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TITLE: Hydrodynamics of Three-Phase Slurry Bubble Column Reactors for Fischer-Tropsch Synthesis

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OBJECTIVE: To determine the effects of bubble column diameter, distributor design, operating conditions (i.e. temperature, gas flow rate, and liquid upflow), and solids concentration on hydrodynamics of slurry bubble column reactors for the Fischer-Tropsch synthesis using a molten paraffin wax as the liquid medium.

TECHNICAL APPROACH: Proper design and scale-up of slurry bubble column reactors requires knowledge of the effects of operating conditions and system geometry on the hydrodynamic parameters. The hydrodynamic parameters of interest in this study are average and axial gas hold-ups, axial solids distribution, flow regime transitions, and bubble size distribution.

Gas hold-ups (axial and average), axial solids distribution, and flow regime transitions will be determined by both conventional techniques (i.e. analysis of pressure signals and slurry samples withdrawn along the column) and the use of a dual energy gamma radiation density gauge. The density gauge will also be used to obtain qualitative information on the bubble size distribution.

SIGNIFICANT ACCOMPLISHMENTS: Two stainless steel bubble columns (2" ID and 9" ID, 10 ft in height) have been modified for continuous liquid flow experiments. The assembly mechanism for axial and radial movement of the gamma radiation density gauges has been designed and constructed.

Experiments were conducted in the small stainless steel bubble column using FT-300 wax as the liquid medium at 265 °C using up to 30 wt% 0 - 5 μm iron oxide and silica particles, and with 35 - 44 μm iron oxide particles. There was a substantial decrease in the gas hold-up for experiments conducted in the continuous mode of operation ($u_l = 0.5$ or 2.0 cm/s) as compared to the batch mode of operation. The solids concentration remained axially uniform throughout the column for all experiments conducted in the continuous mode of operation. For batch experiments, the solids concentration decreased with an increase in height above the distributor.

PUBLICATIONS:

Bukur, D. B. and Daly, J. G., Hydrodynamics of three-phase slurry bubble column reactors for Fischer-Tropsch synthesis, Review Meeting, U. S. Department of Energy, Pittsburgh Energy Technology Center, pp. 137-146, 1986.

INTRODUCTION

Slurry Fischer-Tropsch processing is considered a potentially economic method to convert coal derived synthesis gas into liquid fuels. The slurry process has several potential advantages over conventional vapor phase processes due to its relatively simple reactor design, improved thermal efficiency, and ability to process CO-rich synthesis gas.

The scale-up of slurry bubble column reactors is subject to uncertainty because important hydrodynamic parameters change with scale (i.e. reactor dimensions). Commercial size bubble column reactors are expected to operate in the heterogeneous (churn-turbulent) flow regime, and the extrapolation of results obtained in small diameter columns, where the homogeneous or slug flow regimes exist, to large scale units may not be warranted. The specific gas-liquid interfacial area, as well as the gas and liquid phase mixing are different in the different flow regimes. These parameters have an effect on the secondary reactions and consequently product selectivities obtained in the different flow regimes may differ significantly.

The overall objectives of our study are to determine the effect of solids (up to 30 wt %) and small upward liquid flow (up to 0.02 m/s) on the average and axial gas hold-up and the solids distribution along the column height (Fig. 1). Also, an effort will be made to quantify flow regime transitions and obtain some information of the bubble size distribution.

EXPERIMENTAL CONDITIONS AND OPERATING PROCEDURE

We will determine several important hydrodynamic parameters at typical processing conditions using molten wax as the liquid medium and nitrogen as the gas. The independent variables and range of experimental conditions that will be employed throughout the course of our investigations are presented in Fig. 2. Two stainless steel bubble columns (0.051 m ID and 0.214 m ID, and 3 m tall) will be employed in the hydrodynamic studies. Fig. 3 is a schematic of the bubble column apparatus. So far, experiments

have only been conducted in the small (0.051 m ID) column. A brief description of the operating procedure used for experiments performed in the small column follows.

Prior to experiments with a given batch of wax, the mass flow meter and the pressure transducers are calibrated over the entire operating range. The mass flow meter is calibrated with a wet test meter hooked up in series with it. The pressure transducers are calibrated, while they are at their respective locations on the column wall, by filling up the column to different heights with distilled water and recording the transducer meter readings.

The wax granules are charged in the storage tank and brought up to temperature by heating the tank. Once the solid wax melts, the stirrer is switched on to improve the heating process. For runs conducted with solids, the necessary quantity of solid particles are added to the molten wax. The slurry is heated to a temperature of 220-240°C before it is transported to the column. Once the storage tank reaches the desired temperature, slurry samples are withdrawn and the slurry height in the tank is measured. The column is heated up to the desired operating temperature (265°C) before the wax is introduced. For all experiments, batch and continuous, the wax is transported to the column using a slight overpressure of nitrogen in the storage tank. For the continuous mode of operation, the pump is switched on only after the column is at least half filled with wax. This is done to prevent any solids, settled in the storage tank, from clogging the pump. Throughout the preheating period and during transportation of wax to the column, a small flow of nitrogen is maintained through the distributor. Once the wax is in the column, the temperatures of the various units are allowed to stabilize before the actual run is started. For experiments conducted in the batch mode, only the column is maintained at the operating temperature using two temperature controllers, one for each half of the column (top and bottom). The exit lines and expansion unit are maintained at around 200°C. The scrubber, which is filled with a mineral spirit to

recover components of wax that evaporate from the column, is maintained at 100°C. The gas inlet line and the distributor section are maintained between 220-240°C. The lines connected to the pressure transducers and the slurry withdrawal lines were maintained at 200°C. For continuous mode of operation, all lines and vessels carrying the slurry, including the column, expansion unit, overflow line, calibration chamber, storage tank, slurry feed line, and the slurry pump are maintained at the operating temperature. The remaining temperatures are the same as those used for the batch case. All temperatures are monitored regularly, every half hour during the preheating period (i.e. while wax is in the column and being heated up) and every hour once temperatures have stabilized.

All experiments are conducted using pre-purified nitrogen as the gas. Superficial gas velocities of 0.02, 0.04, 0.06, 0.09 and/or 0.12 m/s were employed in all runs. A duration of one and a half hours is used for each gas velocity. Pressure measurements are made three times for every gas velocity (i.e. every half hour), with the first measurement made half an hour after the gas velocity is changed. After the last pressure measurement, slurry samples are withdrawn from the column at five different locations. In addition to this, two samples are also withdrawn from the storage tank (top and bottom ports), and the height of slurry in the tank is measured. The gas flow rate is then changed to the next setting. For experiments conducted in the continuous mode of operation, the superficial liquid velocity is monitored using the calibration chamber. The desired liquid flow rate is set by varying the pump speed. Liquid flow rate checks are made three times at each gas velocity. Once the slurry samples are withdrawn into the sampling cylinders, they are allowed to cool and solidify before being removed. The cylinders are then cleaned with a solvent and reinstalled. The weight fraction of solids is determined using the Archimedean Principle (the apparent loss in weight of a solid body, when completely immersed in a liquid, equals the weight of the displaced fluid).

Following the completion of a run, the slurry is withdrawn into the storage tank

by using a slight vacuum in the tank (the pump is switched off for runs conducted in the continuous mode). Slurry samples are withdrawn from the storage tank and the slurry height measured once all of the slurry is back in the tank. If a new run is conducted with the same batch of wax the next day, all temperatures are lowered to around 200°C and nitrogen is allowed to flow through the distributor. If the run is the last one for the current batch of wax, the procedure is extended to include the cleaning of the system. The wax in the storage tank is drained into a pan, the drain below the distributor is opened to drain the distributor section and the region just above the distributor, and all temperatures are lowered to about 100°C. Once the system is at this temperature, solvent (toluene) is introduced into the column through a nozzle just above the distributor and the gas flow rate is increased to agitate the solvent. Sufficient amount of solvent is added so that some of it is carried into the expansion unit, overflow lines and the calibration chamber. The spent solvent is pulled into the slurry storage tank after approximately 45 minutes and drained. The process is repeated if deemed necessary. Following the cleaning process, the system is kept at 130-150°C overnight with nitrogen flowing through the distributor to evaporate any remaining solvent. The system is now ready for the next batch of experiments.

MEASUREMENT OF HYDRODYNAMIC PARAMETERS

The effects of operating conditions (liquid and gas superficial velocity and temperature), distributor design, column diameter, and solids concentration on hydrodynamic parameters will be determined using both conventional techniques (i.e. pressure transducers and slurry samples) and by the use of a dual energy nuclear density gauge (see Fig. 4). The nuclear density gauge will only be used for experiments in the large column.

Measurement of Hydrodynamic Parameters by Conventional Techniques

Experiments were conducted in the small stainless steel column using FT-300 as

the liquid medium and nitrogen as the gas. All experiments were made with a 2 mm single hole orifice plate at a temperature of 265 °C. Results illustrating the effect of slurry velocity and solids type and concentration on the average gas hold-up, axial gas hold-up, and axial solids distribution are presented.

Average Gas Hold-up

Fig. 5 shows the effect of slurry velocity on the average gas hold-up for experiments conducted with a 30 wt %, 0 – 5 μm , iron oxide slurry. Foam was produced for the batch case with gas hold-up values as high as 32 % at a gas velocity of 0.04 m/s. However, gas hold-up values decreased significantly for gas velocities in the range 0.04 – 0.09 m/s when the experiment was conducted in the continuous mode of operation using a superficial slurry velocity of 0.005 m/s. A further decrease was observed when the superficial slurry velocity was increased to 0.02 m/s, however the change was less significant. Average gas hold-up values at a gas velocity of 0.02 m/s from all three runs are very similar. At this gas velocity the flow regime is expected to be the same for all three cases (predominantly homogeneous bubbly flow). At a gas velocity of 0.12 m/s hold-ups from all three runs once again approach the same value. The foam produced in the batch mode appears to have dissipated at this gas flow rate, and hold-ups have converged to values similar to those for the continuous mode of operation. Our earlier experiments in the glass column (Bukur et al., 1987) have shown that slug flow dominates for gas velocities in this range, and hold-ups are determined by the size of these slugs. Similar trends were observed with 0, 10 and 20 wt % slurries of iron oxide particles, as well as with a 20 wt % 0 – 5 μm silica slurry.

The above results indicate that small liquid circulation tends to lower gas hold-ups, however, further increases in the liquid flow rates do not have significant effect on the average gas hold-up values. The significant difference in hold-ups between the batch mode of operation and the continuous mode of operation is caused by changes in the

foaming characteristics of the medium. For the batch case, the foam accumulates at the top and this increases the gas hold-up. However, as slug flow develops, the foam disappears and the hold-up profiles flatten out. In the continuous mode of operation, any foam that accumulates at the top is carried back down by the circulating slurry and is dispersed. With an increase in the liquid circulation, the rate of dispersion increases, decreasing the gas hold-up.

Fig. 6 shows the effect of solids type on average gas hold-up for experiments conducted in the continuous mode of operation ($u_l = 0.005$ m/s) with 20 wt %, 0 – 5 μ m iron oxide and silica slurries. Gas hold-ups were lower for experiments conducted in the presence of solids and lowest for experiments with silica slurries. Since the density of silica is less than iron oxide (2.65 as opposed to 5.1 g/cc), for the same weight fraction slurry, the volume fraction of silica is greater than that of iron oxide. This increase in the volume of solid particles, causes an increase in the slurry viscosity which produces lower hold-ups.

Two interesting trends were observed for experiments conducted in the batch mode of operation (See Fig. 7). First, for experiments conducted in increasing order of gas velocities, gas hold-ups for experiments conducted in the presence of solids were greater than gas hold-ups observed with pure FT-300. Secondly, for the experiment with large silica particles conducted in a decreasing order of gas velocities, no foam was observed and the hold-ups were similar to those obtained for experiments conducted in the continuous mode of operation with small silica particles. A similar trend was observed in our previous studies for experiments conducted in a decreasing order of gas velocities in a 0.051 m diameter glass column (Bukur et al., 1987).

Fig. 8 shows the effect of solids concentration on gas hold-up for experiments with 0 – 5 μ m iron oxide particles at a superficial slurry velocity of 0.005 m/s. In general, there is a slight decrease in the gas hold-up with an increase in solids concentration.

The highest hold-ups are observed with pure FT-300 and the lowest are obtained with a slurry containing 30 wt % solids. A similar trend was observed for experiments conducted at a superficial slurry velocity of 0.02 m/s; however, the decrease in hold-up with an increase in solids concentration was less pronounced.

Axial Gas Hold - ups

Fig. 9 shows the effect of slurry velocity on axial gas hold-up for results obtained with a 20 wt %, 0 - 5 μm iron oxide slurry at slurry velocities of 0 (batch) and 0.005 m/s. In general, the gas hold-up increases with height above the distributor and with an increase in gas velocity. For the experiment conducted in the batch mode of operation, the foam at the top of the dispersion is responsible for the significantly higher hold-ups in the upper section, compared to values obtained in the continuous mode of operation. Thus, the axial gas hold-up profiles are affected by the superficial slurry velocity. For batch experiments, the profiles are non-uniform (low hold-ups at the bottom of the column and higher values at the top). However, as the slurry velocity is increased, the axial gas hold-up profiles tend to become more uniform. In general, the results were qualitatively the same for all systems studied.

Fig. 10 shows the effect of solids concentration (0 and 20 wt %) on axial gas hold-up for experiments conducted with 0 - 5 μm silica particles at a superficial slurry velocity of 0.005 m/s. In general, there is not a significant effect of solids concentration on axial gas hold-up.

Axial Solids Distribution Profiles

Fig. 11 shows the effect of slurry velocity (0 (batch) and 0.005 m/s) on axial solids concentration profile for experiments conducted with a 20 wt %, 0 - 5 μm iron oxide slurry. For the experiment conducted in the batch mode of operation, the weight fraction of solids decreased with an increase in height above the distributor. According to the one-dimensional sedimentation dispersion model, the solids concentration should

decrease exponentially along the column height. However, for all experiments conducted in the batch mode of operation with small particles, the decrease in solids concentration was most pronounced at the top of the column. The sedimentation model describes the behavior of solids in a liquid slurry; whereas, for experiments conducted in the batch mode of operation, the solids are dispersed in foam at the top of the column. This is probably the reason for the discrepancy between the predicted and observed trends. A slight increase in the slurry velocity to 0.005 m/s is sufficient to maintain a uniform suspension of solids.

Fig. 12 shows the effect of solids size on the axial distribution of solids for experiments conducted with 0 - 5 μm and 35 - 44 μm iron oxide particles in the batch mode of operation. For the experiment conducted with large iron oxide particles, the decrease in solids concentration is more pronounced than with small particles, as expected. Some experiments were conducted in the continuous mode of operation with large iron oxide particles; however, due to a substantial amount of settling in the system, a direct comparison between results obtained with small and large iron oxide particles in the continuous mode of operation cannot be made. However, a slurry flow rate of 0.005 m/s was sufficient to maintain a uniform suspension of large iron oxide particles.

Application of a Gamma Radiation Density Gauge for Determining Hydrodynamic Parameters

The dual energy nuclear density gauge will be used to obtain various hydrodynamic parameters in the large stainless steel column. The movable assembly mechanism which will be used to transport the gauges both axially and radially along the column has been constructed and tested. Fig. 13 is a schematic of the movable assembly mechanism.

The high energy and low energy sources we plan to use throughout the course of our investigations are Cesium-137, and Americium-241. The sources have been installed on the movable assembly mechanism and some initial tests have been performed using

a two-phase (air-water) system. Gas hold-up values obtained from the nuclear density gauge are comparable to those obtained from the DP system.

We are initiating test with a three-phase (air-water-sand) system. Once satisfactory results are obtained with the cold system, we will begin tests using wax as the liquid medium and iron oxide as the solid phase.

CONCLUSIONS

Significant conclusions from our studies are summarized in Fig. 14. Studies with FT-300 wax in a 0.051 m ID by 3 m tall bubble column were conducted using iron oxide and silica particles (up to 30 wt %) for slurry velocities ranging from 0 (batch) to 0.02 m/s. Results from these experiments indicate that the superficial slurry velocity has a significant effect on the average gas hold-up when it is increased to 0.005 m/s. For experiments conducted in the batch mode of operation, a significant amount of foam is produced; whereas, for experiments conducted in the continuous mode of operation the foam is dispersed by the circulation of the slurry. Further increase in the slurry velocity to 0.02 m/s has a less pronounced effect.

The addition of solids, iron oxide and silica ($< 53 \mu\text{m}$), causes a slight increase in the average gas hold-up for experiments conducted in the batch mode of operation. For experiments conducted in the continuous mode of operation, the addition of solids causes a decrease in the gas hold-up. Experiments with silica yielded slightly lower hold-ups than those with iron oxide.

Axial gas hold-up increased with height above the distributor and with increasing gas velocity. The increase in hold-up with height above the distributor was most pronounced for experiments conducted in the batch mode of operation. The substantial increase in gas hold-up in the upper section of the column may be attributed to the presence of foam. A slight upward slurry flow rate (0.005 m/s) is sufficient to cause the foam to disperse.

Solid concentration profiles remain uniform for experiments conducted in the continuous mode of operation. For experiments with small particles ($0 - 5 \mu\text{m}$) the solids concentration decreased substantially in the foam layer. However, at lower heights (i.e. below the foam interface), the solids concentration remained fairly uniform. For experiments conducted in the batch mode of operation with large iron oxide and silica particles there was a substantial decrease in the solids concentration along the entire height of the column.

FUTURE WORK

Plans for future work for the current contract are shown in Fig. 15. Pressure signals recorded during experiments in the small stainless steel column will be analyzed to gain information on flow regimes and flow regime transitions. Also, axial solids dispersion coefficients will be obtained for experiments conducted in the small stainless steel column. Experimental studies on the effect of operating conditions and distributor design will be initiated in the large stainless steel column, once the nuclear density gauge is calibrated and tested with a three-phase system.

REFERENCES

Bukur, D.B., Daly, J.G., Patel, M.L. and Taterson, G.B., "Hydrodynamics of Fischer-Tropsch Synthesis in Slurry Bubble Column Reactors," Final Report to the Department of Energy for Contract No. DE-AC22-84PC70027 (1987).

FIGURE 1. OBJECTIVES

TO DETERMINE THE EFFECT OF :

- **BUBBLE COLUMN DIAMETER**
- **DISTRIBUTOR DESIGN**
- **GAS FLOW RATE**
- **LIQUID FLOW RATE**
- **SOLIDS CONCENTRATION**

**ON HYDRODYNAMICS OF SLURRY BUBBLE COLUMN
REACTORS FOR THE FISCHER-TROPSCH SYNTHESIS
USING A MOLTEN PARAFFIN WAX AS THE LIQUID MEDIUM.**

FIGURE 2. BUBBLE COLUMN DIMENSIONS AND EXPERIMENTAL CONDITIONS

COLUMN DIMENSIONS			
DIAMETER (cm)	5.1	22.9	
HEIGHT (cm)	300	300	
GAS DISTRIBUTOR	2 mm ORIFICE	PERFORATED PLATE BUBBLE CAPS	
GAS	NITROGEN	NITROGEN	
LIQUID	MOLTEN WAX	MOLTEN WAX	
SOLIDS	IRON OXIDE (< 70 μm) SILICA (< 70 μm)	IRON OXIDE (< 70 μm) SILICA (< 70 μm)	
VARIABLES			
PRESSURE (atm)	1	1	
TEMPERATURE ($^{\circ}\text{C}$)	265	265	
SUPERFICIAL GAS VELOCITY (cm/s)	2 - 12	2 - 15	
LIQUID UPFLOW VELOCITY (cm/s)	0 - 2	0 - 2	
SOLIDS CONCENTRATION (wt%)	0 - 30	0 - 30	

FIGURE 3. BUBBLE COLUMN APPARATUS

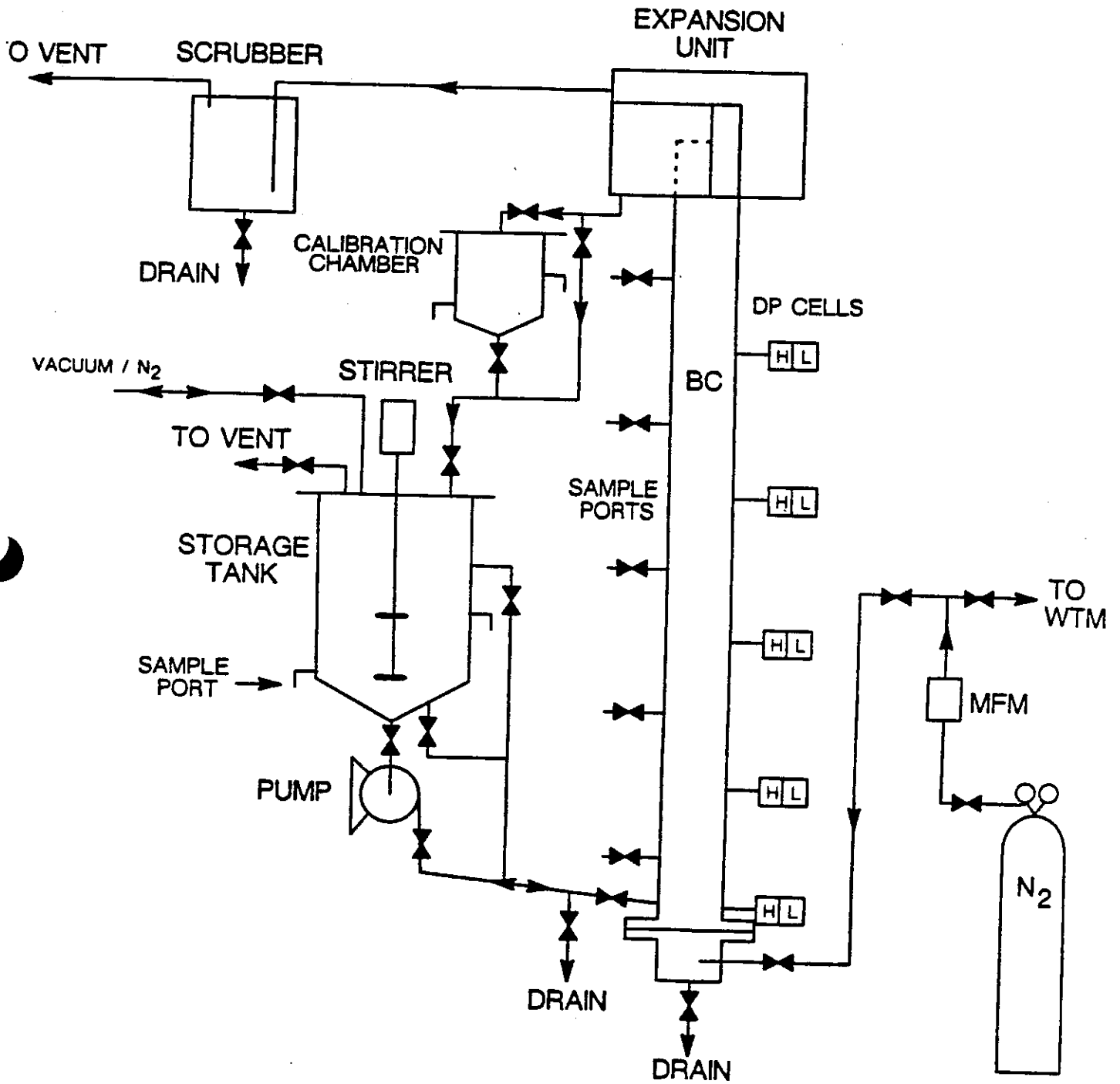


FIGURE 4. DEPENDENT VARIABLES AND EXPERIMENTAL TECHNIQUES

MEASURED QUANTITY	TECHNIQUE
AVERAGE GAS HOLD-UP	DP, NDG
AXIAL GAS HOLD-UP	DP, NDG
SOLIDS CONCENTRATION PROFILE	SLURRY SAMPLING, NDG
BUBBLE SIZE DISTRIBUTION	NDG
FLOW REGIME CHARACTERIZATION	DP, NDG

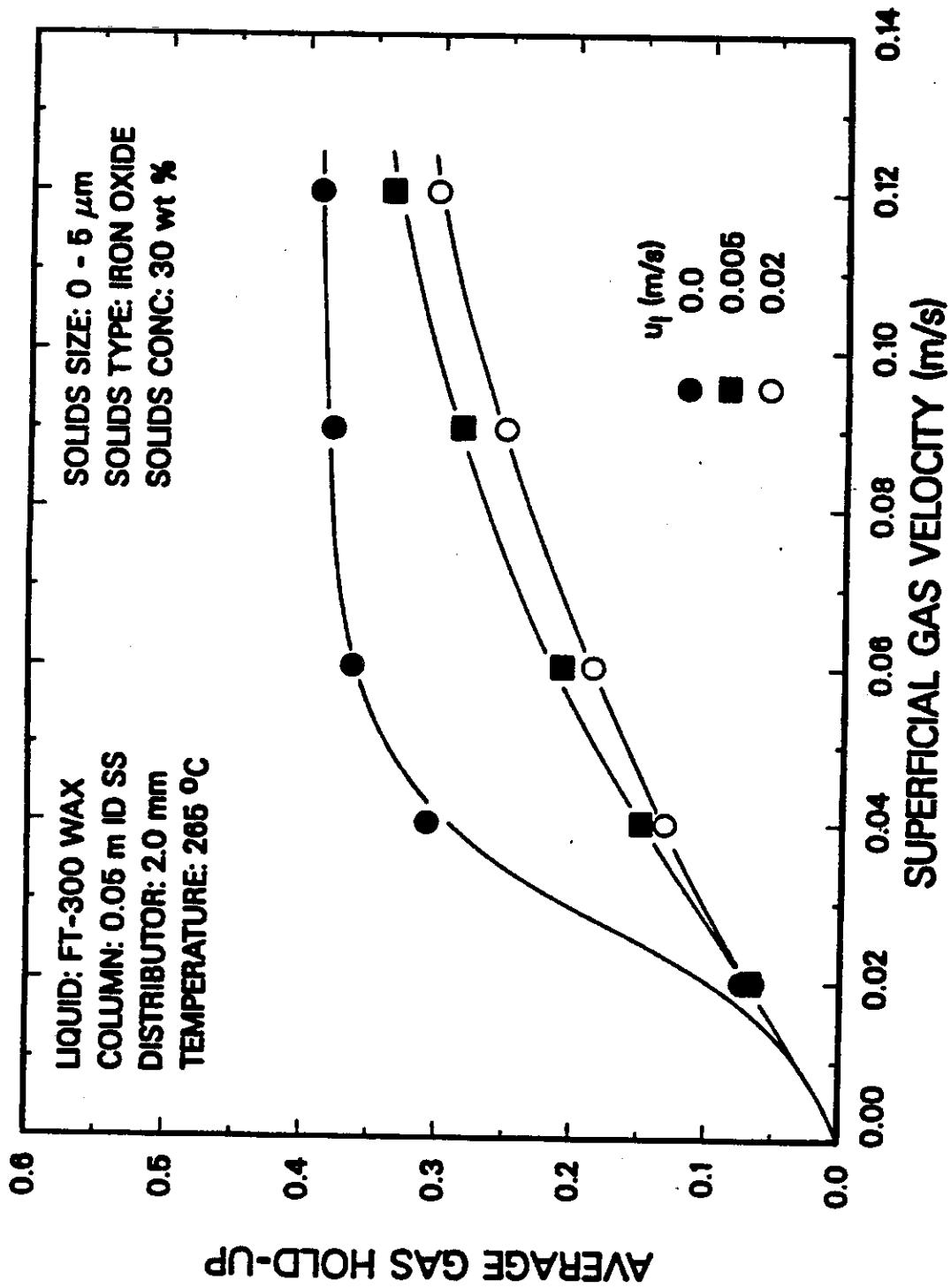


Figure 5. Effect of slurry velocity on average gas hold-up.

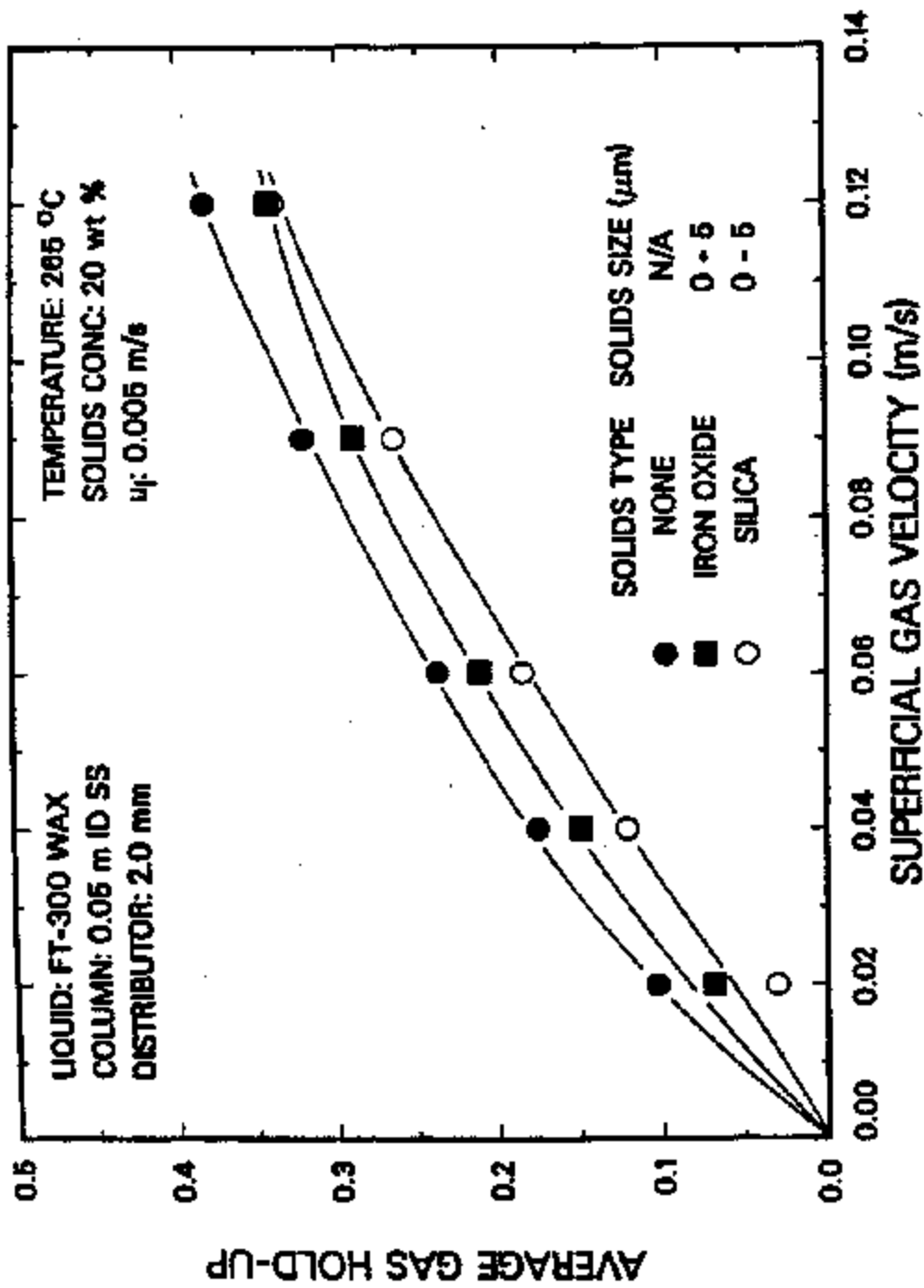


Figure 6. Effect of solids type on average gas hold-up.

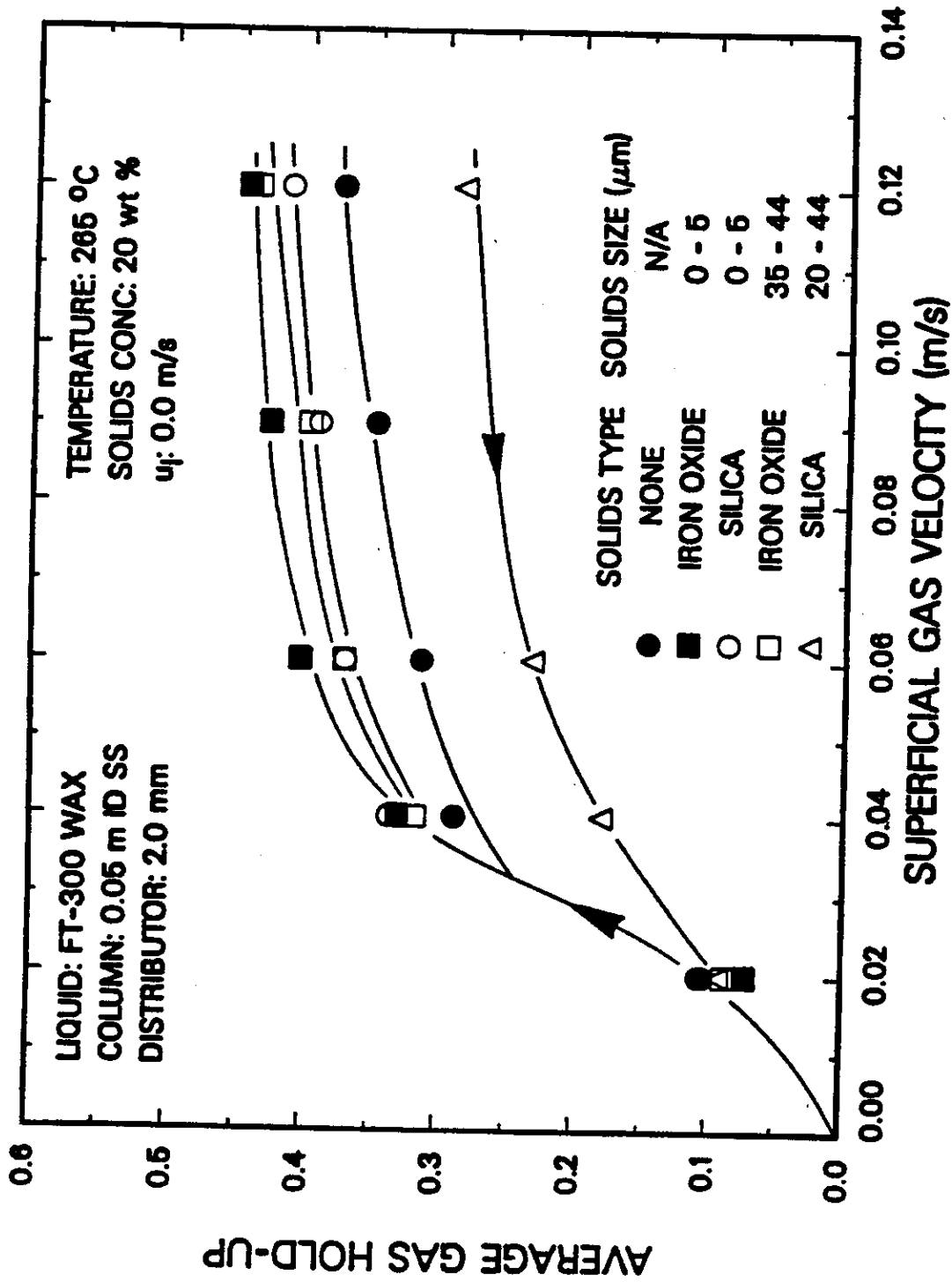


Figure 7. Effect of solids type and size on average gas hold-up.

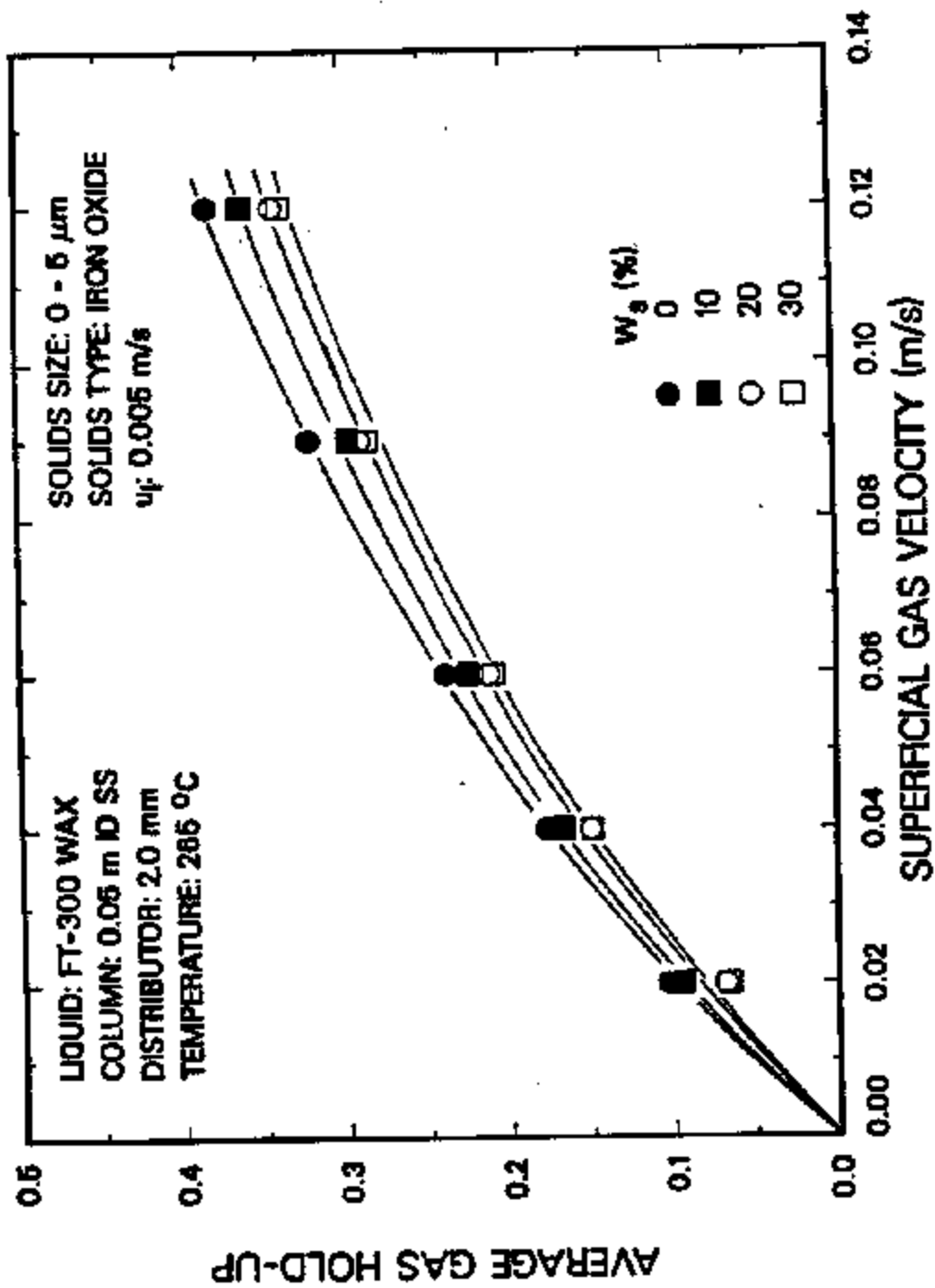
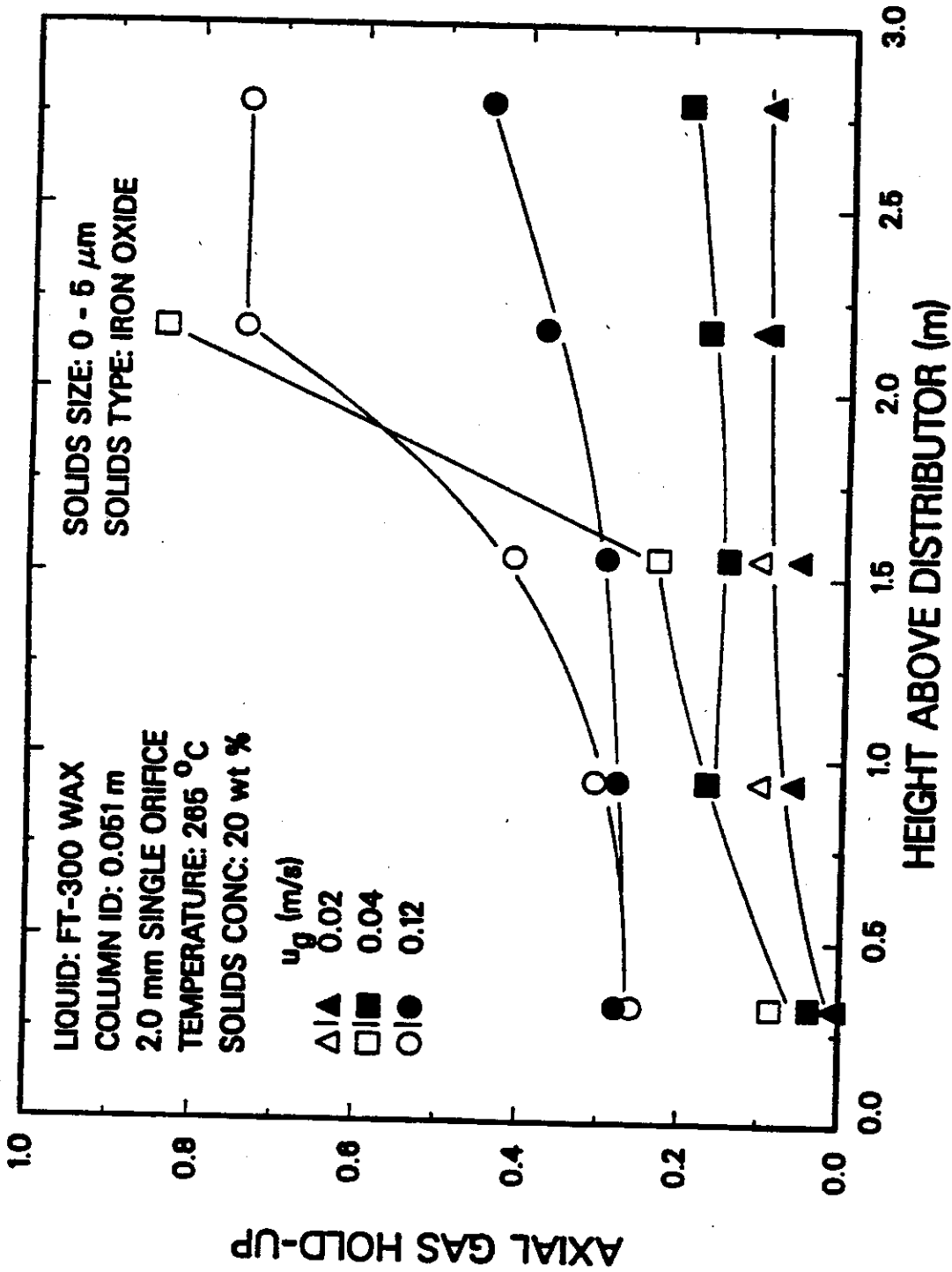
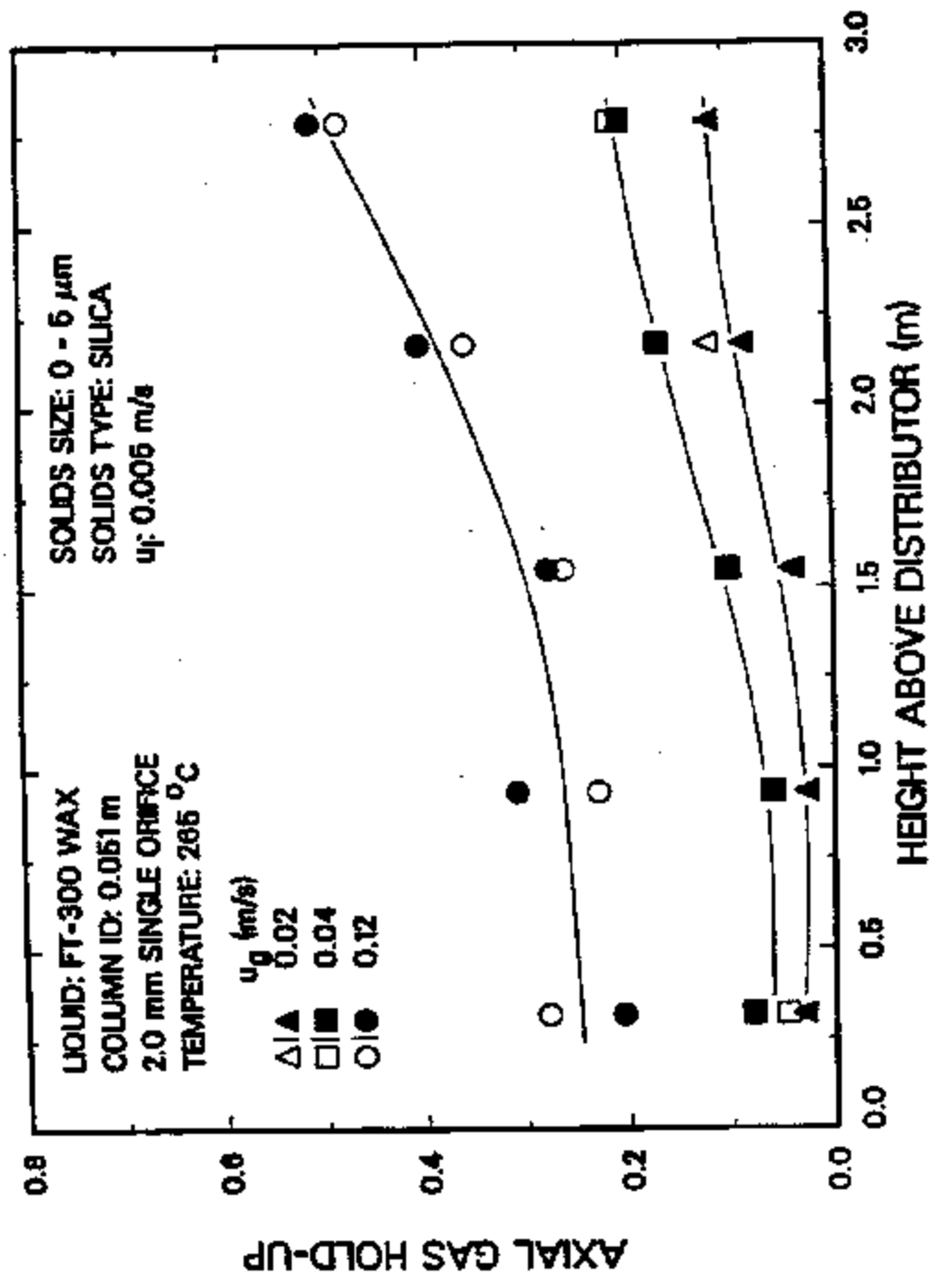


Figure 8. Effect of solids concentration on average gas hold-up.



(Open Symbols - $u_j = 0.0$ m/s, Closed symbols - $u_j = 0.005$ m/s)

Figure 9. Effect of slurry velocity on axial gas hold-up.



(Open Symbols - $w_s = 0$ wt %. Closed symbols - $w_s = 20$ wt %)

Figure 10. Effect of solids concentration on axial gas hold-up.

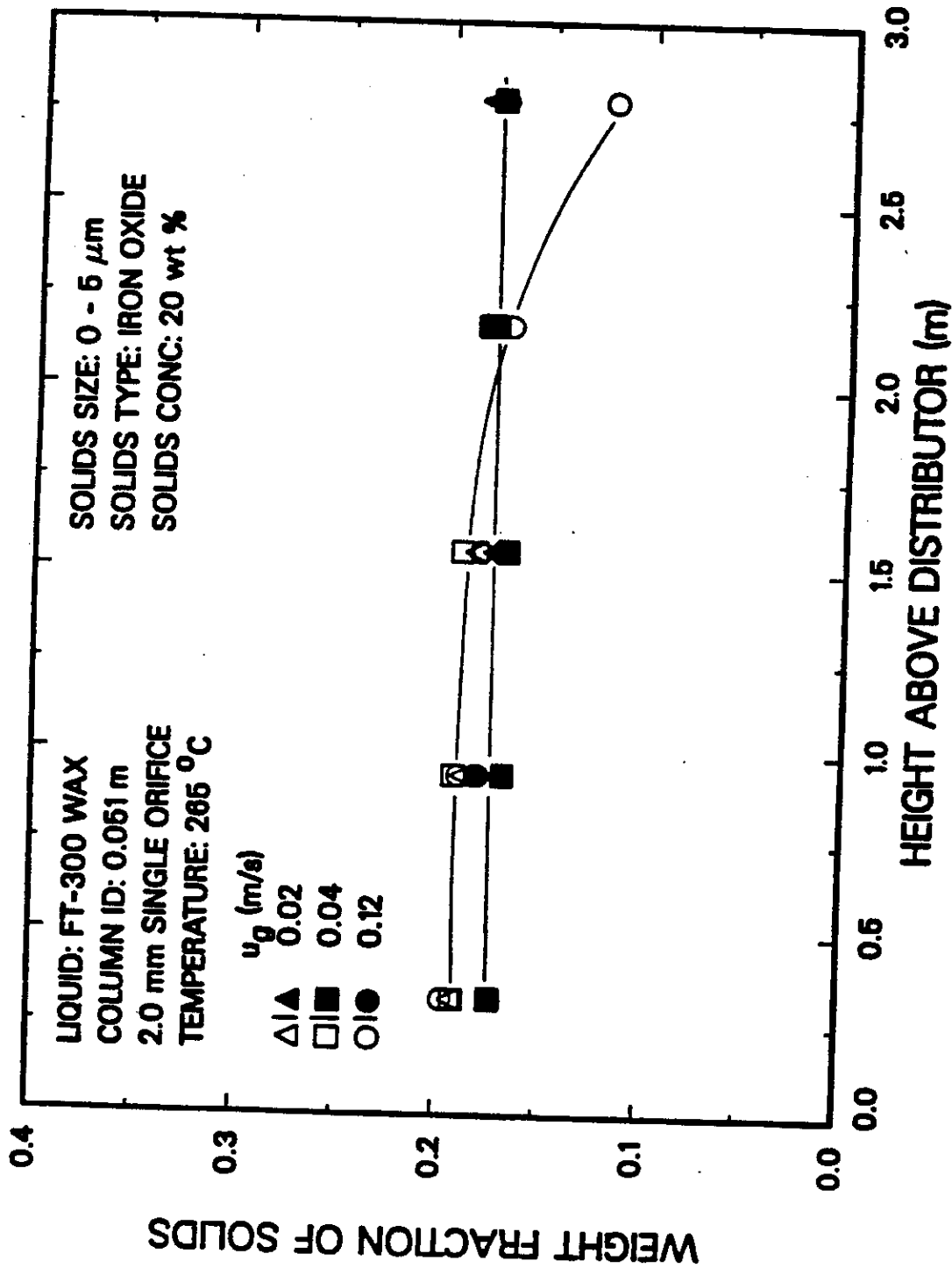
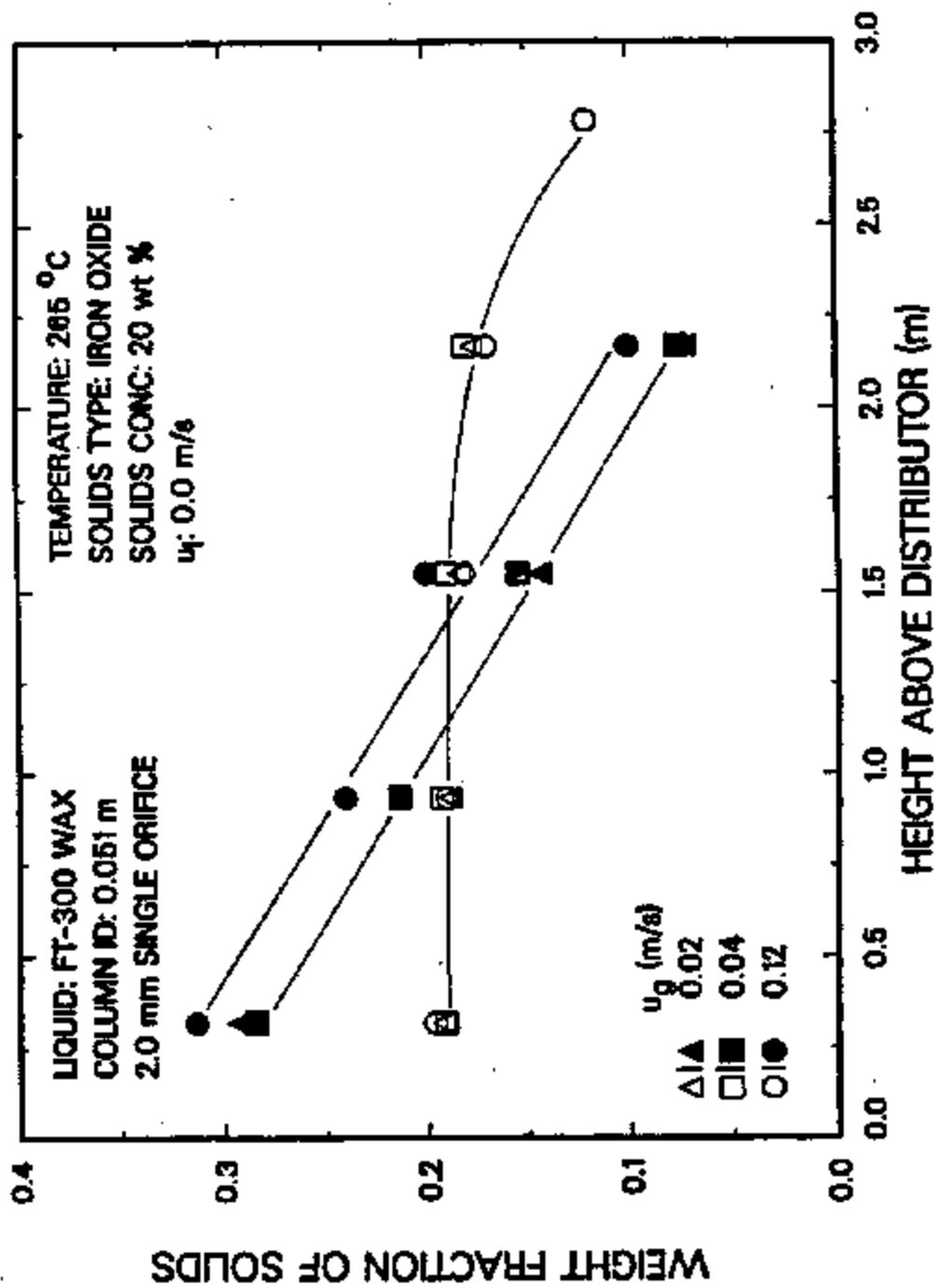


Figure 11. Effect of slurry velocity on axial solids distribution.



(Open Symbols - $d_p = 0 - 5 \mu m$, Closed symbols - $d_p = 44 - 63 \mu m$)

Figure 12. Effect of solids size on axial solids distribution.

FIGURE 13. NUCLEAR DENSITY GAUGE APPARATUS

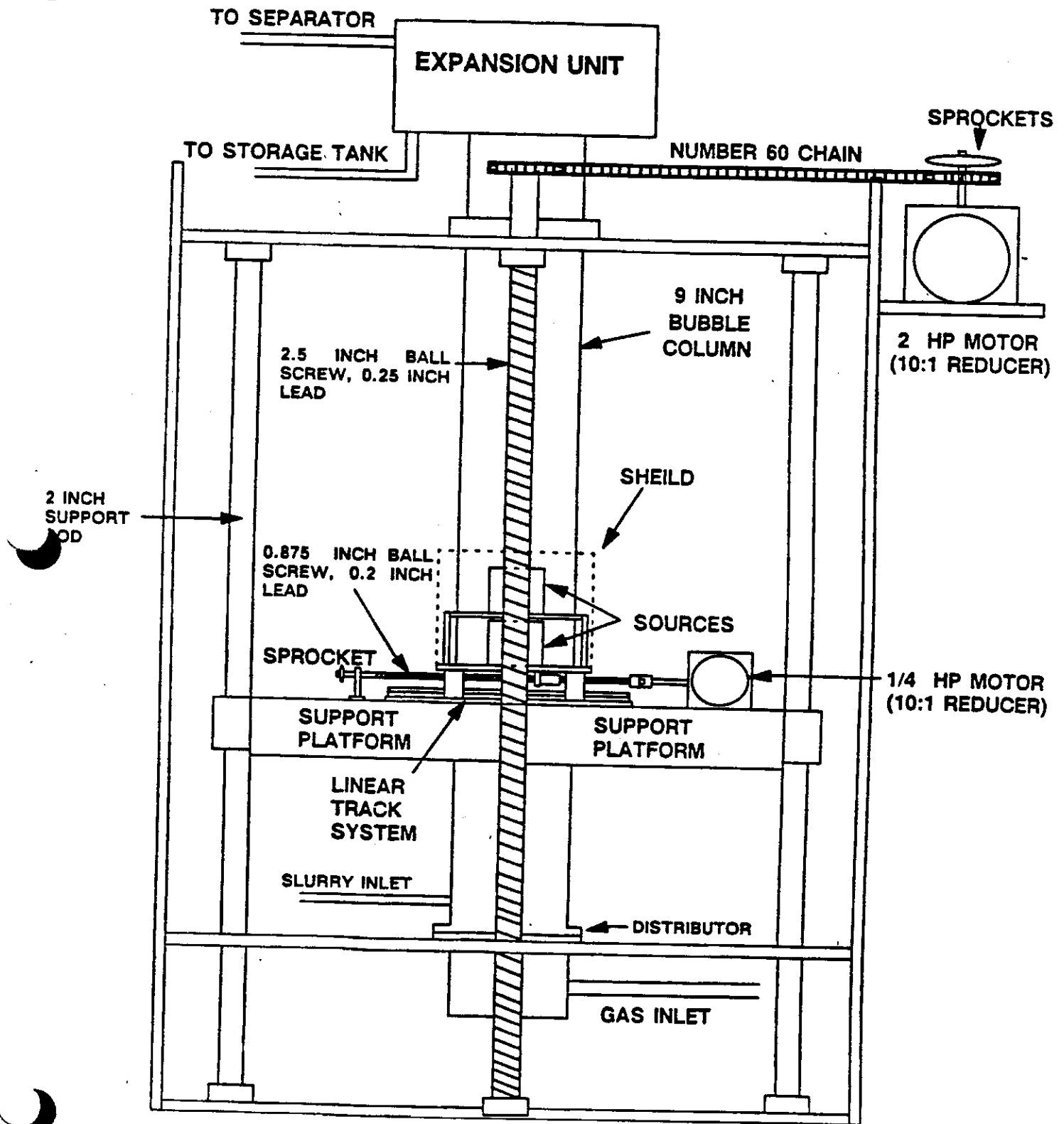


FIGURE 14. CONCLUSIONS

- INCREASE IN SLURRY FLOW RATE CAUSES A DECREASE IN GAS HOLD-UP
- ADDITION OF SOLIDS CAUSES A SLIGHT INCREASE IN GAS HOLD-UP FOR BATCH EXPERIMENTS
- NO SIGNIFICANT EFFECT OF SOLIDS TYPE OR SIZE ON GAS HOLD-UP IN THE CONTINUOUS MODE OF OPERATION
- AXIAL GAS HOLD-UP - NON-UNIFORM FOR BATCH
- UNIFORM FOR CONTINUOUS
- SMALL UPFLOW OF LIQUID IS SUFFICIENT TO MAINTAIN A UNIFORM SUSPENSION OF IRON OXIDE PARTICLES LESS THAN 53 μm

FIGURE 15. FUTURE WORK

- **ANALYZE DATA FROM DP CELLS TO GAIN INFORMATION ON FLOW REGIMES**
- **DETERMINE AXIAL SOLIDS DISPERSION COEFFICIENTS**
- **INITIATE EXPERIMENTS IN THE LARGE COLUMN**