L < 0$.^c D_L is very large.

Table 2.7. RTD measurements using 3000 g of 4.6-mm-diam glass beads

Run No.	Electrode spacing, L (cm)	Superficial gas velocity, U_G (cm/sec)	Superficial liquid velocity, U_L (cm/sec)	From pressure gradient		From RTD curve		Peclet number, Pe	Axial dispersion coefficient, D_L (cm ² /sec)
				Gas holdup, ϵ_G	Liquid holdup, ϵ_L	Gas holdup, ϵ_G	Liquid holdup, ϵ_L		
51	26.5	0	4.18	-0.026	0.374	-0.034	0.387	57.0	5.01
52	26.5	4.01	4.18	0.095	0.323	0.089	0.335	9.51	34.7
53	26.5	7.85	4.18	0.133	0.313	0.162	0.260	4.27	99.6
54	26.5	11.8	4.18	0.159	0.292	0.148	0.312	3.91	90.8
55	26.5	15.8	4.18	0.177	0.289	0.187	0.270	2.03	202
56	26.5	0	5.96	-0.007	0.458	-0.023	0.486	a	b
57	26.5	3.96	5.96	0.080	0.386	0.250	0.080	1.85	1069
58	26.5	7.75	5.96	0.120	0.365	0.200	0.221	0.815	879
59	26.5	11.7	5.96	0.139	0.372	0.134	0.381	1.49	279
60	26.5	15.6	5.96	0.172	0.369	0.107	0.487	1.93	168
61	35.5	0	7.99	0.004	0.515	-0.013	0.544	65.0	8.02
62	35.5	4.01	7.99	0.073	0.478	0.155	0.328	0.909	954
63	35.5	7.84	7.99	0.110	0.446	0.161	0.354	4.42	182
64	35.5	11.8	7.99	0.142	0.413	0.168	0.372	2.39	319
65	35.5	15.8	7.99	0.182	0.410	0.201	0.377	4.58	164
66	42.0	0	10.0	-0.005	0.586	-0.022	0.615	83.0	8.24
67	42.0	4.00	10.0	0.095	0.523	0.275	0.199	10.1	210
68	42.0	7.84	10.0	0.131	0.506	0.210	0.365	2.31	500
69	42.0	11.8	10.0	0.147	0.502	0.180	0.442	7.14	133
70	42.0	15.7	10.0	0.190	0.474	0.220	0.421	6.52	153
71	48.0	0	11.9	-0.003	0.641	-0.026	0.681	30.2	27.9
72	48.0	4.00	11.9	0.099	0.595	0.202	0.410	5.95	235
73	48.0	7.83	11.9	0.134	0.563	0.176	0.489	8.01	146
74	48.0	11.8	11.9	0.175	0.536	0.191	0.507	4.38	258
75	48.0	15.7	11.9	0.216	0.500	0.258	0.424	2.70	500

^a Pe < 0.

^b D_L is very small.

Table 2.8. RTD measurements using 1500 g of 3.2-mm-diam glass beads

Run No.	Electrode spacing, L (cm)	Superficial gas velocity, U_G (cm/sec)	Superficial liquid velocity, U_L (cm/sec)	From pressure gradient		From RTD curve		Peclet number, Pe	Axial dispersion coefficient, D_L (cm ² /sec)
				Gas holdup, ϵ_G	Liquid holdup, ϵ_L	Gas holdup, ϵ_G	Liquid holdup, ϵ_L		
76	7.0	0	3.22	0.048	0.364	0.029	0.399	a	b
77	7.0	4.04	3.22	0.123	0.333	0.207	0.182	0.962	129
78	7.0	7.91	3.22	0.135	0.359	0.135	0.359	1.24	50.7
79	7.0	11.9	3.22	0.136	0.390	0.245	0.195	a	b
80	7.0	15.9	3.22	0.187	0.323	0.183	0.332	0.819	83.0
81	9.5	0	4.18	0.078	0.378	0.017	0.488	30.7	2.64
82	9.5	4.04	4.18	0.011	0.455	0.161	0.186	0.224	953
83	9.5	7.91	4.18	0.109	0.410	0.304	0.058	a	b
84	9.5	11.9	4.18	0.116	0.397	0.171	0.300	0.541	245
85	9.5	15.9	4.18	0.151	0.391	0.007	0.650	1.29	47.3
86	9.5	0	5.96	0.013	0.528	0.085	0.399	a	b
87	9.5	4.04	5.96	0.060	0.450	-0.166	0.357	1.29	51.3
88	9.5	7.90	5.96	0.107	0.419	0.412	c	0.394	343
89	9.5	11.9	5.96	0.154	0.394	0.271	0.185	1.39	221
90	9.5	16.0	5.96	0.157	0.391	0.124	0.451	0.579	217
91	14.5	0	7.35	0.005	0.618	0.029	0.576	2.98	67.5
92	14.5	4.04	7.99	0.079	0.524	-0.002	0.670	1.51	114
93	14.5	7.90	7.99	0.100	0.513	0.188	0.355	1.35	242
94	14.5	11.9	7.99	0.115	0.493	0.135	0.458	1.17	216
95	14.5	15.9	7.99	0.159	0.483	0.231	0.353	3.02	109
96	26.0	0	11.9	0.010	0.702	0.022	0.681	179	2.54
97	26.0	4.04	11.9	0.093	0.678	0.243	0.407	a	b
98	26.0	7.90	11.5	0.119	0.659	0.408	0.137	a	b
99	26.0	11.9	11.5	0.159	0.622	0.298	0.372	19.1	43.7
100	26.0	15.9	11.5	0.218	0.547	0.234	0.517	3.57	168

^a $Pe < 0$.^b D_L is very small.^c $\epsilon_L < 0$.

Table 2.9. RTD measurements using 2250 g of 3.2-mm-diam glass beads

Run No.	Electrode spacing, L (cm)	Superficial gas velocity, U_G (cm/sec)	Superficial liquid velocity, U_L (cm/sec)	From pressure gradient		From RTD curve		Peclet number, Pe	Axial dispersion coefficient, D_L (cm ² /sec)
				Gas holdup, ϵ_G	Liquid holdup, ϵ_L	Gas holdup, ϵ_G	Liquid holdup, ϵ_L		
101	18.5	0	3.22	0.024	0.373	-0.007	0.428	74.5	1.87
102	18.5	4.04	3.22	0.122	0.313	0.074	0.401	3.65	40.8
103	18.5	7.89	3.22	0.149	0.300	0.065	0.452	2.83	46.6
105	18.5	15.9	3.22	0.199	0.257	0.330	0.022	a	b
106	18.5	0	4.18	0.009	0.454	-0.004	0.476	540	0.300
107	18.5	4.02	4.18	0.082	0.368	0.228	0.105	0.329	2240
108	18.5	15.9	4.18	0.128	0.348	0.069	0.453	1.36	126
109	18.5	11.9	4.18	0.149	0.326	0.252	0.142	0.421	1290
111	25.0	0	5.96	0.016	0.515	0.009	0.529	34.5	8.16
112	25.0	4.02	5.96	0.065	0.457	0.291	0.050	a	b
113	25.0	7.87	5.96	0.098	0.384	0.272	0.071	a	b
114	25.0	11.9	5.96	0.118	0.382	0.198	0.237	1.01	621
115	25.0	15.8	5.96	0.141	0.381	0.214	0.248	6.07	99.1
116	25.0	0	7.99	0.045	0.569	0.085	0.497	22.3	18.1
117	25.0	4.02	7.99	0.072	0.521	0.166	0.351	1.57	362
118	25.0	7.87	7.99	0.100	0.507	0.171	0.379	1.67	317
119	25.0	11.9	7.99	0.129	0.491	0.307	0.170	0.561	2090
120	25.0	15.8	7.99	0.173	0.454	0.230	0.351	1.39	408
121	41.0	0	11.9	0.019	0.716	0.008	0.735	22.4	29.7
122	41.0	4.03	11.9	0.088	0.668	0.268	0.344	a	b
123	41.0	7.86	11.9	0.129	0.631	0.230	0.450	3.80	286
124	41.0	11.9	11.9	0.175	0.583	0.236	0.473	3.54	292

^aPe < 0.^b D_L is very small.

Table 2.10. RTD measurements using 3000 g of 3.2-mm-diam glass beads

Run No.	Electrode spacing, L (cm)	Superficial gas velocity, U_G (cm/sec)	Superficial liquid velocity, U_L (cm/sec)	From pressure gradient		From RTD curve		Peclet number, Pe	Axial dispersion coefficient, D_L (cm ² /sec)
				Gas holdup, ϵ_G	Liquid holdup, ϵ_L	Gas holdup, ϵ_G	Liquid holdup, ϵ_L		
126	25.0	0	3.22	-0.126	0.487	-0.069	0.385	40.5	5.17
127	25.0	4.03	3.22	0.119	0.342	0.136	0.313	6.41	40.2
128	25.0	7.84	3.22	0.159	0.292	0.176	0.261	2.04	151
129	25.0	11.8	3.22	0.197	0.279	0.263	0.160	0.748	674
130	25.0	15.8	3.22	0.223	0.271	0.247	0.227	1.17	302
132	25.0	4.00	4.18	0.089	0.367	0.274	0.033	0.064	c
133	25.0	7.82	4.18	0.134	0.342	0.279	0.081	0.408	3180
134	25.0	11.8	4.18	0.175	0.332	0.347	0.022	a	b
135	25.0	15.7	4.18	0.204	0.307	0.212	0.292	0.797	449
136	33.0	0	5.96	0.013	0.529	-0.008	0.565	76.2	4.58
137	33.0	3.98	5.96	0.075	0.436	0.022	0.530	42.4	8.76
138	33.0	7.82	5.96	0.114	0.409	0.287	0.097	a	b
139	33.0	11.8	5.96	0.149	0.393	0.241	0.226	54.3	16.1
140	33.0	15.7	5.96	0.191	0.364	0.245	0.267	2.00	367
141	39.5	0	7.99	0.009	0.604	0.031	0.565	79.2	7.05
142	39.5	3.99	7.99	0.069	0.508	0.083	0.484	3.09	211
143	39.5	7.82	7.99	0.121	0.490	0.137	0.451	2.78	246
144	39.5	11.8	7.99	0.157	0.455	0.230	0.321	41.1	23.9
145	39.5	15.7	7.99	0.189	0.468	0.269	0.323	12.4	79.0
146	62.0	0	11.9	0.006	0.734	0.018	0.713	42.4	24.5
147	62.0	3.99	11.9	0.110	0.622	0.073	0.688	8.43	128
148	62.0	7.81	11.9	0.187	0.513	0.159	0.564	12.0	109

^a Pe < 0.^b D_L is very small.^c D_L is very large.

Table 2.11. RTD measurements using 1500 g of 5.2-mm-diam glass beads

Run No.	Electrode spacing, L (cm)	Superficial gas velocity, U_G (cm/sec)	Superficial liquid velocity, U_L (cm/sec)	From pressure gradient		From RTD curve		Peclet number, Pe	Axial dispersion coefficient, D_L (cm ² /sec)
				Gas holdup, ϵ_G	Liquid holdup, ϵ_L	Gas holdup, ϵ_G	Liquid holdup, ϵ_L		
170	8.0	0	4.89	0.028	0.343	0.051	0.301	7.29	17.8
171	8.0	4.03	4.89	0.092	0.349	0.106	0.324	2.70	44.7
172	8.0	7.88	4.89	0.120	0.359	0.262	0.256	3.90	38.2
173	8.0	11.9	4.89	0.162	0.359	0.203	0.284	2.23	62.0
174	8.0	15.9	4.89	0.180	0.317	0.208	0.266	1.86	78.9
175	8.0	0	5.96	-0.012	0.432	0.010	0.391	1.94	62.8
176	8.0	4.03	5.96	0.101	0.404	0.223	0.179	0.922	289
177	8.0	7.89	5.96	0.133	0.364	0.230	0.186	37.8	6.80
178	8.0	11.9	5.96	0.169	0.360	0.206	0.291	0.863	190
179	8.0	0	7.99	0.209	0.354	0.331	0.129	a	b
180	11.5	0	7.99	-0.003	0.532	0.115	0.313	8.33	35.2
181	11.5	4.03	7.99	0.069	0.481	0.192	0.253	0.490	740
182	11.5	7.88	7.99	0.126	0.430	0.241	0.219	5.91	71.1
183	11.5	11.9	7.99	0.157	0.406	0.254	0.227	0.722	561
184	11.5	15.9	7.99	0.175	0.411	0.284	0.220	1.81	240
185	12.5	0	10.0	-0.003	0.578	0.064	0.455	3.49	78.8
186	12.5	4.03	10.0	0.072	0.541	0.286	0.146	1.42	601
187	12.5	7.88	10.0	0.132	0.486	0.312	0.153	0.977	835
188	12.5	11.9	10.0	0.155	0.486	0.128	0.536	3.00	78.1

^a $Pe < 0$.

^b D_L is very large.

where

U_L = superficial liquid velocity,

L = length between measurement points.

The second moment about each mean, calculated from the following, gives the variance, σ^2 , of each curve:

$$\sigma_i^2 = \frac{\int_0^\infty c(t - \mu_i)^2 dt}{\int_0^\infty c dt} \approx \frac{\sum c_j (t_j - \mu_i)^2 \Delta t}{\sum c_j \Delta t} \quad (4)$$

The difference between the variance of the two curves for an open system is then related to the Peclet number, Pe , as follows:

$$Pe = (\sigma_2^2 - \sigma_1^2) / 2\tau^2, \quad (5)$$

where

$$Pe = \bar{U}_L L / D_L,$$

$$\bar{U}_L = U_L / \epsilon_L = L / \tau = \text{real liquid velocity.}$$

Thus the liquid-phase axial dispersion coefficient, D_L , is found from

$$D_L = L^2 / \tau Pe. \quad (6)$$

Figure 2.24 shows the effect of gas velocity on D_L for the 4.6-mm-diam glass beads. While no clear differences exist for the gas velocities used, the amount of axial dispersion present in the liquid phase was increased by one to two orders of magnitude where gas was present in the bed (as compared to a liquid-fluidized bed only). For the case of no gas flow, the degree of axial dispersion increased slightly as the liquid velocity was increased.

Fig. 2.24. Effect of gas velocity on the liquid-phase axial dispersion coefficient.

For a constant gas velocity and bed mass loading, Fig. 2.25 indicates results scattered over about three orders of magnitude. Similarly, the results shown in Fig. 2.26 for experiments with different bed mass loadings at zero gas velocity are scattered over two orders of magnitude. Even the effect of liquid velocity on D_L is difficult to determine for these two figures.

Because of the scatter in the dispersion data, as well as the disagreement in the liquid holdup calculated by the two methods (Tables 2.5-2.11), RTD experiments were conducted in the 7.62-cm-ID column with liquid only (i.e., with no gas or solid phases present). In a liquid-only system, the liquid holdup is equal to unity. Liquid holdups are fairly well centered around unity for liquid velocities of 6 cm/sec and higher; they are very much below unity for liquid velocities of less than 4.2 cm/sec. Such results could result from laminar flow if the tracer were injected principally into the center of the column where the velocity would be twice the mean velocity. However, based on a liquid density of 1 g/cm³ and a liquid viscosity of 0.01 g/cm·sec, the liquid velocity necessary to achieve a Reynolds number of 2100 in the 7.62-cm-ID column would be 2.8 cm/sec. Although a liquid velocity of 2.8 cm/sec does not agree exactly with Fig. 2.27, the lower holdups are undoubtedly influenced, in part, by velocity profiles. In any case, in two- and three-phase beds, the presence of the solids reduces the liquid holdups and thus causes the real liquid velocities to be high enough so that laminar flow is avoided.

Rather than being related to the velocity profile in the column, the scatter in the RTD data, especially with solids present, may be attributed to two other causes: (1) interaction between the two sets of electrodes

Fig. 2.25. Effect of particle diameter on the liquid-phase axial dispersion coefficient.

Fig. 2.26. Effect of bed mass loading on the liquid-phase axial dispersion coefficient.

Fig. 2.27. Liquid holdups in a single-phase column calculated from the RTD curves.

and (2) equipment response times that are too long in comparison to the residence time of the tracer between each set of electrodes. In some cases, the second set of electrodes actually responded to a pulse of tracer before the first set of electrodes. This effect, which occurred mainly in highly turbulent beds in which the electrodes were closely spaced, could be reduced by separating the two sets of electrodes axially in the columns or by redesigning the electrodes so that the individual plates would be closer together. The cocurrent flow of the tracer with the liquid and gas phases resulted in very short residence times. However, precision was also limited by the fast response time required of the equipment. For example, at a superficial liquid velocity of 5 cm/sec, the liquid holdup would be typically less than 0.5, giving a real liquid velocity greater than 10 cm/sec. Thus, for an electrode spacing of 30 cm, the residence time would be less than 3 sec. Worse yet, the tracer pulse would pass through each set of electrodes (1 cm x 1 cm in size) in less than 0.1 sec. The problem of residence time through the electrode itself will require more sophisticated equipment than is currently available.

Mass transfer. The liquid-phase mass transfer data were analyzed using both the PF and CSTR models as described previously.³⁶ Tables 2.12-2.15 present the results for the three sizes of glass beads and the single size of plexiglass beads.

The effect of gas velocity on the overall volumetric mass transfer coefficient, $K_L a$, for beds of 6.3-mm-diam plexiglass beads is shown in Fig. 2.28. The mass transfer coefficient increased with both increasing liquid and gas velocities. This result is qualitatively typical of those found for each of the solids studied (Figs. 2.29-2.31). However, as these

Table 2.12. Mass transfer data for beds of 4.6-mm-diam glass beads

RUN NUMBER	GAS VEL. (CM/S)	LIQUID VEL. (CM/S)	PORT HEIGHT (CM)	NTU ^a PF	NTU ^a CSTR	KLA PF (1/S)	KLA CSTR (1/S)
G04APV3	4.47	2.98	33.0	0.639	0.893	0.058	0.081
G05APX3	5.17	6.20	49.0	0.224	0.251	0.028	0.032
G06APX3	4.83	6.20	33.0	0.007	0.007	0.001	0.001
G06APX3	4.83	6.20	49.0	0.311	0.365	0.039	0.046
G07APW3	4.53	5.25	49.0	0.295	0.343	0.032	0.037
G08APW3	4.48	5.25	49.0	0.874	1.388	0.094	0.149
G08APW3	4.48	5.25	33.0	0.759	1.131	0.121	0.180
G08APW3	4.48	5.25	17.0	0.388	0.474	0.120	0.146
G09APW3	4.49	5.25	49.0	0.695	1.000	0.074	0.107
G09APW3	4.49	5.25	33.0	0.681	0.972	0.108	0.155
G09APW3	4.49	5.25	17.0	0.447	0.563	0.138	0.174
G10APX3	4.50	6.20	49.0	0.676	0.962	0.086	0.122
G10APX3	4.50	6.20	33.0	0.669	0.949	0.126	0.178
G10APX3	4.50	6.20	17.0	0.427	0.531	0.156	0.194
G11APY3	4.49	8.35	49.0	0.634	0.880	0.108	0.150
G11APY3	4.49	8.35	33.0	0.624	0.861	0.158	0.218
G11APY3	4.49	8.35	17.0	0.371	0.449	0.182	0.220
G12APV3	4.47	10.27	49.0	0.662	0.933	0.139	0.196
G12APV3	4.47	10.27	33.0	0.601	0.818	0.187	0.255
G12APV3	4.47	10.27	17.0	0.366	0.441	0.221	0.267
G13BPW3	8.99	5.25	49.0	0.889	1.428	0.095	0.153
G13BPW3	8.99	5.25	33.0	0.905	1.466	0.144	0.233
G13BPW3	8.99	5.25	17.0	0.795	1.210	0.245	0.374
G14BPX3	9.00	6.20	49.0	0.815	1.255	0.103	0.159
G14BPX3	9.00	6.20	33.0	0.861	1.359	0.162	0.255
G14BPX3	9.00	6.20	17.0	0.727	1.066	0.265	0.389
G15BPY3	9.00	8.35	49.0	0.733	1.078	0.125	0.184
G15BPY3	9.00	8.35	33.0	0.707	1.023	0.179	0.259
G15BPY3	9.00	8.35	17.0	0.477	0.610	0.234	0.300
G16AW3	4.99	5.25	49.0	0.675	0.961	0.072	0.103
G16AW3	4.99	5.25	33.0	0.643	0.899	0.102	0.143
G16AW3	4.99	5.25	17.0	0.277	0.319	0.086	0.099
G17AX3	4.99	6.20	49.0	0.687	0.984	0.087	0.125
G17AX3	4.99	6.20	33.0	0.673	0.957	0.127	0.180
G17AX3	4.99	6.20	17.0	0.357	0.429	0.130	0.157
G18AY3	4.99	8.35	49.0	0.632	0.878	0.108	0.150
G18AY3	4.99	8.35	33.0	0.609	0.835	0.154	0.211
G18AY3	4.99	8.35	17.0	0.203	0.225	0.100	0.110
G19AZ3	4.99	12.33	49.0	0.718	1.040	0.181	0.262
G19AZ3	4.99	12.33	33.0	0.701	1.006	0.262	0.376
G19AZ3	4.99	12.33	17.0	0.243	0.274	0.176	0.199
G20BW3	9.86	5.25	49.0	0.890	1.430	0.095	0.153
G20BW3	9.86	5.25	33.0	0.964	1.614	0.153	0.257
G20BW3	9.86	5.25	17.0	0.902	1.459	0.278	0.451
G21BX3	9.85	6.20	49.0	0.889	1.428	0.113	0.181
G21BX3	9.85	6.20	33.0	0.882	1.410	0.166	0.265
G21BX3	9.85	6.20	17.0	0.806	1.235	0.294	0.451
G22BY3	9.85	8.35	49.0	0.776	1.168	0.132	0.199
G22BY3	9.85	8.35	33.0	0.729	1.070	0.185	0.271
G22BY3	9.85	8.35	17.0	0.597	0.815	0.293	0.400
G23BZ3	9.71	12.33	49.0	0.804	1.227	0.202	0.309
G23BZ3	9.71	12.33	33.0	0.717	1.044	0.268	0.390
G23BZ3	9.71	12.33	17.0	0.539	0.712	0.390	0.516
G24CW3	14.79	5.25	49.0	1.085	1.952	0.116	0.209
G24CW3	14.79	5.25	33.0	1.156	2.167	0.184	0.345
G24CW3	14.79	5.25	17.0	0.956	1.598	0.295	0.493
G25CX3	14.80	6.20	49.0	1.017	1.759	0.129	0.223
G25CX3	14.80	6.20	33.0	1.006	1.727	0.189	0.325
G25CX3	14.80	6.20	17.0	0.734	1.081	0.268	0.394
G26CY3	14.79	8.35	49.0	0.850	1.335	0.145	0.228
G26CY3	14.79	8.35	33.0	0.834	1.298	0.211	0.328
G26CY3	14.79	8.35	17.0	0.652	0.918	0.320	0.451
G27CY3	14.78	10.27	49.0	0.838	1.306	0.176	0.274
G27CY3	14.78	10.27	33.0	0.793	1.206	0.247	0.375
G27CY3	14.78	10.27	17.0	0.582	0.789	0.352	0.476
G28CZ3	14.63	12.33	49.0	0.827	1.280	0.208	0.322
G28CZ3	14.63	12.33	33.0	0.786	1.190	0.294	0.445
G28CZ3	14.63	12.33	17.0	0.570	0.767	0.413	0.556

Table 2.12 (Cont'd)

RUN NUMBER	GAS VEL. (CM/S)	LIQUID VEL. (CM/S)	PORT HEIGHT (CM)	NTU ^a PF	NTU ^a CSTR	KLA PF (1/S)	KLA CSTR (1/S)
G04APV3	4.47	2.98	33.0	0.639	0.893	0.058	0.081
G05APX3	5.17	6.20	49.0	0.224	0.251	0.020	0.032
G06APX3	4.83	6.20	33.0	0.007	0.007	0.001	0.001
G06APX3	4.83	6.20	49.0	0.311	0.365	0.039	0.046
G07APW3	4.53	5.25	49.0	0.295	0.343	0.032	0.037
G08APW3	4.48	5.25	49.0	0.874	1.388	0.094	0.149
G08APW3	4.48	5.25	33.0	0.759	1.131	0.121	0.180
G08APW3	4.48	5.25	17.0	0.388	0.474	0.120	0.146
G09APW3	4.49	5.25	49.0	0.695	1.000	0.074	0.107
G09APW3	4.49	5.25	33.0	0.681	0.972	0.108	0.155
G09APW3	4.49	5.25	17.0	0.447	0.563	0.138	0.174
G10APX3	4.50	6.20	49.0	0.676	0.962	0.086	0.122
G10APX3	4.50	6.20	33.0	0.669	0.949	0.126	0.178
G10APX3	4.50	6.20	17.0	0.427	0.531	0.156	0.194
G11APY3	4.49	8.35	49.0	0.634	0.880	0.108	0.150
G11APY3	4.49	8.35	33.0	0.624	0.861	0.158	0.218
G11APY3	4.49	8.35	17.0	0.371	0.449	0.182	0.220
G12APV3	4.47	10.27	49.0	0.662	0.933	0.139	0.196
G12APV3	4.47	10.27	33.0	0.601	0.818	0.187	0.255
G12APV3	4.47	10.27	17.0	0.366	0.441	0.221	0.267
G13BPW3	8.99	5.25	49.0	0.889	1.428	0.095	0.153
G13BPW3	8.99	5.25	33.0	0.905	1.466	0.144	0.233
G13BPW3	8.99	5.25	17.0	0.795	1.210	0.245	0.374
G14RPX3	9.00	6.20	49.0	0.815	1.255	0.103	0.159
G14RPX3	9.00	6.20	33.0	0.861	1.359	0.162	0.255
G14RPX3	9.00	6.20	17.0	0.727	1.066	0.265	0.389
G15BPY3	9.00	8.35	49.0	0.733	1.078	0.125	0.184
G15BPY3	9.00	8.35	33.0	0.707	1.023	0.179	0.259
G15BPY3	9.00	8.35	17.0	0.477	0.610	0.234	0.300
G16AW3	4.99	5.25	49.0	0.675	0.961	0.072	0.103
G16AW3	4.99	5.25	33.0	0.643	0.899	0.102	0.143
G16AW3	4.99	5.25	17.0	0.277	0.319	0.086	0.099
G17AX3	4.99	6.20	49.0	0.687	0.984	0.087	0.125
G17AX3	4.99	6.20	33.0	0.673	0.957	0.127	0.180
G17AX3	4.99	6.20	17.0	0.357	0.429	0.130	0.157
G18AY3	4.99	8.35	49.0	0.632	0.878	0.108	0.150
G18AY3	4.99	8.35	33.0	0.609	0.835	0.154	0.211
G18AY3	4.99	8.35	17.0	0.203	0.225	0.100	0.110
G19AZ3	4.99	12.33	49.0	0.718	1.040	0.181	0.262
G19AZ3	4.99	12.33	33.0	0.701	1.006	0.262	0.376
G19AZ3	4.99	12.33	17.0	0.243	0.274	0.176	0.199
G20BW3	9.86	5.25	49.0	0.890	1.430	0.095	0.153
G20BW3	9.86	5.25	33.0	0.964	1.614	0.153	0.257
G20BW3	9.86	5.25	17.0	0.902	1.459	0.278	0.451
G21RX3	9.85	6.20	49.0	0.889	1.428	0.113	0.181
G21RX3	9.85	6.20	33.0	0.882	1.410	0.166	0.265
G21RX3	9.85	6.20	17.0	0.806	1.235	0.294	0.451
G22BY3	9.85	8.35	49.0	0.776	1.168	0.132	0.199
G22BY3	9.85	8.35	33.0	0.729	1.070	0.185	0.271
G22BY3	9.85	8.35	17.0	0.597	0.815	0.293	0.400
G23RZ3	9.71	12.33	49.0	0.804	1.227	0.202	0.309
G23RZ3	9.71	12.33	33.0	0.717	1.044	0.268	0.390
G23RZ3	9.71	12.33	17.0	0.539	0.712	0.390	0.516
G24CW3	14.79	5.25	49.0	1.085	1.952	0.116	0.209
G24CW3	14.79	5.25	33.0	1.156	2.167	0.184	0.345
G24CW3	14.79	5.25	17.0	0.956	1.598	0.295	0.493
G25CX3	14.80	6.20	49.0	1.017	1.759	0.129	0.223
G25CX3	14.80	6.20	33.0	1.006	1.727	0.189	0.325
G25CX3	14.80	6.20	17.0	0.734	1.081	0.268	0.394
G26CY3	14.79	8.35	49.0	0.850	1.335	0.145	0.228
G26CY3	14.79	8.35	33.0	0.834	1.298	0.211	0.328
G26CY3	14.79	8.35	17.0	0.652	0.918	0.320	0.451
G27CY3	14.78	10.27	49.0	0.838	1.306	0.176	0.274
G27CY3	14.78	10.27	33.0	0.793	1.206	0.247	0.375
G27CY3	14.78	10.27	17.0	0.582	0.789	0.352	0.476
G28CZ3	14.63	12.33	49.0	0.827	1.280	0.208	0.322
G28CZ3	14.63	12.33	33.0	0.786	1.190	0.294	0.445
G28CZ3	14.63	12.33	17.0	0.570	0.767	0.413	0.556

^a NTU = number of transfer units.

Table 2.13. Mass transfer data for beds of
3.2-mm-diam glass beads

RUN NUMBER	GAS VEL. (CM/S)	LIQUID VEL. (CM/S)	PORT HEIGHT (CM)	NTU ^a PF	NTU ^a CSTR	KLA PF (1/S)	KLA CSTR (1/S)
C01AXP3	5.02	5.25	49.0	0.351	0.420	0.038	0.045
C01AXP3	5.02	5.25	33.0	0.296	0.344	0.047	0.055
C01AXP3	5.02	5.25	17.0	0.183	0.201	0.056	0.062
C02AY3	5.02	6.20	49.0	0.316	0.371	0.040	0.047
C02AY3	5.02	6.20	33.0	0.280	0.323	0.053	0.061
C02AY3	5.02	6.20	17.0	0.216	0.241	0.079	0.088
C03AZ3	5.02	8.35	49.0	0.283	0.327	0.048	0.056
C03AZ3	5.02	8.35	33.0	0.275	0.317	0.070	0.080
C03AZ3	5.02	8.35	17.0	0.219	0.244	0.107	0.120
C04AZP3	4.95	12.33	49.0	0.409	0.503	0.103	0.127
C04AZP3	4.95	12.33	33.0	0.405	0.498	0.151	0.186
C04AZP3	4.95	12.33	17.0	0.354	0.424	0.257	0.307
C05BXP3	9.85	5.25	49.0	0.560	0.750	0.060	0.080
C05BXP3	9.85	5.25	33.0	0.556	0.742	0.088	0.118
C05BXP3	9.85	5.25	17.0	0.458	0.581	0.142	0.179
C06BY3	9.87	6.20	49.0	0.542	0.718	0.069	0.091
C06BY3	9.87	6.20	33.0	0.467	0.595	0.088	0.112
C06BY3	9.87	6.20	17.0	0.372	0.450	0.136	0.164
C07RZ3	9.85	8.35	49.0	0.473	0.604	0.081	0.103
C07BZ3	9.85	8.35	33.0	0.381	0.463	0.096	0.117
C07BZ3	9.85	8.35	17.0	0.309	0.362	0.152	0.178
C08BZP3	9.74	12.33	49.0	0.572	0.770	0.144	0.194
C08BZP3	9.74	12.33	33.0	0.485	0.623	0.181	0.233
C08BZP3	9.74	12.33	17.0	0.398	0.488	0.288	0.354
C09CXP3	14.83	5.25	49.0	0.711	1.035	0.076	0.111
C09CXP3	14.83	5.25	33.0	0.667	0.947	0.106	0.151
C09CXP3	14.83	5.25	17.0	0.596	0.814	0.184	0.251
C10CY3	14.90	6.20	49.0	0.661	0.936	0.084	0.118
C10CY3	14.90	6.20	33.0	0.551	0.734	0.104	0.138
C10CY3	14.90	6.20	17.0	0.488	0.628	0.178	0.229
C11CZ3	14.90	8.35	49.0	0.574	0.774	0.098	0.132
C11CZ3	14.90	8.35	33.0	0.463	0.588	0.117	0.149
C11CZ3	14.90	8.35	17.0	0.384	0.468	0.189	0.230
C12CW3	14.86	3.58	49.0	0.935	1.544	0.068	0.113
C12CW3	14.86	3.58	33.0	1.013	1.750	0.110	0.190
C12CW3	14.86	3.58	17.0	1.080	1.939	0.227	0.408
C13CX3	14.06	4.29	49.0	0.834	1.305	0.073	0.114
C13CX3	14.86	4.29	33.0	0.813	1.252	0.106	0.163
C13CX3	14.86	4.29	17.0	0.880	1.409	0.222	0.356
C14AW3	5.05	3.58	49.0	0.438	0.549	0.032	0.040
C14AW3	5.05	3.58	33.0	0.392	0.479	0.042	0.052
C14AW3	5.05	3.58	17.0	0.195	0.215	0.041	0.045
C15AX3	5.05	4.29	49.0	0.387	0.471	0.034	0.041
C15AX3	5.05	4.29	33.0	0.426	0.531	0.055	0.069
C15AX3	5.05	4.29	17.0	0.252	0.286	0.064	0.072
C16BX3	9.92	4.29	49.0	0.606	0.833	0.053	0.073
C16BX3	9.92	4.29	33.0	0.692	0.995	0.090	0.130
C16BX3	9.92	4.29	17.0	0.702	1.016	0.177	0.257
C17BW3	9.92	3.58	49.0	0.712	1.037	0.052	0.076
C17BW3	9.92	3.58	33.0	0.830	1.292	0.090	0.140
C17BW3	9.92	3.58	17.0	0.604	0.830	0.127	0.175

Table 2.13. (Cont'd)

RUN NUMBER	GAS VEL. (CM/S)	LIQUID VEL. (CM/S)	PORT HEIGHT (CM)	NTU ^a PF	NTU ^a CSTR	KLA PF (1/S)	KLA CSTR (1/S)
C01AXP3	5.02	5.25	49.0	0.351	0.420	0.038	0.045
C01AXP3	5.02	5.25	33.0	0.296	0.344	0.047	0.055
C01AXP3	5.02	5.25	17.0	0.183	0.201	0.056	0.062
C02AY3	5.02	6.20	49.0	0.316	0.371	0.040	0.047
C02AY3	5.02	6.20	33.0	0.280	0.323	0.053	0.061
C02AY3	5.02	6.20	17.0	0.216	0.241	0.079	0.088
C03AZ3	5.02	8.35	49.0	0.283	0.327	0.048	0.056
C03AZ3	5.02	8.35	33.0	0.275	0.317	0.070	0.080
C03AZ3	5.02	8.35	17.0	0.219	0.244	0.107	0.120
C04AZP3	4.95	12.33	49.0	0.409	0.503	0.103	0.127
C04AZP3	4.95	12.33	33.0	0.405	0.498	0.151	0.186
C04AZP3	4.95	12.33	17.0	0.354	0.424	0.257	0.307
C05BXP3	9.85	5.25	49.0	0.560	0.750	0.060	0.080
C05BXP3	9.85	5.25	33.0	0.556	0.742	0.088	0.118
C05BXP3	9.85	5.25	17.0	0.458	0.581	0.142	0.179
C06BY3	9.87	6.20	49.0	0.542	0.718	0.069	0.091
C06BY3	9.87	6.20	33.0	0.467	0.595	0.088	0.112
C06BY3	9.87	6.20	17.0	0.372	0.450	0.136	0.164
C07BZ3	9.85	8.35	49.0	0.473	0.604	0.081	0.103
C07BZ3	9.85	8.35	33.0	0.381	0.463	0.096	0.117
C07BZ3	9.85	8.35	17.0	0.309	0.362	0.152	0.178
C08BZP3	9.74	12.33	49.0	0.572	0.770	0.144	0.194
C08BZP3	9.74	12.33	33.0	0.485	0.623	0.181	0.233
C08BZP3	9.74	12.33	17.0	0.398	0.488	0.288	0.354
C09CXP3	14.83	5.25	49.0	0.711	1.035	0.076	0.111
C09CXP3	14.83	5.25	33.0	0.667	0.947	0.106	0.151
C09CXP3	14.83	5.25	17.0	0.596	0.814	0.184	0.251
C10CY3	14.90	6.20	49.0	0.661	0.936	0.084	0.118
C10CY3	14.90	6.20	33.0	0.551	0.734	0.104	0.138
C10CY3	14.90	6.20	17.0	0.488	0.628	0.178	0.229
C11CZ3	14.90	8.35	49.0	0.574	0.774	0.098	0.132
C11CZ3	14.90	8.35	33.0	0.463	0.588	0.117	0.149
C11CZ3	14.90	8.35	17.0	0.384	0.468	0.189	0.230
C12CW3	14.86	3.58	49.0	0.935	1.544	0.068	0.113
C12CW3	14.86	3.58	33.0	1.013	1.750	0.110	0.190
C12CW3	14.86	3.58	17.0	1.080	1.939	0.227	0.408
C13CX3	14.86	4.29	49.0	0.836	1.305	0.073	0.114
C13CX3	14.86	4.29	33.0	0.813	1.252	0.106	0.163
C13CX3	14.86	4.29	17.0	0.880	1.409	0.222	0.356
C14AW3	5.05	3.58	49.0	0.438	0.549	0.032	0.040
C14AW3	5.05	3.58	33.0	0.392	0.479	0.042	0.052
C14AW3	5.05	3.58	17.0	0.195	0.215	0.041	0.045
C15AX3	5.05	4.29	49.0	0.387	0.471	0.034	0.041
C15AX3	5.05	4.29	33.0	0.426	0.531	0.055	0.069
C15AX3	5.05	4.29	17.0	0.252	0.286	0.064	0.072
C16BX3	9.92	4.29	49.0	0.606	0.833	0.053	0.073
C16BX3	9.92	4.29	33.0	0.692	0.995	0.090	0.130
C16BX3	9.92	4.29	17.0	0.702	1.016	0.177	0.257
C17BW3	9.92	3.58	49.0	0.712	1.037	0.052	0.076
C17BW3	9.92	3.58	33.0	0.830	1.292	0.090	0.140
C17BW3	9.92	3.58	17.0	0.604	0.830	0.127	0.175

^a NTU = number of transfer units.

Table 2.14. Mass transfer data for beds of 6.2-mm-diam glass beads

RUN NUMBER	GAS VEL. (CM/S)	LIQUID VEL. (CM/S)	PORT HEIGHT (CM)	NTU ^a PF	NTU ^a CSTR	KLA PF (1/S)	KLA CSTR (1/S)
K01AW3	5.02	6.20	49.0	0.765	1.143	0.097	0.145
K01AW3	5.02	6.20	33.0	0.707	1.022	0.133	0.192
K01AW3	5.02	6.20	17.0	0.266	0.305	0.097	0.111
K02AX3	5.02	7.40	49.0	0.733	1.074	0.111	0.162
K02AX3	5.02	7.40	33.0	0.664	0.937	0.149	0.210
K02AX3	5.02	7.40	17.0	0.301	0.351	0.131	0.153
K03AY3	5.02	9.98	49.0	0.691	0.989	0.141	0.201
K03AY3	5.02	9.98	33.0	0.516	0.673	0.156	0.203
K03AY3	5.02	9.98	17.0	0.269	0.308	0.158	0.181
K04AZ3	5.00	14.97	49.0	0.670	0.945	0.205	0.289
K04AZ3	5.00	14.97	33.0	0.545	0.721	0.247	0.327
K04AZ3	5.00	14.97	17.0	0.382	0.464	0.337	0.409
K05BW3	9.97	6.20	49.0	0.783	1.184	0.099	0.150
K05BW3	9.97	6.20	33.0	0.831	1.291	0.156	0.243
K05BW3	9.97	6.20	17.0	0.485	0.624	0.177	0.228
K06RX3	9.97	7.40	49.0	0.765	1.145	0.115	0.173
K06RX3	9.97	7.40	33.0	0.899	1.450	0.202	0.325
K06RX3	9.97	7.40	17.0	0.549	0.731	0.239	0.318
K07BY3	9.94	9.98	49.0	0.762	1.138	0.155	0.232
K07BY3	9.94	9.98	33.0	0.765	1.143	0.231	0.346
K07BY3	9.94	9.98	17.0	0.546	0.724	0.320	0.425
K08BZ3	9.86	14.97	49.0	0.867	1.368	0.265	0.418
K08BZ3	9.86	14.97	33.0	0.750	1.110	0.340	0.503
K08BZ3	9.86	14.97	17.0	0.503	0.652	0.443	0.574
K09CW3	15.03	6.20	49.0	0.995	1.698	0.126	0.215
K09CW3	15.03	6.20	33.0	1.445	3.209	0.272	0.603
K09CW3	15.03	6.20	17.0	0.833	1.298	0.304	0.474
K10CX3	15.03	7.40	49.0	0.947	1.572	0.143	0.237
K10CX3	15.03	7.40	33.0	0.903	1.461	0.202	0.328
K10CX3	15.03	7.40	17.0	0.738	1.089	0.321	0.474
K11CY3	14.81	9.98	49.0	0.849	1.333	0.173	0.271
K11CY3	14.81	9.98	33.0	0.778	1.174	0.235	0.355
K11CY3	14.81	9.98	17.0	0.585	0.794	0.344	0.466
K12CZ3	14.61	14.97	49.0	0.851	1.334	0.260	0.407
K12CZ3	14.61	14.97	33.0	0.767	1.148	0.348	0.520
K12CZ3	14.61	14.97	17.0	0.600	0.820	0.528	0.722

^aNTU = number of transfer units.

Table 2.15. Mass transfer data for beds of
6.3-mm-diam plexiglass beads

RUN NUMBER	GAS VEL. (CM/S)	LIQUID VEL. (CM/S)	PORT HEIGHT (CM)	NTU ^a PF	NTU ^a CSTR	KLA PF (1/S)	KLA CSTR (1/S)
P01AW3	5.11	2.15	49.0	0.750	1.114	0.033	0.049
P01AW3	5.11	2.15	33.0	0.829	1.287	0.054	0.084
P01AW3	5.11	2.15	17.0	0.757	1.130	0.096	0.143
P02AX3	5.08	2.62	49.0	0.693	0.997	0.037	0.053
P02AX3	5.08	2.62	33.0	0.700	1.011	0.056	0.080
P02AX3	5.08	2.62	17.0	0.586	0.796	0.090	0.123
P03AY3	5.08	3.46	49.0	0.624	0.865	0.044	0.061
P03AY3	5.08	3.46	33.0	0.546	0.725	0.057	0.076
P03AY3	5.08	3.46	17.0	0.383	0.466	0.078	0.095
P04AZ3	5.08	5.25	49.0	0.482	0.619	0.052	0.066
P04AZ3	5.08	5.25	33.0	0.387	0.473	0.062	0.075
P04AZ3	5.08	5.25	17.0	0.227	0.255	0.070	0.079
P05BW3	9.96	2.15	49.0	1.177	2.236	0.052	0.098
P05BW3	9.96	2.15	33.0	1.224	2.394	0.080	0.156
P05BW3	9.96	2.15	17.0	0.926	1.522	0.117	0.192
P06BX3	9.97	2.62	49.0	1.159	2.180	0.062	0.117
P06BX3	9.97	2.62	33.0	1.088	1.961	0.086	0.156
P06BX3	9.97	2.62	17.0	0.827	1.284	0.128	0.198
P07BY3	9.96	3.46	49.0	1.040	1.822	0.073	0.129
P07BY3	9.96	3.46	33.0	0.957	1.600	0.100	0.168
P07BY3	9.96	3.46	17.0	0.639	0.893	0.130	0.182
P08BZ3	9.90	5.25	49.0	0.899	1.452	0.096	0.156
P08BZ3	9.90	5.25	33.0	0.687	0.987	0.109	0.157
P08BZ3	9.90	5.25	17.0	0.447	0.563	0.138	0.174
P09CW3	15.15	2.15	49.0	1.422	3.134	0.062	0.137
P09CW3	15.15	2.15	33.0	1.500	3.467	0.098	0.226
P09CW3	15.15	2.15	17.0	1.073	1.922	0.136	0.243
P10CX3	15.15	2.62	49.0	1.359	2.881	0.073	0.154
P10CX3	15.15	2.62	33.0	1.348	2.840	0.107	0.226
P10CX3	15.15	2.62	17.0	0.931	1.534	0.144	0.237
P11CY3	15.12	3.46	49.0	1.190	2.278	0.084	0.161
P11CY3	15.12	3.46	33.0	1.154	2.165	0.121	0.227
P11CY3	15.12	3.46	17.0	0.789	1.199	0.161	0.244
P12CZ3	15.00	5.25	49.0	0.948	1.576	0.102	0.169
P12CZ3	15.00	5.25	33.0	0.866	1.373	0.138	0.218
P12CZ3	15.00	5.25	17.0	0.550	0.733	0.170	0.226

^a NTU - number of transfer units.

Fig. 2.28. Effect of gas velocity on the overall volumetric mass transfer coefficient in beds of 6.3-mm-diam plexiglass beads.

Fig. 2.29. Effect of gas velocity on $K_L a$ in beds of 3.2-mm-diam glass beads.

Fig. 2.30. Effect of gas velocity on $K_L a$ in beds of 4.6-mm-diam glass beads.

Fig. 2.31. Effect of gas velocity on $K_L a$ in beds of 6.2-mm-diam glass beads.

figures show, the relationship between $K_L a$ and the fluid velocities is apparently exactly the same in any of the systems. For example, Fig. 2.28 indicates a less than linear dependence of $K_L a$ on the liquid velocity, whereas Fig. 2.29 indicates a greater than linear dependence. In Fig. 2.28 the increase in $K_L a$ for an increase in the velocity from 5.1 to 10 cm/sec is much larger than that observed for a similar gas velocity change in the other systems. Figure 2.31 illustrates that the curves for gas velocities of 5.0 and 9.9 cm/sec are joined at a liquid velocity of 6 cm/sec, but as the liquid velocity is increased to 15 cm/sec, the curve for a gas velocity of 9.9 cm/sec diverges until it merges and actually crosses the curve for a gas velocity of 14.8 cm/sec.

Figure 2.32 shows the effect of particle size and density on $K_L a$, at a constant gas velocity of 5.0 cm/sec. The mass transfer coefficient increases with both increasing particle diameter and density. Apparently, the larger diameter of the plexiglass beads coupled with their much lower particle density results in mass transfer behavior similar to that exhibited by the 3.2-mm-diam glass beads. Figure 2.33 presents a similar example in which the gas velocity was kept constant at 9.9 cm/sec.

These results can be explained in terms of the type of bubble flow regime encountered in a three-phase fluidized bed. Large or heavy solids tend to break up the gas bubbles, giving rise to a "bubble-breakup" or "bubble-disintegration" regime. Small or light solids, however, do not break up the gas bubbles but allow them to coalesce; this is termed the "bubble-coalescence" regime. In the former regime, the bubbles are small (hence the surface area is very large), which increases the volumetric mass transfer coefficient. In the latter regime, the bubbles are large

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Fig. 2.32. Effect of particle size and density on $K_L a$ at a constant gas velocity of 5 cm/sec.

Fig. 2.33. Effect of particle size and density on $K_L a$ at a constant gas velocity of 9.9 cm/sec.

(hence the surface area is low) which decreases $K_L a$. Thus, use of the 3.2-mm-diam glass beads (small diameter) and the 6.3-mm-diam plexiglass beads (large diameter and low solid density) results in lower mass transfer coefficients than those obtained using the 4.6- and 6.2-mm-diam glass beads.

These mass transfer results were obtained by ignoring the effect of dispersion in the liquid phase as well as the column entrance and end effects. Future mass transfer experiments will attempt to deal with these phenomena. Experiments with the 15.2-cm-ID column are also planned. These will study the effect of column diameter and will use aqueous glycerol solutions to study the effect of liquid viscosity on the overall volumetric mass transfer coefficient.

2.5.3 Correlation of results

The results shown in the previous section and in previous reports^{1,2,7} for MF velocities, overall phase holdups, and local phase holdups were correlated with the physical parameters of the systems studied by using multiple linear regression. Dimensional correlations were tried first and were followed by dimensionless correlations whenever possible. The predictive equations presented in this section represent the best of the many correlations that were attempted.

Minimum fluidization. The MF velocities shown in Fig. 2.23, along with the previously reported MF results in aqueous glycerol, were correlated with the system parameters and resulted in the following dimensionless correlation:

$$Re_{mf} = a Ar^b Fr_G^c, \quad (7)$$

where

$$Re_{mf} = \text{Reynolds number} = \rho_L U_{L,mf} d_p / \mu_L ,$$

$$Ar = \text{Archimedes number} = d_p^3 \rho_L (\rho_S - \rho_L) g / \mu_L^2 ,$$

$$Fr_G = \text{Froude number} = U_G^2 / g d_p ,$$

$$\rho_L = \text{liquid density,}$$

$$d_p = \text{particle diameter,}$$

$$\mu_L = \text{liquid viscosity,}$$

$$\rho_S = \text{solid density,}$$

$$g = \text{acceleration due to gravity,}$$

$$U_G = \text{gas velocity,}$$

and the constants and their 95% confidence limits are

$$a = 0.005131 \pm 0.002,$$

$$b = 0.661 \pm 0.034,$$

$$c = -0.120 \pm 0.025.$$

Equation (7) had a correlation coefficient of 0.94 and an F-value of 478 using a total of 135 points; it is shown in Figs. 2.34-2.36 as predicted versus experimental MF data. Although the overall correlation is very good, significant deviations can be seen between the predicted and experimental results under some conditions. Considering the range of conditions covered, though, the correlation is satisfactory. Several correlations were tested but Eq. (7) gave the best results. Note that Eq. (7) is not valid for a zero gas rate where it would predict a liquid MF velocity of zero. As Figures 2.34-2.36 show, however, if a predicted MF curve is generated starting with gas velocities just greater than zero, the MF curves can be reliably extrapolated back to zero gas flow. Alternatively, at zero gas velocity, the two-phase correlation of Wen and Yu³⁷ can be used to predict the MF velocity.

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Fig. 2.34. Predicted vs experimental MF data for the glass and alumino-silicate beads.

Fig. 2.35. Predicted vs experimental MF data for the glass, plexiglass, and alumina beads.

Fig. 2.36. Effect of liquid viscosity on the predicted vs experimental MF data.

Overall phase holdups. Measurements of the overall solid holdup, $\bar{\epsilon}_S$, from this study were combined with 1355 points from the literature³⁸⁻⁴⁷ to develop the following dimensional correlation in centimeter-gram-second (cgs) units:

$$1 - \bar{\epsilon}_S = a U_L^b U_G^c (\rho_S - \rho_L)^d d_p^e \mu_L^f D_c^g, \quad (8)$$

where D_c = column diameter and the constants and their 95% confidence limits are

$$\begin{aligned} a &= 0.371 \pm 0.013, & e &= -0.268 \pm 0.008, \\ b &= 0.271 \pm 0.008, & f &= 0.055 \pm 0.006, \\ c &= 0.041 \pm 0.004, & g &= -0.033 \pm 0.010. \\ d &= -0.316 \pm 0.008, \end{aligned}$$

Figure 2.37 presents the results of this study in a parity plot. The equation was based on a total of 2381 data points and has a correlation coefficient of 0.87 and an F-value of 1178. Although the considerable data scatter is evident, these correlations show considerable improvement over previous ones presented in the literature.

Combining the data for overall gas holdup, $\bar{\epsilon}_G$, with 169 data points available from the literature,^{38,41-43,45} we developed the following correlation:

$$\bar{\epsilon}_G = a U_G^b d_p^c D_c^d, \quad (9)$$

where the constants and their 95% confidence limits are

$$\begin{aligned} a &= 0.048 \pm 0.008, & c &= 0.168 \pm 0.046, \\ b &= 0.720 \pm 0.021, & d &= -0.125 \pm 0.067. \end{aligned}$$

Again, cgs units are used for each parameter. Equation (9) is based on a total of 913 points and has a correlation coefficient of 0.93 and an

CORRELATION OF $1 - \bar{\epsilon}_s$

Fig. 2.37. Predicted vs experimental overall solid holdup values.

F-value of 1793. The results of this correlation, which are shown in a parity plot in Fig. 2.38, represent a significant improvement in existing correlations, principally because this study has greatly increased the range of conditions studied.

Local holdups. The local holdup versus column position shown previously¹ clearly indicated that each of the holdups is approximately constant in two regions: the lower portion of the bed and the gas-liquid region above the bed. The transition region between these two extremes depends on the gas velocity and the physical characteristics of the solid particles. An inflection point was observed on each curve with a spread about that point proportional to the width of the transition region. If each curve were differentiated, these two parameters would correspond to the mean and standard deviation of the normalized Gaussian curves. An error function was used to fit the gas- and solid-holdup curves, and the liquid-holdup curve was determined as the residual of the following:

$$\epsilon_G + \epsilon_L + \epsilon_S = 1 , \quad (10)$$

where

ϵ = phase holdup

and subscripts

G = gas phase,

L = liquid phase,

S = solid phase.

Use of the error function was essentially equivalent to use of the probability integral, since the two are related by the following:

$$\text{erf}(x) = 2\Phi(\sqrt{2}x) , \quad (11)$$

CORRELATION OF $\bar{\varepsilon}_G$

Fig. 2.38. Predicted vs experimental overall gas holdup values.

where

$\text{erf}(x)$ = error function,

$$\frac{2}{\sqrt{\pi}} \int_0^x e^{-z^2} dz ,$$

$\Phi(x)$ = probability integral,

$$\frac{1}{\sqrt{2\pi}} \int_0^x e^{-w^2/2} dw .$$

Thus the gas holdup curves were fitted by the following:

$$\epsilon_G = [(P_G - 1)/-2]\epsilon_G''' + [(P_G + 1)/2]\epsilon_G'' , \quad (12)$$

where

''' = three-phase region of the column,

'' = two-phase (gas-liquid) region of the column,

$$P_G = \text{erf} [(h - I_G)/\sigma_G] , \quad (13)$$

h = axial column position,

I = inflection point in local holdup versus height curve,

σ = standard deviation in local holdup versus height curve.

The solid holdup was fitted similarly using the error function and the knowledge that the solid holdup in the gas-liquid region of the column is zero:

$$\epsilon_S = [(P_S + 1)/2]\epsilon_S''' , \quad (14)$$

where

$$P_S = -\text{erf} [(h - I_S)/\sigma_S] . \quad (15)$$

The liquid holdup at each point was obtained from the residual to Eq. (10).

Thus, knowledge of seven parameters — ϵ_G''' , ϵ_G'' , ϵ_S''' , σ_S , σ_G , I_S , and I_G — allows description of each of the phase holdups at all axial

column positions. Figure 2.39 shows an example of such a fit. For the example system shown, the seven parameters were

$$\begin{aligned}\epsilon_G''' &= 0.072, & I_G &= 45.7 \text{ cm}, \\ \epsilon_G'' &= 0.129, & \sigma_S &= 2.83 \text{ cm}, \\ \epsilon_S''' &= 0.551, & \sigma_G &= 2.64 \text{ cm}. \\ I_S &= 45.7 \text{ cm},\end{aligned}$$

Treatment of the experimental data in this way and correlation of the seven parameters with fluid and solid properties and experimental conditions using least-squares multiple linear regression analysis resulted in a predictive equation for each parameter.

The gas holdup in the three-phase region of the column was successfully correlated by the following:

$$\epsilon_G''' = a[U_G^5(\rho_S - \rho_L)U_L g \sigma_{LV}]^b, \quad (16)$$

where σ_{LV} = interfacial tension and constants a and b and their 95% confidence limits are 0.159 ± 0.008 and 0.150 ± 0.006 respectively. Equation (16), shown as a parity plot in Fig. 2.40, had a correlation coefficient of 0.89 and an F-value of 2155 and was based on a total of 555 points.

Data on the gas holdup in the two-phase portion of the column (above the bed) were used to develop the following dimensionless correlation:

$$\epsilon_G'' = a[U_G^4(\rho_S - \rho_L)/g\sigma_{LV}]^b, \quad (17)$$

where constants a and b and their 95% confidence limits are 0.237 ± 0.010 and 0.185 ± 0.006 respectively. Equation (17) had a correlation coefficient of 0.93 and an F-value of 4266. The 634 points on which it was based are shown as a parity plot in Fig. 2.41. Most of the scatter shown in the

Fig. 2.39. Fit of local holdup profiles for the air-water-glass beads.

CORRELATION OF ε_G'''

Fig. 2.40. Predicted vs experimental values of the gas holdup in the three-phase region.

CORRELATION OF ε''_G

Fig. 2.41. Predicted vs experimental values of the gas holdup in the two-phase region.

figure results from the low-density (and low-density-difference) plexiglass data.

The solid holdup in the bed was correlated as follows:

$$1 - \epsilon_S''' = a Ar^b Re_L^c (H/H_O)^d, \quad (18)$$

where

$$Re_L = \rho_L U_L d_p / \mu_L,$$

H = expanded bed height (i.e., the height at which the pressure gradients in the two- and three-phase regions intersect),

H_O = static bed height,

and the constants and their 95% confidence limits are

$$\begin{aligned} a &= 1.990 \pm 0.273, & c &= 0.197 \pm 0.011, \\ b &= -0.178 \pm 0.012, & d &= 0.298 \pm 0.018. \end{aligned}$$

Figure 2.42 shows a parity plot of Eq. (18), which has a correlation coefficient of 0.95 and an F-value of 2529 and was based on 762 points.

Equation (18) requires a value for the expanded bed height; this was also correlated with the system properties and resulted in the following equation:

$$H/H_O = a Fr_G^b Re_L^c Ar^d [(\rho_S - \rho_L)/\rho_L]^e, \quad (19)$$

where the constants and their 95% confidence limits are

$$\begin{aligned} a &= 10.483 \pm 5.7, & d &= -0.295 \pm 0.039, \\ b &= 0.069 \pm 0.005, & e &= -0.305 \pm 0.027. \\ c &= 0.429 \pm 0.025, \end{aligned}$$

Equation (19), based on a total of 706 points, had a correlation coefficient of 0.90 and an F-value of 762; it is shown as a parity plot in Fig. 2.43. Again, most of the scatter occurs in the data from the plexiglass solids.

CORRELATION OF $1 - \epsilon_s'''$

Fig. 2.42. Predicted vs experimental values of the solid holdup in the three-phase region.

CORRELATION OF H/H_0

Fig. 2.43. Predicted vs experimental expanded bed height values.

The inflection point in the solid holdup curve followed the calculated bed height fairly closely and could be correlated by the following:

$$I_S = a U_G^b U_L^c D_c^d H^e, \quad (20)$$

where the constants and their 95% confidence limits are

$$\begin{aligned} a &= 2.354 \pm 0.440, & d &= 0.061 \pm 0.031, \\ b &= 0.017 \pm 0.008, & e &= 0.628 \pm 0.045. \\ c &= 0.247 \pm 0.017, \end{aligned}$$

Equation (20), shown as a parity plot in Fig. 2.44, had a correlation coefficient of 0.92 and an F-value of 875 and was based on a total of 689 points. The agreement is very good except for the plexiglass data.

Similarly, the inflection point in the gas holdup curve followed that in the solid holdup curve, yielding the following correlation:

$$I_G/H_o = a(\rho_S - \rho_L)^b d_p^c D_c^d I_S^e, \quad (21)$$

where the constants and their 95% confidence limits are

$$\begin{aligned} a &= 0.027 \pm 0.006, & d &= 0.170 \pm 0.045, \\ b &= -0.250 \pm 0.026, & e &= 0.875 \pm 0.049. \\ c &= -0.145 \pm 0.123, \end{aligned}$$

Equation (21) is based on a total of 635 points, and the results are shown as a parity plot in Fig. 2.45. The correlation coefficient was 0.849 and the F-value was 408.

The standard deviations in the local holdups versus height curves were the most difficult parameters to measure since a slight variation in the local holdup affected the standard deviation considerably; this variation would make the standard deviations more difficult to correlate. The

CORRELATION OF I_s

Fig. 2.44. Predicted vs experimental values of the inflection points of the solid holdup curve.

CORRELATION OF I_G/H_0

Fig. 2.45. Predicted vs experimental values of the inflection points of the gas holdup curve.

standard deviation in the solid holdup curve can be estimated from the following correlation:

$$\sigma_S/H_o = aC_D^b Fr_H^c, \quad (22)$$

where

$$C_D = \text{drag coefficient} = (\rho_S - \rho_L)d_p/\rho_L U_G^2,$$

$$Fr_H = \text{Froude number based on bed height} = U_G^2/gH,$$

and the constants and their 95% confidence limits are

$$a = 5.510 \times 10^{-6} \pm 3.3 \times 10^{-6},$$

$$b = -1.015 \pm 0.052,$$

$$c = -0.840 \pm 0.048.$$

Figure 2.46 presents Eq. (22) as a parity plot. The equation had a correlation coefficient of 0.84 and an F-value of 752 and was based on a total of 635 points. Although the data scatter was considerable, the data are useful and important because they represent the only data and the only correlation which attempts to describe axial variation in column properties.

Unfortunately, the standard deviation in the gas holdup curve was even more difficult to correlate than σ_S . A very rough estimate of σ_G can be obtained from the following correlation:

$$\sigma_G/H_o = a(\epsilon_G'' - \epsilon_G''')^b (\rho_S - \rho_L)^c d_p^e H^f \sigma_S^f, \quad (23)$$

where the constants and their 95% confidence limits are

$$a = 0.005 \pm 0.004,$$

$$d = -0.861 \pm 0.461,$$

$$b = 0.132 \pm 0.061,$$

$$e = 0.693 \pm 0.242,$$

$$c = -0.362 \pm 0.094,$$

$$f = 0.429 \pm 0.090.$$

CORRELATION OF σ_s/H_0

Fig. 2.46. Predicted vs experimental values of the standard deviations of the solid holdup curve.

Equation (23), based on a total of 609 points, had a correlation coefficient of only 0.66 and an F-value of only 93. The parity plot, shown in Fig. 2.47, illustrates the large variation between the measured and calculated values of σ_G . Much of the variation was due to the two plexi-glass-bead systems. With their small solid-liquid density difference, these beads made the pressure gradient, and thus the holdups, difficult to measure; hence, there was a large amount of scatter in the parity plot.

Reduction of parameters. Because of the scatter in the experimental data, using the different parameters to describe the local holdup of each phase was difficult to justify. In the fitting of the local holdup versus height curves, the inflection points and standard deviations of the gas and solid phases were similar. Thus, it might be more appropriate to estimate the inflection point and the standard deviation in the gas-phase curves by equating them to the predicted solid-phase values rather than by using Eqs. (21) and (23).

The inflection points in the gas-holdup curves are shown in Fig. 2.48 plotted against the solid-holdup inflection points. Similarly, the standard deviations in the gas-holdup curves are plotted against those in the solid holdup curves as shown in Fig. 2.49. Although a good deal of scatter is evident in Fig. 2.48 and, especially, in Fig. 2.49, data from Figs. 2.45 and 2.47, representing least-square fits, are also scattered. In fact, because of the scatter in the correlated fits, it is recommended that both the inflection point and the standard deviation of each of the three holdup curves be estimated by a single equation. For the standard deviation in the holdup curves, Eq. (22) should be used.

For the inflection point in the holdup curves, a further simplification can be made. As mentioned previously, the inflection point in the

CORRELATION OF σ_g/H_0

Fig. 2.47. Predicted vs experimental values of the standard deviations of the gas holdup curve.

CORRELATION OF I_G vs I_S

Fig. 2.48. Inflection points of the gas holdup curve vs inflection points of the solid holdup curve.

CORRELATION OF σ_G VS σ_S

Fig. 2.49. Standard deviations of the gas holdup curve vs standard deviations of the solid holdup curve.

solid holdup curve followed the calculated bed height closely. The two parameters are shown plotted against each other in Fig. 2.50. The agreement between the two is quite good, as expected, since the calculated bed height represents that height in the column of an equivalent homogeneous bed. Disagreements occur chiefly for beds of plexiglass beads, and particularly for highly expanded beds.

Figure 2.51 presents an example of an expanded bed of plexiglass beads. For this specified set of conditions, the concentration of solids dropped very gradually to zero, giving a solid-holdup inflection point of 36 cm. However, the pressure gradient over the two- and three-phase regions yielded a calculated bed height of 49 cm. As mentioned previously, the low solid-liquid density difference of the plexiglass beads made calculation of the bed heights and pressure drops subject to potentially larger errors than those associated with the other solids studied. Thus, with the possible exception of very low solid-liquid density difference systems, Eq. (19) should be used to predict both the expanded bed heights and the inflection points in the three holdup curves.

In summary, it is recommended that the following dimensionless correlations be used to construct phase-holdup curves versus column position curves: (1) that Eqs. (16)-(18) be used to estimate the gas and solid holdups in the two- and three-phase regions; (2) that Eq. (19) be used to determine the inflection point in each of the three holdup curves; and (3) that Eq. (22) be used to determine the standard deviation in each of the three holdup curves.

Centimeter-gram-second units were used in all of the parameters employed in these correlations [Eqs. (16)-(23)]. The correlations were

CORRELATION OF I_s vs H

Fig. 2.50. Inflection points of the solid holdup curve vs calculated bed heights.

Fig. 2.51. Axial variation of phase holdups in a bed of plexiglass beads.

based on a varying number of total points, depending on how many of the points used were zero (i.e., ϵ_G''' , ϵ_G'' , σ_G , and I_G) and how many were associated with zero gas-flow rates. Such points could not be logarithm transformed and hence could not be used in the multiple linear regression analysis. Also, a number of experimental conditions were used such that the bed height was above the highest manometer tap. For such conditions, the transition between the three- and two-phase regions could not be determined, so only the solid holdup was measured.

2.5.4 Conclusions

The minimum gas and liquid velocities required to fluidize various types of solids have been determined and correlated as a function of particle size, particle density, and liquid viscosity. No effect of the initial bed height or column diameter was found.

Overall phase holdups determined from a homogeneous bed model were combined with similarly determined literature data to yield correlations for the overall solid and gas holdups. The overall solid holdup was primarily a function of the liquid velocity, solid-liquid density difference, and the particle diameter; it varied proportionally with the latter two parameters and inversely with the liquid velocity. The overall gas holdup was primarily a function of the gas velocity and was almost proportional to it.

Using the seven parameters determined from the local gas and solid holdup profiles, it was possible to fit each of the holdup versus column height curves. Use of the dimensionless correlations of just five of these parameters — ϵ_G''' , ϵ_G'' , ϵ_S''' , σ_S , and H — should give a reactor designer more information concerning important phase distributions than that available

from the simpler homogeneous bed model and thereby aid in the rational design of reactors in which local conditions throughout the bed must be considered.

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3. FUSION ENERGY

The work of the Chemical Technology Division in fusion energy is closely coordinated with that of the ORNL Fusion Energy Program and includes studies of fuel handling, processing, and containment. Current studies are concerned with the development of vacuum pumps for fusion reactors and experiments and the evaluation of techniques for recovering tritium from solid or liquid breeding blankets. The more fundamental studies of blanket processing are supported by the DOE/Office of Basic Energy Sciences, and the remaining, more applied, studies are supported by the DOE/Office of Fusion Energy.

3.1 Cryosorption Vacuum Pumping

P. W. Fisher

During the past six months, the cryosorption vacuum pumping program continued its efforts to determine the optimal choice of adsorbents for fusion reactor applications. After completing pumping speed measurements for the molecular sieve 5A (MS-5A) cryosorption panel reported previously,¹ a molecular sieve Na-Y (MS-NaY) panel was installed for testing. At the tested feed rate, it was found that the MS-NaY panel reached much higher speeds than did the MS-5A panel at temperatures below 25 K. Above 25 K the performance of the two panels appears to be identical. During this time, several modifications and improvements were made to the experimental apparatus. These included replacing the stainless steel chevron with a copper chevron, modifying the flow of coolant to the back of the cryosorption panel, and adding the automatic data acquisition capability of a PDP/11 computer. While these hardware improvements will allow the

apparatus to operate at lower temperatures and permit experiments to be run with greater efficiency, making these improvements did significantly, though temporarily, delay the experimental program.

3.1.1 Experimental apparatus

In the course of taking data with the MS-5A panel, it was found that the temperature at the center of the chevron was between 120 and 140 K rather than the desired 77 K. The chevron assembly, previously all stainless steel, was modified; the stainless steel chevron panels were replaced with copper panels. Bolting on the new chevron and covering the interface between the copper and stainless steel with high-thermal-conductivity potting compound failed to give adequate thermal contact. Some experimental runs were made with this assembly, but chevron temperatures below 175 K could not be reached. Disassembly and inspection of the pieces showed that the potting compound did not remain bonded to the stainless steel. Subsequently, the chevron was silver-soldered to the dewar and now goes rapidly to 77 K when liquid N_2 is added. The temperature rises to only 79 K when all the vacuum gauges are turned on.

Because there have also been difficulties in reaching molecular panel temperatures below 12 K during the MS-5A runs, modifications were made to the heater and baffle plate behind the cryopanel. These changes provided greater volume and decreased the helium velocity across the back of the panel, thus permitting the accumulation of liquid helium. However, the desired result was not realized; the minimum temperature went up to 18 K. As a result, the baffle plate has again been redesigned and replaced, and the direction of gas flow behind the cryopanel reversed. Liquid helium now drips directly onto the center of the panel and is directed radially outward to the edge of the cryopanel.

Interconnecting cables have been installed between our laboratory and the PDP/11 computer for automatic data acquisition. The computer's industrial control system (ICS) is being implemented for this purpose. This system is capable of reading signals as high as 10 V with an accuracy of 0.05%. Eight gains, ranging from 1 to 1000, are available to vary the sensitivity of the instrument. Channels for analog input and output, digital output, and a computer terminal have been installed and tested. Programs and subroutines for reading voltages and automatic gain control have been written and tested. A data acquisition program has also been written and will be tested.

Figure 3.1 shows the MS-NaY cryopanel which has been installed in the apparatus for testing. The panel was prepared by Y-12 development. It has 1/16- by 1/16-in. cross-milled grooves identical in design to those used in the previous MS-5A panel. The coating on this panel, however, does not appear to be as thick. Also, the tops of the stainless steel projections are exposed in this panel, whereas they were covered in the MS-5A panel.² Maximum pumping speeds are therefore expected to be only about 75% of those previously measured. In addition, the surface of the panel has become discolored during the hardware modifications. The nature and effect of this possible contamination are unknown at this time.

3.1.2 Experimental results

Table 3.1 summarizes the 22 runs made during this period using the two different copper chevron assemblies discussed above. All runs were made with a hydrogen feed rate of 5.4×10^{-2} torr-liter/sec. Speeds could not be measured at lower feed rates because of a broken leak valve. Time-averaged speeds, pressures, and temperatures were calculated for

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Fig. 3.1. Molecular sieve-NaY cryopanel.

Table 3.1. Time-averaged temperature, speed, and pressure for 5-min runs with a MS-NaY panel

(Runs were made at a hydrogen feed rate of 5.4×10^{-2} torr-liter/sec.)

Run	Quantity of gas accumulated prior to run (torr-liters)	Average surface temperature (K)	Average speed (liters/sec)	Average pressure (torr)	Thermal treatment prior to run ^a	Chevron temperature (K)	Temperature during run
A-1	0.0	21.3	565	9.7×10^{-5}	R	200	Steady
A-2	16.2	35.3	13.6	4.2×10^{-3}	H-50		Rising
A-3	32.4	31.9	15.3	3.6×10^{-3}	C		Rising
A-4	48.6	29.6	146	2.8×10^{-3}	C		Unstable
A-5	64.8	33.6	12.4	4.9×10^{-3}	C		Rising
B-1	0.0	17.9	674	8.1×10^{-5}	R	175	Steady
B-2	16.2	18.2	498	1.1×10^{-4}	H-50		Steady
B-3	32.4	32.2	15.0	4.1×10^{-3}	H-50		Rising
B-4	48.6	18.8	491	1.1×10^{-4}	H-40		Rising
B-5	64.8	19.0	475	1.2×10^{-4}	H-40		Steady
B-6	81.0	22.9	294	2.3×10^{-3}	H-50		Unstable
B-7	97.4	19.5	359	1.5×10^{-4}	H-50		Steady
C-1	0.0	16.3	1180	4.6×10^{-5}	R	79	Steady
C-2	16.2	16.5	1170	4.7×10^{-5}	H-40		Steady
C-3	32.4	20.3	61.6	1.3×10^{-3}	H-40		Rising
C-4	48.6	24.7	33.9	1.6×10^{-3}	H-40		Rising
C-5	64.8	16.5	1064	5.1×10^{-5}	H-40		Steady
C-6	81.0	16.9	807	6.9×10^{-5}	H-50		Steady
C-7	97.2	19.5	105	1.1×10^{-3}	H-40		Rising
C-8	113.4	17.2	636	8.8×10^{-5}	H-40		Steady
C-9	129.6	17.9	327	1.8×10^{-4}	H-40		Steady
C-10	145.9	19.5	425	8.6×10^{-4}	H-40		Sinusoidal

^a R = cooled from room temperature; C = temperature held constant at previous operating temperature between runs; H-40 = panel heated to 40 K and re-cooled to operating temperature prior to run; and H-50 = panel heated to 50 K and re-cooled to operating temperature prior to run.

5-min runs for comparison with the MS-5A data presented previously.¹ Heat treatments to about 40 and 50 K were made between most runs to clear the surface of hydrogen. Discussion of this effect has also been presented previously.¹ It was found that the temperature of the panel could not be held steady during all runs, especially those above about 20 K. During these runs, the temperature sometimes rose monotonically; sometimes underwent wide, random fluctuations; and once showed a sinusoidal-type variation.

Figure 3.2 shows curves representing four typical MS-NaY runs during which the temperature remained nearly constant. These curves can be compared with similar ones presented in a previous report for MS-5A (Ref. 1, Fig. 3.10). Curves at comparable speeds have comparable shapes. Speed curves near 200 liters/sec, for instance, show significant fluctuations for both. It is also apparent from these curves that for a comparable speed, the temperature of the MS-5A panel requires a temperature about 5 K lower than does the MS-NaY panel.

Figure 3.3 shows sets of curves for two MS-NaY runs (A-4 and C-10), during which the temperature could not be controlled and varied sinusoidally and unstably. Pressures during these runs were in the 10^{-4} to 10^{-2} torr range. Run B-6 showed similar behavior to Run A-4. None of the MS-5A runs with similar panels behaved in this manner, although one deuterium run in the 10 K range, measured on the Excalibur pump, also showed rapid sinusoidal fluctuations (Ref. 2, Fig. 3.11). These data additionally show that the surface-clearing mechanism proposed previously for helium,³ hydrogen,⁴ and deuterium² cycles may also be operative for the hydrogen-MS-NaY system. Run A-4, for instance, showed that pumping speeds can begin to increase

Fig. 3.2. Pumping speed as a function of time at various temperatures for hydrogen on MS-NaY.

Fig. 3.3. Pumping speed, pressure, and temperature as a function of time for two runs in which the temperature could not be controlled.

as the temperature decreases but will then fall rapidly at the lowest temperature. Apparently, material is transferred from the surface to the bulk of the adsorbent during the higher temperature part of the cycle, thus allowing the surface to become clear and the speed to increase. As the temperature goes down, the surface coverage again increases, eventually causing the speed to fall. These effects did not appear below 20 K. Above 20 K the equilibrium adsorption pressure may be close to the operating pressure at this feed rate.

Figure 3.4 shows a direct comparison between average pumping speeds measured for both the MS-5A and MS-NaY. Below 20 K the MS-NaY panel shows speeds that are about an order of magnitude higher than those of the MS-5A panel. This behavior is not unexpected because cryosorption pumping speeds in this region appear to be limited by mass transfer; the MS-NaY with its more open structure and, consequently, higher diffusivities should have higher pumping speeds than the MS-5A. Note that the temperature of the chevron does not appear to have a significant effect on performance.

Figures 3.5 and 3.6 show the response of the closed system to a temperature cycle after two different runs. Figure 3.5 shows a run made at about 20 K, and Fig. 3.6 a run below 20 K. These two curves are representative of behavior observed after other runs. These curves cannot be compared directly with those presented previously for the MS-5A (Ref. 1, Figs. 3.13 and 3.14) because they were recorded after accumulation of far less material during the run (0.02 torr-liter as opposed to 16.2 torr-liters in the runs presented here).

The curve in Fig. 3.5 begins at the pressure and temperature at which the pump was operating when the leak was terminated. The pressure falls

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Fig. 3.4. Comparison of average pumping speeds and temperatures for 5-min runs on the MS-5A and MS-NaY.

Fig. 3.5. Response of the closed system to a temperature cycle after a run at about 20 K.

Fig. 3.6. Response of the closed system to a temperature cycle after a run below 20 K.

rapidly and the temperature also decreases slightly as the heat load on the panel is reduced. Panel heating begins and the pressure rises steadily until cooling is resumed at about 40 K. It is important to observe that the curve forms a closed hysteresis loop. (Curves presented in Ref. 1 did not close on themselves but returned to a much lower pressure.) This means that the panel is returning to the same equilibrium point after the temperature cycle. Hence, mass transfer resistance did not hamper approach to equilibrium with the bulk of the adsorbent after the run. The closed hysteresis loop can be fully explained in terms of the heat of adsorption. As the panel is heated, material desorbs from the surface; this is an endothermic process which cools the panel and retards the heating rate. As the panel is cooled, material readsorbs on the surface. This is an exothermic process which heats the panel and retards the cooling rate. Hence, this hysteresis loop forms as a result of dynamic effects. The fact that the curve closes on itself at 20 K indicates that this is a true equilibrium point.

The curve in Fig. 3.6 also begins at the temperature and pressure at which the pump was operating when the leak was terminated. Note that the pump was operating slightly below 20 K, and the pumping speed was quite high during the run (449 liters/sec). The heating and cooling curve has two distinct loops which do not form a closed curve. Following the curve from the beginning (termination of leak), it can be seen that the pressure first increases very rapidly with a slight increase in temperature and then decreases rapidly with a continued slight increase in temperature. Continuation of heating causes the pressure to rise a second time, and the start of cooling at about 40 K causes the pressure to decrease and

ultimately reach much lower pressures than those observed near the beginning of the curve. Apparently, during the run, most of the hydrogen accumulated at or near the surface; the temperature at that point is too low to allow rapid diffusion into the bulk of the adsorbent. The hydrogen adsorbed on the surface desorbs rapidly with only a slight increase in temperature and is readsorbed into the bulk of the adsorbent. Reexamination of the recovery data for the MS-5A after runs at this feed rate shows that a double peak also occurs for that material.

Figure 3.7 compares equilibrium curves for hydrogen at about the same coverage on the MS-5A and MS-NaY panels. The two materials show the same equilibrium behavior at 18 K. Presumably, they would continue to be similar below 18 K. However, above 20 K, the MS-NaY shows equilibrium pressures which are orders of magnitude higher than those of the MS-5A at the same temperature. A comparison of Figs. 3.4 and 3.7 suggests that below 20 K, pumping speeds on the MS-NaY are limited by mass transfer and that above 20 K, they are limited by equilibrium. This is in contrast to MS-5A speeds which, for the temperature range examined, always appear to be limited by mass transfer.

3.1.3 Program status

Pumping speed measurements on the MS-NaY panel are continuing and should be complete in the near future. An MS-BX cryosorption panel is ready for installation and testing. Some additional tests may be performed on an MS-NaY panel with a renewed surface for comparison with the present data.

Fig. 3.7. Comparison between equilibrium curves for the MS-NaY and MS-5A; 165 torr-liters adsorbed on the MS-NaY panel and 99 torr-liters on the MS-5A panel.

3.2 Tritium Sorption from Liquid Metals

S. D. Clinton and J. B. Talbot

3.2.1 Introduction

Molten lithium appears to be the most promising blanket material for breeding tritium in fusion reactors. Three recovery techniques are currently being considered for the removal of tritium from liquid lithium: (1) extraction by a molten salt, (2) permeation through a niobium window, and (3) sorption on a hydrogen-gettering metal. Tritium sorption from molten lithium and potassium (potential blanket coolant) has been studied in a batch contactor at temperatures of 250 to 400°C using metal sorbent samples of yttrium and zirconium. Yttrium has shown significant removal rates from both molten lithium and potassium; however, the sorption rates observed from potassium are too slow for a practical recovery process. At 300°C a yttrium sample reduced the concentration of tritium in lithium by a factor of 2 in 24 min (effective film mass transfer coefficient of 6×10^{-4} cm/sec), whereas the half-life of tritiated lithium in contact with a similar yttrium sample at 400°C was about 50 min (effective film mass transfer coefficient of 3×10^{-4} cm/sec). At the higher temperature, the lower sorption rate may be due to a reduced concentration driving force. Although forced convection data are needed to complete the analysis, the results to date demonstrate the feasibility of such a blanket-recovery system.

3.2.2 Experimental equipment

A schematic diagram of the equipment used to contact tritiated liquid metals with selected metal sorbents has been published.⁵ The equipment

consists of a liquid metal reservoir containing dissolved tritium, two sampling valves, two isolated contacting chambers (volume, ~20 cc each), a vacuum source, and an argon supply. The tritiated lithium can be drawn into the two contacting chambers at a temperature between 200 and 400°C. One chamber contains the metal sorbent, and the other chamber serves as a control. To terminate an experiment, the lithium samples are removed from the contactor chambers, dissolved in water, and analyzed for tritium by liquid scintillation counting.^{3,6}

3.2.3 Results and discussion

To prepare tritiated yttrium samples for the regeneration experiments, yttrium-metal foil obtained from Research Chemicals was sawed into seven coupons (0.16 x 0.64 x 1.26 cm each). The total weight of the yttrium was 3.83 g (average weight of each coupon, 0.55 g). Twelve batch-contactor runs were made with tritiated lithium (733 ppb tritium) and the seven yttrium coupons at 300°C. The contact times ranged from one to three days. Tritium accumulation in the yttrium, estimated from the concentrations in the lithium control and sorber samples after each of the 12 sorption runs, was estimated to be 0.336 Ci (0.088 Ci/g).

At the end of the sorption runs, the yttrium coupons were removed from the contactor chamber and rinsed with water to remove any lithium adhering to the sample. The total tritium recovered from the lithium-water dissolution was 5.4×10^{-4} Ci. One of the seven coupons was dissolved in dilute hydrochloric acid to check the tritium content of the yttrium. After counting the solution in a liquid scintillation spectrometer, the tritium concentration in the yttrium was found to be 0.090 Ci/g. The six remaining yttrium coupons (about 0.050 Ci/coupon) were stored for future high-temperature (500 to 800°C) tritium-recovery experiments.

3.2.4 Program status

Sorption on a hydrogen-gettering metal appears to be one of the more promising techniques for tritium recovery from liquid lithium. Although the studies are not complete, the results to date demonstrate the feasibility of such a blanket-recovery process system. During the next six months, the batch-contactor system will be dismantled and replaced by a forced-convection tritium sorption experiment. An electromagnetic pump and a flow meter have been received for use in the proposed flow system.

3.3 References for Section 3

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4. RESOURCE RECOVERY

The Resource Recovery Program is concerned with the recovery of valuable minerals from energy-related waste streams and the recovery of minerals important to energy production from new or secondary ores. Current efforts are focused on the recovery of metals from fly ash produced by coal combustion. The work reported here is supported by the DOE/Office of Basic Energy Sciences.

4.1 Resource Recovery from Coal Wastes

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4.1.1 Recovery of resource materials from coal combustion wastes

The objectives of this program are to develop and evaluate potential processes for the recovery of resource materials from coal combustion wastes and to identify those candidates that appear most feasible from both technical and economic points of view. The studies presented here have been directed primarily toward resource material recovery from fly ash generated as waste by coal-burning power plants. The program is carried out in cooperation with the Separations Systems Research group of the Chemical Development Section. In the United States, coal conversion and utilization residues currently total about 10^8 tons and are expected to become a major disposal problem in the future. Hence, the extraction of metal values from these residues with accompanying waste-volume reduction is desirable.

Laboratory-scale tests of methods for the recovery of aluminum and other metal values from fly ash have included reported processes such as

lime-sinter, lime-soda-sinter, and the obvious direct-acid leach methods, as well as two new combination sinter-dilute-acid leach methods. In the first, fly ash is sintered with a $\text{NaCl-Na}_2\text{CO}_3$ mixture at 800°C , followed by successive leaches with water and 1 N HNO_3 or H_2SO_4 . In the second, fly ash is sintered with a $\text{CaSO}_4\text{-CaCO}_3$ mixture at 1200°C , after which the sinter cake is pugged with 36 N H_2SO_4 and then diluted to 4 N for a second leaching period. Both of these new methods are capable of recovering more than 95% of the aluminum, of yielding a pure Al_2O_3 product if a solvent extraction circuit is included, and of providing for product option flexibility in that Fe, Ti, Mn, U, and Th can be recovered.

4.1.2 Salt-soda-sinter-acid leach system

Sintering with a $\text{NaCl-Na}_2\text{CO}_3$ mixture, as is used for opening up the aluminum silicates in fly ash, is a modification of a fusion method developed at ORNL for the recovery of cesium from Pollucite. In the development of the salt-soda-sinter process, the fusion mixture, $\text{NaCl-Na}_2\text{CO}_3$ in a ratio of 2:1, was mixed with fly ash in a ratio of 3:1, heated to sintering temperatures of 500 to 850°C , and then leached with various solutions. Figure 4.1 shows aluminum recovery as a function of sintering temperature; a generalized, conceptual flowsheet for the process is shown in Fig. 4.2. In tests designed to determine the optimum salt-soda mixture for the most effective recovery of aluminum from fly ash, a series of experiments was conducted in which the ratios of NaCl , Na_2CO_3 , and fly ash were varied. Results show that maximum aluminum recovery is achieved at a $\text{NaCl:Na}_2\text{CO}_3$ ratio of 2:1 and a salt mixture:fly-ash ratio of 3:1. If 8 N acid is used instead of 1 N , the latter ratio can be lowered to 2:1. In all these tests, the salt-fly-ash mixture, along with 4% H_2O , was

Fig. 4.1. Effect of sintering temperature on aluminum recovery in the salt-soda-sinter process. Test conditions: programmed increase, 2 hr at maximum temperature; fusion mix: 50 wt % NaCl, 25 wt % Na₂CO₃, 25 wt % fly ash; leaches: No. 1, H₂O; No. 2, 1 N HNO₃.

Fig. 4.2. Generalized flowsheet for the salt-soda-sinter process.

compressed into pellets at 10,000 psi and sintered at 800°C for 1.5 hr. A programmed increase (and decrease) in furnace temperature improved the leaching qualities of the sinter cake; therefore, the procedure that was followed in the tests reported here provided for an initial temperature increase to 400°C in 1 hr and a subsequent rate of increase of 100°C/hr until the desired temperature had been reached (Fig. 4.3). After sintering, the cake was subjected to a combination of an initial H₂O leach for the purpose of recovering unreacted salts. This was followed by a leach with solutions of either HNO₃ or H₂SO₄ at varying concentrations and pulp density. Aluminum recovery is reduced from 80 to 30% when the pulp density is increased from 10 to 30%.

4.1.3 CaSO₄-CaCO₃-sinter (Calsinter) process

The CaSO₄-CaCO₃-fly ash sintering system, a new process developed at ORNL, is an alternative method for opening up the refractory silicates in fly ash. Its advantages are (1) use of sulfate as a single anion in the leaching system (thus reducing acid recovery and corrosion problems, (2) use of the CaSO₄-CaSO₃ sludge from a lime scrubber designed for the removal of sulfur dioxide from stack gases, and (3) high metal-values recovery. In the investigation of the CaSO₄-CaCO₃-sinter process, the fusion mixture (using reagent-grade salts) and the fly ash were sintered in various ratios at temperatures ranging from 800 to 1250°C. A programmed increase in furnace temperature was used here as in the salt-soda process described in the previous section. Leaching of the sinter cake consisted of pugging the material with 36 N H₂SO₄ for 3 hr and diluting the slurry to 10% solids, followed by an additional leaching period of 16 hr at reflux temperature. Various acid concentrations were tested to determine optimum aluminum

Fig. 4.3. Programmed furnace temperature for sintering fly ash with NaCl-Na₂CO₃ mixtures.

recovery. Though arbitrary and not necessarily optimum, the most favorable conditions for this testing were found to be a sinter mixture containing CaSO_4 - CaCO_3 -fly ash in the ratio of 1:1:1, a sintering temperature in the range of 1100 to 1200°C, a pugging leach followed by a dilution leach at 10% solids, and a final H_2SO_4 concentration of 4 N. Both leaches were made at reflux temperatures for 3 and 16 hr respectively. Two scanning electron photomicrographs (Fig. 4.4) show evidence of the complete conversion by this technique of the refractory glass-type spheroids, which make up the fly ash originally into a completely crystalline structure. Aluminum recovery is plotted as a function of sintering temperature and the ratio of fusion mixture composition to fly ash composition in Fig. 4.5. Figure 4.6 shows that adding MgCO_3 to the sinter mixture improves aluminum recovery above the level obtained from use of the CaSO_4 alone, but not as much as does adding CaCO_3 . Further, the addition of MgSO_4 to a mixture of CaSO_4 - CaCO_3 appears to repress aluminum recovery in the temperature region of 1000°C, while the addition of MgSO_4 in the absence of CaCO_3 apparently enhances its recovery. Table 4.1 shows aluminum recovery as a function of H_2SO_4 concentration, both with and without the initial plugging leach. For the former condition, surprisingly small differences in aluminum recovery resulted when the concentration of the leaching acid was varied from 2 to 16 N. For example, after samples of fly ash had been sintered at 1100°C with a CaSO_4 - CaCO_3 mixture, recoveries ranged from 79 to 88%. Aluminum recovery for several low-melting sintering agents is shown in Table 4.2.

A generalized, conceptual flowsheet for the Calsinter process is shown in Fig. 4.7. No material balance has been determined as yet for the H_2SO_4 ; thus, the recycle-to-makeup ratio is not known.

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FLY ASH AS RECEIVED

ORNL-PHOTO 1218-78

SINTERED/LEACHED SOLIDS

Fig. 4.4. Conversion of fly ash from glassy spheroids to crystalline structure after treatment by the CaSO_4 - CaCO_3 sinter-acid leach process.

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Fig. 4.5. Effect of sinter-mix composition and temperature on aluminum recovery from fly ash.

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Fig. 4.6. Effects of sintering temperature and fusion mixture composition on aluminum recovery from fly ash.

	Weight Ratios				Fly Ash
	CaSO ₄	CaCO ₃	MgSO ₄	MgCO ₃	
1.	2	-	-	-	1
2.	1	1	-	-	1
3.	1	-	1	-	1
4.	0.7	0.7	0.7	-	1
5.	1	-	-	1	1

Table 4.1. Effect of sulfuric acid concentration
on aluminum recovery

Preparative conditions: sinter, CaSO_4 - CaCO_3 -fly
ash (1:1:1); temperature, 1100°C; time, 2 hr;
leach and pugging, 3 hr; dilute, 16 hr;
temperature, reflux.

H_2SO_4 conc. (N)	Initial pugging leach	Aluminum leached (%)
2	No	79
4	No	79
8	No	80
16	No	99
2	Yes	82
4	Yes	86
8	Yes	86
16	Yes	86

^a Note that these results are not at optimum recovery conditions in order to emphasize differences in leachability of the sinter cake.

Table 4.2. Recovery of aluminum from fly ash using low-melting eutectic mixtures as sintering agents^a

Test no.	Eutectic mixtures	Mixture composition (mole %)	Mix-fly ash ratio (wt %)	Leach acid	Aluminum recovered (%)
SFA-12	CaSO ₄ -K ₂ SO ₄	42:58	2:1	H ₂ SO ₄	61
SFA-13	CaSO ₄ -K ₂ SO ₄ -MgSO ₄	4.9:20.8:74:3	2:1	H ₂ SO ₄	40
SFA-14	CaSO ₄ -Na ₂ SO ₄	50:50	2:1	H ₂ SO ₄	23
SFA-15	CaSO ₄ -Na ₂ CO ₃ -CaCO ₃	36:38:26	2:1	H ₂ SO ₄	38
SFA-16	CaCO ₃ -Ca(OH) ₂	35.8:64.2	2:1	H ₂ SO ₄	3
SFA-17	CaCO ₃ -Ca(OH) ₂	35.8:64.2	2:1	HNO ₃	5
SFA-18	K ₂ SO ₄ -MgSO ₄	64.5:35.5	2:1	H ₂ SO ₄	47

^aTest conditions: sintered under programmed temperature increase and decrease; maximum temperature: 800°C for 1.5 hr; leached at 10% pulp density for 16 hr at reflux temperature with 1 N solutions of specified acids.

Fig. 4.7. Generalized, conceptual flowsheet for the Calsinter process.

4.1.4 Test of the Calsinter process using scrubber-slurry sludge

One current method for removing sulfur dioxide from coal-fired power plant stack-gases is to scrub the gas with a lime slurry (Fig. 4.8). The resulting waste slurry is a mixture of CaSO_4 , CaSO_3 , and CaCO_3 . The components of a typical scrubber sludge are shown in Table 4.3. The possibility of combining the two waste materials, stack-gas scrubber sludge and fly ash, in the recovery of useful resource materials while simultaneously reducing the total volume of waste is extremely attractive. Accordingly, samples of dewatered stack-gas scrubber sludge were obtained and tested as a sintering material for the recovery of metal values from fly ash. In these tests, the dewatered sludge was mixed with varying proportions of fly ash and, in some cases, additional CaCO_3 . This mixture was then pelletized, and the pellets were sintered at various temperatures. The sintered pellets were then crushed and leached with 8 N H_2SO_4 in standard pugging and dilution leaches. The results of these tests show that aluminum recovery generally improved as the sintering temperature was increased in the range of 800 to 1100°C (Fig. 4.5). Further, adding CaCO_3 increased the amount of aluminum that can be removed by leaching. Figure 4.9 shows aluminum recovery as a function of sinter-mix composition at 1100°C. Aluminum recovery increased as the ratio of sludge solids to fly ash increased; however, note that since the fly ash contained 15% aluminum and the sludge solids contained 4% aluminum, the total aluminum present in the tested systems decreased as the ratio of the sludge solids to fly ash increased. This information is represented by a broken line in Fig. 4.9.

4.1.5 Sintering fly ash with low-melting eutectic mixtures

Since mixtures of NaCl - Na_2CO_3 and CaSO_4 - CaCO_3 were so successful in displacing the aluminum from the complex silicate structure of fly ash,

Fig. 4.8. Limestone scrubber system.

Table 4.3. Analyses of typical limestone scrubber-sludge solids

Wet-chemical analyses					
Constituent	wt %		mole %		
Ca	21.6		30.6		
Al	4.02		8.5		
SiO ₂	20.4		19.2		
SO ₄ ²⁻	4.95		2.9		
SO ₃ ²⁻	14.7		11.0		
CO ₃ ²⁻	28.6		27.0		

Spark-source mass spectrometric analyses					
Constituent	wt %	Constituent	wt %	Constituent	wt %
Al	>10	K	1.5	Rb	0.18
B	0.01	Li	0.02	Si	>10
Ba	0.1	Mg	1.5	Sn	0.07
Ca	>10	Mn	0.08	Sr	0.5
Co	0.0075	Mo	0.01	Ta	0.05
Cr	0.05	Na	1.0	Ti	0.1
Cu	0.03	Ni	0.03	V	0.04
Fe	0.6	Pb	0.02	Zn	0.02

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Fig. 4.9. Effect of sinter-mix composition on aluminum recovery at 1100°C.

it seemed expedient to try other mixtures, particularly those which exhibit lower melting points because of their formation of eutectic mixtures.

Therefore, a series of sintering tests was made in which known eutectic mixtures were combined with fly ash, pelletized at 10,000 psi, and sintered at 800°C; the sinter cake was then leached with 1 N solutions of either HNO_3 or H_2SO_4 . Several sinter cakes were preleached with H_2O to remove soluble acid-consuming compounds. Standard leaching conditions of 16 hr at reflux temperature and 10% pump density were used for all the tests reported in Table 4.3. The test data indicate only moderate recovery of aluminum with these eutectic mixtures.

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