interstitial liquid velocity, and found downflow near the wall and upflow in the center of the column. This circulation pattern and its associated large eddies tend to cause bubble clustering in the center of the column which further drives the liquid circulation pattern.

Zuber and Findlay (63) have suggested that n in Equation 23 is zero for the churn-turbulent flow regime. Thus:

$$V_{CD} = U_t \epsilon_g \tag{26}$$

Zuber (63) has suggested that U_t is given by the expression for Region 4 in Table III. U_t might also be given by Equation 15.

Slug Behavior.--When the diameter of the bubbles becomes of the same order as that of the tube, the flow regime is referred to as slug flow. In this regime, round-nosed slugs of gas separated by regions of liquid rise through the system. Davies and Taylor (27) have determined the rising velocity of these slugs in stagnant liquid. They found:

$$U_{sl} = 0.35\sqrt{gD} \tag{27}$$

where: U_{sl} = the velocity of the slug
D = tube diameter

In the case where there is a net flow of gas and liquid, Nicklin, Wilkes, and Davidson (52) have shown that the velocity of the slug is given by:

$$U_{sl} = 1.2(U_g + U_l) + 0.35\sqrt{gD} \tag{32}$$

Nicolitsas and Murgatroyd (54) have confirmed the values of the two constants in Equation 28 as 1.2 and 0.35, respectively.

Zuber and Findlay (63) give the value of the drift flux for slug flow as:

$$V_{CD} = 0.35(gD)^{1/2}\epsilon_g \tag{29}$$

Gas/Liquid/Solid Fluidized Systems

The addition of gas to a liquid fluidized bed increases the complexity of the system considerably. Many of these complexities have direct analogs in the corresponding two-phase system. For instance, Kim, Baker, and Bergougnou (78) and Darton and Harrison (70) report the existence of two distinct types of gas/liquid flow regimes: the ideal bubbly and churn-turbulent. Kim, et al. (78) describe these as the "bubble disintegrating" and "bubble coalescing" regimes. Other complexities are unique to the three-phase systems. Turner (105) was the first to report the contraction of some liquid fluidized beds upon the addition of gas. Stewart and Davidson (103) have proposed that the contraction occurs because of the formation of particle-free liquid wakes behind the bubbles which move through the bed at the bubble velocity. This action reduces the interstitial liquid velocity in the

rest of the bed, thus causing its contraction. Ostergaard (93) has proposed a similar mechanism. However, he contends that the particle concentration in the wake is the same as in the remainder of the bed. These mechanisms will be discussed in detail later.

This section will first consider the behavior of gas bubbles in the presence of solid particles. Data and correlations of three-phase fluidized systems will then be discussed.

Bubble Behavior in Gas/Liquid/Solid Systems.--Topics discussed in this section will follow the same order as the section on vertical gas/liquid systems.

a) Rising Velocity of Single Bubbles.--Several studies on the rise velocity of single bubbles in fluidized beds have been reported in the literature. A summary of experimental conditions is shown in Table IV.

Darton and Harrison (71) analyzed their bubble velocity data in terms of the following equation:

$$C_D = E + \frac{\delta}{\rho_l U_b d_e} \qquad (30)$$

where $E \cong 2.65$

They assumed that the bubble had rigid surfaces. Thus:

$$\delta = 24\mu_e$$

where μ_e = effective bed viscosity

The effective bed viscosity was found to decrease with increasing bed expansion. The authors correlated their bed viscosity data and bed viscosity data obtained by Rigby, et al. (100) and Henriksen (76) via the relation suggested by Mooney (193). Using the effective bed viscosity to calculate bubble Reynolds numbers, the authors found the following limiting relationships for C_D:

$$C_D = 2.65 \qquad Re > 100 \qquad (31)$$

$$C_D = 38Re_b^{-1.5} \qquad Re < 2 \qquad (32)$$

The best correlation of C_D and Re_b was obtained when Re_b and C_D were based on bubble velocity relative to liquid velocity.

Massimila, et al. (85) presented the results of their single bubble experiments graphically as plots of bubble rise velocity vs. bubble diameter. They found that for a given bubble diameter the rise velocity increased with increasing bed expansion. This result indicates the bed behaves as a high viscosity fluid, the viscosity decreasing as the bed expands. Verbitskii and Vakhrushev (108) also found that the

effective bed viscosity decreased with increasing bed expansion. These authors correlated their data in a format similar to that used by Darton and Harrison (71). They propose the following relationships:

$$C_D = \frac{24}{Re_b} \qquad Re_b < 1 \tag{33}$$

and $$C_{D_b} = 21.2 Re_b^{-0.32} \qquad 2 < Re_b < 10 \tag{34}$$

Henriksen and Ostergaard (77) used two-dimensional beds to measure the velocity of spherical cap bubbles in fluidized beds. For the cases where the bed could be considered inviscid, they found the following relation:

$$U_t = K''(gR)^{1/2} \tag{35}$$

where: K'' = constant dependent on particle size and bed expansion
R = radius of curvature of spherical cap.

b) Bubble Wakes.--As will be discussed later, bubble wakes are of great importance in explaining bed contraction in three-phase systems. Stewart and Davidson (103) and Rigby and Capes (99) have investigated the structure of wakes from spherical cap bubbles in two-dimensional beds fluidized with water. In Reference 103, glass ballotini, iron, and lead shot (0.46 mm diameter) were fluidized. In Reference 99, glass ballotini and sand (0.120 to 0.775 mm in diameter) were fluidized. In these studies, the following observations of bubble wakes in beds of particle diameter greater than 0.46 mm were made:

1) For sufficiently large bubbles, a small region of water free of particles follows the bubble.
2) The wake contains vortices which are shed either simultaneously or in a zig-zag manner similar to that reported by Narayanan, et al. (133) (Class IV wakes).
3) The vortices contain a lower concentration of particles than the rest of the bed; the particles are centrifuged out by the vortex action.
4) The upward velocity of the vortices is lower than that of a bubble.

For particles less than 0.26 mm, Rigby and Capes (99) observed little or no particle-free liquid wake associated with the bubbles, although the vortices were still present.

Rigby and Capes (99) estimated the wake-to-bubble-volume ratio from pictures, and concluded that this ratio decreased with increasing bubble size. Using an impedance probe, Darton and Harrison (70) have measured this ratio. Their findings agree with those of Rigby and Capes (99).

c) Bubble Coalescence.--The effect of particle size on the rate of bubble coalescence has been pointed out by Kim, et al. (78) and by Ostergaard (88,94). In general, small particles promote coalescence

and reduce gas holdup. Hence, small particles favor the churn-turbulent (bubble coalescence) flow regime. Large particles, on the other hand, tend to reduce bubble coalescence and increase gas holdup. Numerous investigators (64,82,85,95,109) have found evidence to support these statements. The experimental conditions used by these are listed in Table V. Table V indicates that the critical particle size between coalescing and non-coalescing beds is between 3 and 4 mm for the conditions studied.

This particle size effect and its influence on the gas/liquid flow regime is further illustrated by Darton and Harrison's (70) drift flux analysis of Ostergaard's data (86) presented in Figure 11. For the 6 mm particles, the flow regime remains ideal bubbly up to relatively large gas holdups (0.2 to 0.3). The flow regime for the 3 mm particles is ideal bubbly only for ϵ_g less than 0.1. The flow regime for the 1 mm particles is always churn-turbulent. Excellent pictures of the churn-turbulent and ideal bubbly flow regimes for the 1 mm and 6 mm particles, respectively, have been presented by Ostergaard (92).

Massimilla, et al. (85) and Ostergaard (95) have further observed that for a given particle size the rate of coalescence decreases with increasing bed expansion. These authors argue that this effect is caused by a decline in bed viscosity with expansion; high viscosity favors coalescence. The experiments of Calderbank, et al. (17) support this argument.

d) Bubble Breakup.--The results discussed in the previous section also indicate the importance of particle size on bubble breakup. Two mechanisms of bubble breakup in three-phase fluidized beds have been proposed. Henriksen and Ostergaard (75), following the work of Clift and Grace (19), argue that bubbles break up due to a Taylor instability which develops on the roof of the bubble. Lee (81) proposes that bubbles break up if a particle is able to penetrate the roof of the bubble.

In order to test these mechanisms, Henriksen and Ostergaard (75) dropped steel spheres (5 mm diameter) and glass spheres (3mm or 6 mm diameter) through bubbles with equivalent diameters of 20 mm. The bubbles were held stationary by a downward flow of water. In none of the experiments did the bubble disintegrate when the sphere fell through them. Jets were also used to introduce disturbances on the tops of spherical cap bubbles held stationary by a downflow of water or methanol in a two-dimensional column (0.9 cm thick). In this case bubble breakup occurred; the breakup was easier in methanol. Large bubbles were also injected into water-fluidized beds of glass spheres of 0.2, 1, or 3 mm. Bubble breakup occurred only in the presence of the 3 mm spheres.

These results support Henriksen and Ostergaard's claim that a Taylor instability is responsible for bubble breakup. The jets and fluidized particles must in some way introduce disturbance onto the

upper surface of the bubble. In the case of fluidized particles, the introduction may occur by the particles touching the bubble or by the particles directing eddies at the surface. Once the disturbance has been introduced, Equation 17 indicates these disturbances will grow provided the wavelength is sufficiently large. It is not unreasonable to assume that wavelength is proportional to the particle size. Thus, bubble breakup in three-phase fluidized beds should be expected above some critical particle size. Henriksen and Ostergaard's experiments and the experiments discussed in previous sections support this conclusion. The critical size in air/water fluidized beds is between 3 and 4 mm. Bubble breakup may not have occurred when the 5 and 6 mm spheres fell through the bubbles because the growth of the disturbance was not governed by a Taylor instability, but rather by the inertia of the spheres forcing their way through the bubbles.

e) Swarms of Bubbles.--Three investigations of the rising velocity of bubble swarms in fluidized beds were reviewed. Experimental conditions for these studies are listed in Table VI. Rigby, et al. (100) used a conductivity probe to measure size and velocity, whereas Kim, et al. (78,79) used photographic techniques.

Rigby, et al. (100) present their results as plots of bubble velocity (relative to a stationary observer) vs. bubble length with liquid flow rate as a parameter. The authors found their measured bubble velocities were much larger than the single bubble velocities reported by Massimilla, et al. (85) and Davies and Taylor (27). No satisfactory explanation is offered for this result. An empirical correlation relating bubble velocity to bed porosity, superficial gas and liquid flow rates, and bubble length is presented. This correlation indicates that bubble velocity increases with increasing bed expansion.

Rigby, et al. (100) also measured the distribution of gas holdup as a function of radial position in their column. In the majority of cases, the distribution is non-uniform and similar to the results obtained by Hills (36). These results indicate that the measurements were made in the churn-turbulent flow regime where liquid circulation in the bed is significant. Thus, in comparing their bubble velocity measurements to those for single bubbles, the authors should have measured and subtracted the liquid velocity.

Kim, et al. (78) have also measured the rising velocity of bubbles in swarms. Bubble velocity and size are presented as functions of liquid and gas superficial velocity. Gas and liquid holdup are also measured at the same conditions. Analysis of this data in terms of a three-phase drift flux approach (see Equation 47, below) indicates that the flow regime is also churn-turbulent in these experiments (see Figure 11). Kim, et al. recognize this fact and propose the existence of two distinct flow regimes: the bubble-coalescing and bubble-disintegrating. The former regime is favored by small bed particles, whereas the latter is favored by large bed particles. The authors propose that bed contraction upon the addition of gas only occurs in

the bubble-coalescing regime. In a later publication these authors (79) present empirical correlations for bubble size and rise velocity in two-dimensional, three-phase fluidized beds. The correlations, which are based on data for a wide variety of liquids, relate bubble size and rise velocity to superficial gas and liquid velocities, liquid viscosity, and surface tension.

Data and Correlations.--This section will describe the global behavior of three-phase fluid beds. Existing data and correlating models will be examined.

a) Open Literature Data.--Numerous investigators (98,86,68,69,109,78, 80,66,87,67,90) have collected data on three-phase fluidized beds. Table VII contains a summary of these experiments. Many of the investigators have correlated their data in various forms, as shown in Table VIII. It is suggested that these correlations be used only for the specific system and range of variables from which they are developed. This problem is illustrated by Bruce and Revel-Chion (67), who analyzed their bed porosity data in terms of the correlation proposed by Dakshimamurty, et al. (68). They found this correlation was limited to low gas velocities.

b) HRI and OCR Data.--HRI (201,202,203) has made extensive measurements of bed expansion for three-phase fluidized systems. The bed material in these experiments was cylindrical catalyst particles. System parameters which were varied in the studies include the length-to-diameter ratio of the particles, bed diameter, and gas and liquid flow rates. A summary of experimental conditions is given in Table IX. A synopsis of these reports is given in Table X.

HRI's (203) three-phase data were correlated by plotting the catalyst concentration (lb/ft^3 of bed) vs. the net liquid velocity. The net liquid velocity is defined as the superficial liquid velocity divided by the liquid holdup. The liquid holdup was obtained from the relation:

$$\epsilon_l = 1 - \epsilon_s - \epsilon_g$$

The solids holdup was obtained from the bed height and the gas holdup was estimated from:

$$\epsilon_g = \frac{H_{GL} - H_L}{H_{GL}} \qquad (36)$$

where: H_{GL} = three-phase bed height
H_L = liquid/solid bed height at the same liquid velocity

HRI found that the correlation failed at low and high bed expansions. The failure at low expansions was attributed to channeling and at high expansions to gas slugging in the bed. The data in the report do indicate that in some instances bed contraction occurred upon the addition of gas. This is illustrated in Figure 10, where ϵ_s for expansion of 0.025" diameter cylinders in a 6" diameter bed is plotted as a function of U_l and U_g. For U_l equal to 6.0 cm/sec, ϵ_s increases with the addition of gas, thus indicating a bed contraction. Equation 36 does not hold in this case, as apparently significant liquid wakes are forming.

Zenz (204) has proposed correlating data from the PDU via the Barnea-Mizrahi (1) liquid/solid model reported in Table I. In applying the model, ϵ_s is obtained from bed expansion data; U_r is calculated from the superficial liquid velocity and an estimate of the liquid holdup, which is obtained from ϵ_s and an estimate of ϵ_g. The gas holdup is estimated in a manner similar to that suggested by Equation 36.

Consolidation Coal Company has also studied three-phase fluidization for OCR (205). These experiments were performed in glass columns 3" and 6" in diameter. The particles fluidized were 1/16" diameter glass beads. Nitrogen was used as the gas, and diethylbenzene, water, and soapy water were used as liquids. The principle parameters varied were U_l, U_g, σ, ρ_g, and the orifice diameter on the gas distributor plate. The gas holdup was measured by simultaneously shutting off the flow of gas and liquid to the column.

The data are plotted as gas and liquid holdup as a function of superficial gas velocity, with bed expansion, gas density, and orifice diameter as parameters. In the 3" diameter column, slugging was observed above nitrogen flow rates of 0.04 to 0.09 ft/sec. It was observed that the smaller the bed expansion (more concentrated the solids), the greater the tendency of the gas bubbles to coalesce. Gas holdup was correlated as a function of gas and liquid density.

c) Models.--The correlations presented in Table VIII were developed through empirical observation or dimensional analysis. Models have also been proposed to correlate three-phase fluidization data. These models attempt to take into consideration details of the bed structure, such as bubble rise velocity or bubble wake volume. Often the relations describing these details are empirical.

Ostergaard (93) has proposed a model based on the assumption that the bed consists of a liquid fluidized phase (ϵ_l), a bubble phase (ϵ_g), and a wake phase (ϵ_w). The liquid fluidized phase consists of the solids and the liquid not contained in the wake phase. This is often referred to as the particulate phase. Ostergaard further assumed that the wake phase moves at the gas velocity and has the same porosity as the liquid fluidized phase.

The following procedure is presented for calculating the bed porosity:

1) The bubble velocity (U_b) is estimated by:

$$U_b = 21.7 - 4.6 \ln U_g + U_l \quad (37)$$

where: U_l = superficial liquid velocity
U_b = cm/sec

2) ϵ_g is estimated from:

$$\epsilon_g = U_g/U_b \quad (38)$$

3) ϵ_w is estimated from:

$$\epsilon_w = 0.14\epsilon_g^{1/2}(U_l - U_{lo}) \quad (39)$$

where: U_{lo} = superficial liquid velocity at incipient fluidization.

4) The superficial liquid velocity in the liquid phase, U'_l, is determined from a liquid mass balance and an assumed value of ϵ_l:

$$U'_l = \frac{U_l - U_b\epsilon_w\epsilon_l}{1 - \epsilon_g - \epsilon_w} \quad (40)$$

5) ϵ_l is then calculated from the Richardzon-Zaki correlation for liquid/solid fluidization:

$$\epsilon_l = \left(\frac{U'_l}{U_t}\right)^n \quad (41)$$

6) Steps 4 and 5 are iterated until the values of U'_l and ϵ_l converge.

7) The porosity is then calculated from:

$$\epsilon = \epsilon_l(1 - \epsilon_g) + \epsilon_g \quad (42)$$

Ostergaard compares his model vs. data available for air/water fluidized beds (103,106,89).

This model meets Darton and Harrison's (70) first and second criteria listed above. However, it is not clear that this model will reduce to a suitable gas/liquid model as the solids concentration goes to zero. Darton and Harrison (70) also argue that the model cannot predict bed contraction because the porosity of the wake phase is assumed to equal that of the liquid fluidized phase. They contend that this assumption leads to a stirring of the bed, but based on particle continuity arguments, cannot explain bed contraction.

Darton and Harrison (70) have proposed a model which is based on the work of Stewart (104) and Efremov and Vakrushev (72). They propose that the bubble wakes are particle-free and that the liquid flux in the bubble wakes is given by $\bar{k}U_g$, where $\bar{k}$ is the mean value of the liquid-wake volume/bubble volume ratio. Darton and Harrison develop an empirical correlation for $\bar{k}$ as a function of U_l and U_g:

$$1 + \bar{k} = 1.4(U_l/U_g)^{0.33} \tag{43}$$

The superficial liquid velocity and the liquid holdup in the particulate phase are given by $(U_l - \bar{k}U_g)/(1 - \epsilon_g - \bar{k}\epsilon_g)$ and $(\epsilon_l - \bar{k}\epsilon_g)/(1 - \epsilon_g - \bar{k}\epsilon_g)$, respectively. These expressions are then introduced into the Richardson-Zaki correlation to obtain:

$$\epsilon_l = \left(\frac{U_l}{U_t} - \frac{\bar{k}U_g}{U_t}\right)^{1/n} (1 - \epsilon_g - \bar{k}\epsilon_g)^{1-1/n} + \bar{k}\epsilon_g \tag{44}$$

This equation and the fact that the fractional holdups must sum to unity give two equations with three unknowns.

In order to obtain a third relation, Darton and Harrison use the drift flux approach discussed above in the section on gas/liquid flow. The slip velocity and the drift flux are defined as:

$$U_s = \frac{U_g}{\epsilon_g} - \frac{U_l}{\epsilon_l} \tag{45}$$

$$V_{CD} = U_s\epsilon_g (1 - \epsilon_g) \tag{46}$$

respectively. Combining Equations 45 and 46 gives:

$$V_{CD} = U_g(1 - \epsilon_g) - \frac{U_l\epsilon_g}{\epsilon_l} (1 - \epsilon_g) \tag{47}$$

Darton and Harrison analyzed the fluidization data of Michelson and Ostergaard (86) in terms of Equation 47. A plot of V_{CD} vs. ϵ_g revealed two flow regimes: the ideal bubbly and the churn-turbulent. This plot is reproduced in Figure 11. As can be seen from the figure, the data from the two flow regimes fall along different lines. Typical transition data are indicated by the dashed lines between the two regimes. The data for the ideal bubbly regime fall on the line given by:

$$V_{CD} = 180\epsilon_g(\text{mm/sec}) \tag{48}$$

Equation 48 is identical to the model for bubbly flow proposed previously by Davidson and Harrison. However, all of the data in Figure 11 are for small ϵ_g, where it is difficult to distinguish between the various models for bubbly flow. For the churn-turbulent regime, Darton and Harrison suggest the approach of Zuber and Findlay (63) be used.

The condition for bed contraction can be found by adding ϵ_g to both sides of Equation 44 and then taking the derivative of $(\epsilon_l + \epsilon_g)$ with respect to U_g as $\epsilon_g \rightarrow 0$. The condition for contraction is:

$$(1 + \bar{k})(1 - \epsilon_l + \frac{\epsilon_l}{n}) < \epsilon_l \frac{\bar{k}}{n} \frac{U_b}{U_l} \qquad (49)$$

Epstein (73) has proposed a similar criterion for bed contraction.

Thus, knowing the superficial gas and liquid velocities, the Richardson-Zaki index (n), and the terminal particle velocity, the holdup of each phase in the bed can be calculated. The procedure is as follows:

1) Obtain an estimate of ϵ_l from Equation 1.

2) Assume a gas/liquid flow regime to obtain a relation between V_{cD} and ϵ_g (for instance, Equation 48). Use this relation, Equation 47, and ϵ_l calculated in Step 1 to obtain an estimate of ϵ_g.

3) Use Equation 44 and the estimated ϵ_g, and calculate ϵ_l and check against that found in Step 1.

4) Iterate until ϵ_l converges.

A sample calculation is given by Darton and Harrison in Reference 70. Clearly this model satisfies the four criteria proposed by Darton and Harrison.

Bhatia and Epstein (65) have also proposed a generalized wake model. Following Ostergaard (93), they also propose four distinct phases in the bed: solid, liquid, gas, and the wake phase. The solids concentration in the wake phase can be varied between zero and that in the particulate liquid/solid fluidized phase by means of an adjustable parameter, X_k. The value of X_k ranges between 0 and 1. The wake volume in the three-phase system is related to that in a gas/liquid, two-phase system by an empirical function of solid holdup. The particulate liquid/solid phase is described by a Richardson-Zaki type model. The model also takes into consideration the possible existence of two gas/liquid flow regimes in the bed. Bhatia and Epstein develop six equations for the six unknown systems. These equations and the unknowns are listed in Table XI. The equations must be solved by an iterative procedure. Setting the wake volume fraction equal to zero in this model is equivalent to the assumption made in deriving Equation 36.

The authors test this model vs. the data of Michelson and Ostergaard (86) and data of their own. Their data are for the fluidization of spheres ranging in size from 0.25 to 3 mm. The solid density ranged from 2.5 to 11.1 mg/m^3. The gas used was air, and the liquids were water (1 cp), aqueous glycerol (2.1 cp), or aqueous polyethylene glycol (63 cp). The experiments were carried out in 20 and 50 mm columns. Best agreement between the model and data was obtained when $X_k = 0$ (solids-free wake).

This model, along with the contraction criteria proposed later by Epstein (73), also meets the four criteria suggested by Darton and Harrison. In many respects Bhatia and Epstein's wake model is very similar to the model proposed by Darton and Harrison.

EXPERIMENTAL TECHNIQUES FOR MULTIPHASE SYSTEMS

Experimental techniques for measuring the fluid properties of an ebullated bed involve devices which are either external to the reactor or within the reactor. Devices inside the reactor will interfere to some degree with the fluid flow. Therefore, techniques which are external to the reactor are most desirable. These include gamma-ray scans, radioactive gas, solid and liquid tracers, and some types of sonic probes. Examples of techniques for monitoring the flow by inserting a device inside the reactor include: light, impedance, conductivity, and sampling probes.

Techniques External to the Reactor

Gamma-Ray Scans.--This is an excellent technique for determining the average density in multiphase systems without causing flow disturbances. The use of gamma-rays is based on the differential absorption of radiation by the various materials. The absorption is dependent only on the density and atomic number of the absorbing medium. For a system composed of a gas phase (g), a liquid phase (l), catalyst particles (c), and fines (f), the intensity of the transmitted radiation is given by the following equation:

$$\frac{\log(I_B/I_R)}{d} = \rho_l\alpha_l\epsilon_l + \rho_c\alpha_c\epsilon_c + \rho_f\alpha_f\epsilon_f \qquad (50)$$

where: I_B = transmission through the reactor containing gas only
I_R = measured intensity
α_i = mass absorption coefficient, i = l, c, f
ϵ_i = volume holdup of phasei, i = l, c, f
d = path length
ρ_i = density of phase i, i = l, c, f

Although Equation 50 indicates that measurement of the transmitted radiation alone cannot provide the volume holdup of the individual phases, Blum and Toman (66) and Farley and Ray (147) have shown that Equation 50 can be coupled with other measurements of the system to calculate ϵ_l, ϵ_c, and ϵ_f. Blum and Toman (66) combined Equation 50 with measurements of the fluidized bed height. Farley and Ray (147) assumed a uniform distribution of solids throughout their system.

For the special case when only gas and solid or gas and liquid are present in the reactor, the average holdup of each phase along the absorption path can easily be calculated. Bartholomew and Cassagrande (135) and Hunt, et al. (154) have proposed an algorithm by which these average densities can be used to calculate point densities across the cross-section of a catalyst riser. Calderbank, et al. (140) have also demonstrated the use of the gamma-ray technique to measure densities and thus the gas holdup in a two-phase gas/liquid system.

The various gamma-ray sources which can be used for scans are shown in Table XII. Bartholomew, et al. (135) used a 5 millicurie Cobalt-60 source, while Farley and Ray (147) used a 20 millicurie Cesium-137 source. Both sources have long half-lives, and as a result changes in source intensity with time are not significant. Cobalt-60 is often chosen for scanning industrial reactor sections with thick walls because it has the highest energy radiation. Cameron (141) gives the criteria for selecting the appropriate radiation source size for obtaining meaningful data for various systems. The source size is determined by compromising the opposing requirements of optimum sensitivity and minimal statistical variations.

The detector is another important part of a gamma-ray system. Table XIII reports the advantages and limitations of commonly used detectors. Scintillation counters with sodium iodide crystals have several advantages over other systems. They have much higher detection efficiency, shorter resolving time, and can discriminate between gamma-rays of different energies (158).

An important factor in the successful application of the gamma-ray technique is the integrating time, the length of time during which counts are collected and averaged. Farley and Ray (147) used an integrating time of five seconds. However, it has been previously pointed out by Hancox, et al. (151,152) that different bubble and slug flow regimes result in different void fluctuation periods which may require different integrating times.

Sonic Methods.--McShane and Geil (163) have reviewed three basic sonic techniques. These are: the Doppler shift, the phase time, and dual path methods for measuring both concentration and flow rates of slurries.

In the Doppler shift method, sound waves are projected along a flow path and the frequency shift in the reflected signal from scatterers in the flow is measured. This technique is based on the speed of sound, which varies with the temperature of the medium. Brown (138), Noble (169), and McShane and Geil (163) have reported that results from the Doppler method are often difficult to interpret because of the statistical nature of the reflected signal.

In the phase or transit time technique, two diagonally mounted transducers are used to measure the travel time of a sound wave in a fluid medium. Best results are obtained when sound is transmitted in both directions diagonally across the flowing medium. Noble (169) has shown that with proper cell geometry and the selection of the best sound frequency, this technique can give excellent results in measuring fluid flow.

The dual path probe technique is essentially independent of changes in the speed of sound, and hence temperature changes. Two velocimeters located diagonally opposite each other and exposed to the same flow will

have different output frequencies. The difference in the output frequencies is proportional to the flow velocity.

The sonic impedance (R_s) is the most important factor in assessing the applicability of these sonic methods to the H-Coal fluid dynamics unit. The sonic impedence is proportional to fluid density and the velocity of sound in the fluid. The application of the phase time and dual path sonic probes to multiphase systems is feasible only if the sonic impedence of the phases is similar. If the sonic impedences are not similar, the sound will be reflected instead of transmitted. The Doppler shift method is dependent on having phases with different sonic impedences present. However, too many scatterers in the flow will obscure the sonic beam. In the cases where sonic waves are transmitted, the mean velocity of sound in the mixture will depend on the volume fraction of each phase present. For these cases, sonic probes can be used to determine the relative concentrations of the different phases.

For the H-Coal FDU, sonic probes could be used to determine the coal fine concentration in the slurry and the flow rate of the coal slurry. The sonic impedences of the coal fines and liquids are similar, and so sound is transmitted. The sonic probes cannot be used on the ebullating bed or streams with gas entrained because differences in sonic impedances would cause the signal to be obscured.

Tracers.--Gas, liquid, or solid tracers injected into a flow system can be used to determine the residence time distribution and flow profile for each phase and the extent of solid/gas mixing. Coupled with each tracer is a detection system. Several types of tracer-detection systems can be used to study fluidized beds, and these are discussed in this section.

Gilliland and Mason (150) used helium as the tracer gas in an air fluidized bed. Thermal conductivity cells were used to monitor the helium concentration. Two techniques were used for studying gas mixing. In backmixing studies, tracer gases were introduced into the fluidized bed and samples taken from along the length of the column. For residence time studies, the bed was fluidized with air and the tracer. The addition of tracer was stopped and exit gas composition monitored. Botton (137) performed studies using the same technique, except hydrogen was used as the gas tracer and the exit gases were analyzed with a mass spectrograph. Oxygen in an air fluidized bed analyzed with a Beckman oxygen analyzer has also been similarly used by Chen and Osberg (142).

In all the studies discussed thus far, gases which do not adsorb on the solid catalyst were used. By utilizing both adsorbing and non-adsorbing gases, both residence time and contact time distributions can be determined. It has been shown that the contact time distribution (CTD) plays the same role for heterogeneous reactions that the residence time distribution plays for homogeneous reactions (168). The effect of the degree of absorptive capacity of the tracer on the CTD has been investigated by Nam-Koong and Sae-Ki (167).

Several problems are common to all the tracer methods listed above. Samples taken from the reactor may not be representative of the location from which they were withdrawn. When continuous sampling is employed, sampling line mixing effects may distort the results. Sample removal may also cause disturbance of flow patterns. The use of radioactive tracers which can be detected from outside the reactor circumvents these problems because sampling is not required. Selection of the appropriate tracer and the amount of tracer required is discussed by Kohl, et al. (158).

To be detected from outside the reactor, the tracers used must be gamma-ray emitters. Therefore, the same detection systems discussed for gamma-ray scans would be used.

To determine the quantity of a tracer required, the maximum tolerable error is a primary consideration, and this is related to the signal-to-noise ratio provided by the detector. The physical method of placing the tracer in the system is another important consideration in determining the amount of tracer required. Finally, the counting efficiency of the system must be taken into account. Factors included in the counting efficiency are geometry, absorption and scatter of radiation before reaching the detector, detector efficiency, and yield of detectible radiation from the isotope.

Michelsen and Ostergaard (86) have used both gas and liquid radioactive tracers to determine the holdup of these phases in a three-phase fluidized bed. They employed two scintillation detectors to measure tracer concentration in the column at two horizontal cross-sections.

They encountered two problems with use of the gaseous radiotracers in their system. Argon, which was used as the gaseous tracer, was absorbed in the liquid phase, water. Accurate determination of gas-phase holdup and mixing would have required independent measurement of tracer content in both phases.

Another problem stems from the different rise velocity of the individual gas bubbles. The number of counts recorded during the transit of a single gas bubble depends not only on the amount of tracer in the bubble, but is proportional to the ratio of the amount of tracer in the bubble and the rise velocity of the bubble.

Because of these difficulties, Michelsen and Ostergaard (86) only could give a qualitative description of mixing in the gas phase. They used Bromine-82 (ammonium bromine solution) as the tracer in the liquid phase. No problems were reported with the use of this liquid radioactive tracer, and they obtained quantitative information on liquid-phase holdup.

The use of an untagged liquid tracer which can also be monitored from outside the reactor is discussed by Arunachalam, et al. (134). They used a photochromic dye tracer technique. The photochromic dye changes color when irradiated with a laser. The light is introduced as a focussed flash which results in the formation of a sharp

trace line. The trace line can then be followed with a high-speed movie camera. This method also causes no flow disruption. This technique could not be used in a coal slurry system because the color change would be obscured by the coal fines.

A technique similar to the photochromic dye trace technique, but using solid tracer, is pulse luminescence (166). Luminescent particles are well dispersed in a liquid. The luminescent particles are excited by a narrow pulse of light. The excited particles emit light which is recorded with photographs. The holdup of the liquid phase in the column can be determined as long as the luminescent particles stay well dispersed in the liquid. This technique could not be used in a coal slurry system because coal fines will block light emitted from the luminescent particles.

Radioactive solids can be used to determine catalyst velocity profiles in fluidized beds. Tagged catalyst have been used recently to determine catalyst mixing patterns in commercial fluid catalytic cracking units. Singer, et al. (171) used Scandium-46 and Cerium-144 to tag cracking catalyst. To determine catalyst mixing patterns, catalyst samples were withdrawn from sampling ports and the radioactive content determined with a scintillation dip counter. Use of this technique on other commercial units has been reported by Metcalfe (164). The difficulty in obtaining representative samples is the major disadvantage of this method.

Hull and Von Rosenberg (153) reported an improved technique which they used on a catalytic cracking pilot plant. They used externally mounted detectors to follow the course of the labelled catalyst. Larger quantities of a radioisotope must be employed so that an adequate amount of activity is transmitted through the reactor walls. The sampling problem and any flow disturbance is avoided, however, using this method. More recently, Sorrentino (172) reported usage of externally mounted detectors to monitor the flow of catalyst tagged with a radioactive tracer on commercial catalytic crackers.

Any tracer technique which requires sampling would introduce uncertainty into holdup determinations, and is therefore inferior to a technique using externally mounted tracers.

The use of externally monitored radioactive tracers can be applied to studies of the H-Coal ebullating bed. Slurry and catalyst-phase holdups can be determined by using liquid and solid tracers, respectively. Radioactive gas tracers can be used to investigate gas-phase holdup. However, the problems encountered by Michelson and Ostergaard (86) will have to be considered in evaluating any data.

Techniques Internal to the Reactor

Light Probes.--This technique has wide application for studies of fluidized beds. Several probes have been developed based either on light refraction or transmission through the fluid medium.

The principle of refractive probes is discussed by Geake (149). These probes are based on the difference of the refractive index of the fluid with which they are in contact. However, some of these probes are very large in size, and they would interfere with the liquid flow. Jones and Delhave (155,145) have presented the design principle of a simplified probe. In this case the probe is based on a U-shaped fiber, 40μ in diameter. Thus, minimum flow disruption is caused. This type of probe has several advantages. The probe is very mobile, and its location throughout the bed can be varied. In an ebullated bed it can be used to determine the void fractions of the gas and slurry phases. The light emerges from the probe when submerged in the liquid phase and it is reflected back when the probe is in the gas phase, creating a binary signal.

In the transmission light method, a light source and a light-reflecting probe to detect light transmission are the main components. Nye and Brodkey (170) have reported the use of a single probe to measure liquid holdup using a colored dye. When the dye passed through the probe the light transmission was reduced. Such a technique has limited application to the H-Coal fluid dynamics studies because the coal fines will restrict the light transmission. The size of this probe will also cause considerable flow disruption. Yasui and Johanson (174) used a pair of light probes to determine gas bubble holdup in a fluidized bed. The probe itself was 4 mm in size. Application of this probe could also be considered in the H-Coal fluid dynamics studies.

Impedance and Conductivity Probes.-- Impedance probes are generally used to measure gas-phase holdup, bubble rise time, and size. Conductivity probes are employed when either one of two phases is conductive or a conductive liquid tracer has been added to the system. The progress of the conductive phase is monitored with the probe. There are several configurations of both probe types, and these are discussed below.

An impedance probe with a single contact has been used by several workers for measuring local gas holdup in gas/liquid systems. The impedance or resistance is continuously recorded, and when gas envelops the probe the resistance increases. When a second contact is added to the probe, it is possible to measure bubble rise time by monitoring the delay time between the signal received from each contact. A double probe system can also be used to look at bubble size. The use of a double probe to measure both bubble size and velocity is discussed by Darton and Harrison (144). They used probes with two different tip separations and compared the results from each trial. The system was calibrated by comparing computer-analyzed signals with photographs of the same system. Probe results were usually within 10% of photographic measurements. To derive the bubble size distribution, the relation between the detected bubble chord length and the bubble length was developed. Using this method, the bubble shape must be assumed.

Burgess and Calderbank (139) devised a five-contact probe which eliminates the requirement of assuming a bubble shape. They developed this probe to avoid some of the uncertainties associated with previous

techniques. Five channels were used in order to sense the local bubble interface angle as well as to measure bubble size and velocity. Only those bubbles whose central axes are coincident with the probe axis were analyzed. The five-contact probe arrangement is shown in Figure 12. The probes were connected so that each contact formed part of an electrical circuit as long as the contact is in the conducting phase. If a bubble passes a contact, the circuit is broken. In this way a pulse sequence is generated by the probe assembly.

These types of impedance probes could be used with the H-Coal FDU to determine gas-phase holdup and, if multi-contact probes are employed, bubble rise time and size also could be determined. These probes will only determine the point gas holdup. To determine the overall holdup, data must be collected from several locations in the reactor. A serious disadvantage of these probes is their large size--2 mm--which will result in flow disruption.

Conductivity probes can be used to monitor velocity of weak electrolytes, holdup of a conductive phase, and fluid density fluctuations. Magrini (159) evaluated two probes for flow measurement of weak electrolytes. The probes consisted of two Pt electrodes; one probe had two wire electrodes, and the other two plate electrodes. The plate probe had several advantages: smaller stabilization time, better reproducibility, and higher stability. These advantages are attributed to the lower current density on the plate electrodes because of their larger area.

The effectiveness of different probe types in determining an average cross-section concentration for flow with radial concentration gradients are discussed by Kim and Harris (157). Four different probes were evaluated. A single-contact probe will miss tracer at all but one location in a reactor. A two-point probe can detect the presence of tracer in radial locations, but not consistently. Two-wire probes will give a better representation of the flow, but the location of the wires in the flow will affect the accuracy of the measuring device.

Probes used to measure concentration or density fluctuations are discussed by Keeler, et al. (156) and Alonso (133). To avoid measurement distortion, the following criteria must be satisfied:

1) Instrument response to linear conductivity changes must be linear.

2) The orientation effect of the sensing elements to the flow direction must be as small as possible.

3) The response time of the probe should be small enough to allow the detection of fluctuations in density or concentration.

It was shown that the smaller probes have higher resolution and greater sensitivity and in general did a better job of meeting the above criteria.

Impedance probes could be used in the H-Coal FDU studies to measure gas-phase holdup because gas and liquid phases have different impedances. However, conductivity probes could not be used unless a conductive tracer were added to the system because the fluids being studied are not conductive. Both impedance and conductivity probes would suffer from the disadvantage of possibly distorting flow which would result in unreliable measurements.

PHYSICAL PROPERTIES OF COAL/OIL MIXTURES

In selecting fluids for study in the cold flow unit, it is important to choose liquids with physical properties close to those of the H-Coal slurries at reactor conditions (700 to 900°F, 2000 to 3000 psig). In order to assure this, Amoco will attempt to measure the viscosity and surface tension of H-Coal slurries at reactor conditions. It is therefore important to review the literature on the physical properties of coal/oil mixtures. This area has not been widely researched, and as a result not many papers were found. Most papers are concerned with the viscosity of these mixtures. In addition to a review of these papers, prominent methods of correlating viscosity data of suspensions will also be discussed.

Measurements of Viscosity of Coal/Oil Mixtures

Arco-HRI (207) have measured the viscosity of H-Coal liquid products and slurries at temperatures up to 450°F. The parent liquids were obtained from H-Coal operations on Pittsburgh seam coal. Solids concentration varied between three levels: 0, 18, and 34 wt%. The solids consisted of 64% ash and 36% unconverted coal. The viscosity was determined using both Stormer and Capillary Furol viscometers.

Viscosity was found to be a strong function of the base oil, temperature, and weight per cent solids. The solid-free viscosity at various temperatures was found to correlate well with liquid density at that temperature. This method of correlation is also used to correlate the viscosity of crude fractions and is summarized by Maxwell (191). Solids resulted in an increase of the liquid viscosity by a constant amount over the entire viscosity range. A 6.5% increase in viscosity was found for each weight per cent increase in solids concentration.

Rudyki, Pease, and Weidner (179) have measured the viscosity of various coal oil slurries at temperatures up to 150°F. The base oil was No. 6 fuel oil. The solids consisted of pulverized petroleum coke, anthracite, and bituminous coal. The average particle size varied from 1 to 6μ. The concentration of solids ranged from 0 to 60 wt%. A Brookfield viscometer was used for these measurements.

The authors reported that the viscosity was a strong function of temperature, slurry concentration, and particle type and size. The viscosity increased exponentially with solids concentration below 40 wt%, the rate of increase being greatest for anthracite coal. Above approximately 47 wt%, a gel was formed and an even more dramatic increase

in viscosity with solids concentration and particle size was observed. At 150°F and 45 wt% solid, the kinematic viscosity dropped by an order of magnitude as the average particle size increased from 1 to 4μ. Above 4μ, little change in viscosity was observed with increasing particle size.

Droege, et al. (177) have measured the viscosity of product oils and preheat specimens from the synthoil process. The measurements were made at temperatures up to 450°C and pressures up to 4000 psig. The viscometer consisted of a bob in a concentric cylinder. The gap between the bob and cylinder wall was 1 mm. After the sample was placed in the cylinder, the bob was pulled axially through the cylinder magnetically. From the application of a known force and the measured rate of movement of the bob, an estimate of the viscosity could be obtained. Shear rates as high as 600 sec^{-1} could be achieved in the instrument. High temperature was obtained by placing the apparatus in a furnace. Hydrogen was used to pressurize the system.

Droege reported that the viscosity was a very weak function of pressure, increasing slightly with increasing pressure. As in the other studies, viscosity was a strong function of temperature, decreasing with increasing temperature. The authors developed relationships between the temperature and pressure coefficients of viscosity.

Slurry concentration was not varied in the study. However, the viscosity of filtered samples was measured. Viscosity measurements of both the filtered and unfiltered samples exhibited a yield stress (Bingham fluids). This yield stress was small compared to the shear stresses exerted in the viscometer. Above the yield stress the shear stress increased linearly with increasing rate of shear. The exact cause of the yield stress could not be determined, although it could have been caused by chemical changes due to oxidation of the samples during storage. Evidence is presented that the viscosity of the samples may increase by a factor of 100 during the 15 to 28 months between sampling and measurement.

Exxon (209) plans to measure the viscosity of the coal-solvent slurries to be used in the Donner-Solvent process. In order to accomplish this, they have developed a viscometer capable of operating at temperatures up to 850°F and pressures up to 2500 psi. The viscometer is a couette flow system consisting of a rotating cylinder contained in a stationary cup. The rate of shear is determined from the rotational rate of the cylinder and the shear stress is determined by measuring the torque needed to hold the cup stationary. Shear rates as high as 2100 sec^{-1} can be achieved.

At the present time, Exxon has measured the viscosity of two hydrotreated creosote oil slurries. Only one slurry concentration was investigated. The coal fines were Illinois No. 6, with particle sizes less than 30 mesh. Temperatures in these measurements ranged between room temperature and 425°F. Pressure was the system vapor pressure. It was found that for most cases the slurries exhibit a Newtonian behavior, with the viscosity varying inversely with temperature.

Correlation of Suspension Viscosities

An excellent review of the literature on the rheology of suspensions is given by Jeffrey and Acrivos (188). A review of data and empirical relations used in correlating data is presented. Two of the more prominent empirical correlations are those of Mooney (193) and Krieger and Dougherty (190), respectively:

$$\frac{\mu_s}{\mu_l} = \exp\left(\frac{B\phi}{1 - K\phi}\right) \tag{51}$$

and

$$\frac{\mu_s}{\mu_l} = (1 - K\phi)^{-B/K} \tag{52}$$

where: μ_s = viscosity of suspension
μ_l = viscosity of liquid
ϕ = volume fraction of solids
K,B = adjustable parameters which have to be determined experimentally

In the limit of $\phi \rightarrow 0$, both of these expressions reduce to Einstein's relation:

$$\frac{\mu_s}{\mu_l} = (1 + B\phi) \tag{53}$$

where B is Einstein's coefficient. The value of B for spherical particles lies between 2.5 and 5.

Jeffrey and Acrivos argue that suspensions should be treated as non-Newtonian fluids whose flow properties are characterized by more than just the volume fraction of solids. Other variables which are important are particle size distribution, particle shape, and the presence of electrical charge.

Barnea and Mizrahi (1) have also reviewed empirical methods of correlating viscosity data for suspension with solids volume fraction.