# Removal of Liquid from a Packed Column of Spherical Beads under Centrifugal Force

Surface sulfonated copolymer beads and glass beads of various size distributions were used to study the removal of liquid from a packed column of spherical beads under centrifugal force. At low forces, from 1 G to approximately 20 G, the volume of liquid retained corresponds to the free volume between the packed beads. The liquid level varies with force from about 20 to 400 G. It is shown that the liquid level is a function of the force applied and the size distribution of the beads in the column. At forces from approximately 400 to 1200 G the weight of the liquid on the sample remains constant.

#### GORDON H. FRICKE DONALD ROSENTHAL

Department of Chemistry and Institute of Colloid and Surface Science Clarkson College of Technology Potsdam, New York 13676

### and GEORGE A. WELFORD

Health and Safety Laboratory
U. S. Atomic Energy Commission
New York, New York 10014

#### **SCOPE**

The centrifugation technique has been used to measure the average saturation of samples of limestone and sandstone at various centrifugal accelerations (Hassler and Brunner, 1945) and to study rates of drainage to a constant partial saturation of packed beds of various materials (Haruni and Storrow, 1953a, 1953b; Nenninger and Storrow, 1958; Storrow, 1957). A semiempirical equation based on the capillary rise model for individual capillaries has been used (Batel, 1961) to calculate the height of liquid in partially saturated samples. The capillaries assumed by the researchers above are not connected and are like the capillary rise models of Princen (1969a, 1969b) for circular and triangular capillaries.

It has been suggested that the centrifugation technique can be used to determine pore size distribution curves for disks of porous nickel made from powder. In this analysis (Ksenzhek et al., 1967), it was assumed that upon centrifugation liquid is removed from the larger pores and retained by the smaller pores. At a particular centrifugal force only pores smaller than a certain size will be filled with liquid. It is assumed that liquid remains distributed throughout the sample. The principle is approximately opposite to that of the mercury porosimeter method (Rit-

ter and Drake, 1945; Mayer and Stowe, 1966) of determining the pore size distribution of porous media.

In a previous publication (Fricke et al., 1971), the centrifugation method was used to determine the wet weights of ion exchange resin beads with surface liquid. The ion exchange beads were centrifuged at sufficient forces that only the surface liquid remained on the beads. The method was checked with spherical beads which are impenetrable to the wetting liquid. The amount of liquid which remained on the surface of the solid materials was shown to be dependent on the size distribution of the beads.

In this paper the previous study is extended to include centrifugal forces below the minimum force required to remove all but the surface liquid from spherical beads. The liquid formed a boundary around the beads in the glass tube. When the tube was replaced in a vertical position, the height of the boundary was found to be related to the size distribution of the beads and to the centrifugal force at which the sample had been centrifuged.

The purpose of this paper is to present a model for centrifugation of liquid from a packed column of spherical beads. The results should be applicable to studies of flow in porous media.

#### CONCLUSIONS AND SIGNIFICANCE

A model is presented for the removal of liquid from a packed column of beads under centrifugal force. This model, previously unreported, treats the centrifuge tube as a single capillary broken up by the beads. The total length of the wetted bead boundary at the liquid-air interface can be calculated from an equation which relates the length of this boundary to the height of the liquid in the sample and the centrifugal force. This equation requires no assumption about the shape and size of the capillary or the number of capillaries. The calculated length of the bead boundary is dependent on the size distribution of the beads.

Correspondence concerning this paper should be addressed to D. Rosenthal. G. H. Fricke is with the Department of Chemistry, Indiana University-Purdue University, Indianapolis, Indiana 46205.

At low forces (1 to 20 G) the liquid remaining on the beads represents the interstitial pore volume between the packed beads. The centrifugation results are in good agreement with mercury porosimeter results.

At moderate forces (about 20 to 400 G) the liquid formed a linear boundary around the beads in the centrifuge tube. The length of the boundary was shown to be characteristic of the sample and is related to the way the beads pack in the column.

At high forces (about 400 to 1200 G) the volume percent of liquid at the contacts of the beads is constant and is linearly related to the spread of the size distribution of the beads.

The model presented in this paper was checked with

water and with two solid materials which were completely wetted. Equation (17) is general and should apply to a wide variety of liquids and packed solid materials. The

model and Equation (17) should also apply to flow through any type of porous media where the liquid is predominantly interconnected in the material.

#### **EXPERIMENT**

#### Materials

Glass beads with a high degree of sphericity were purchased from Microbeads Division, Cataphote Corporation. The unsulfonated copolymer beads were obtained from Dow Chemical Company and Ionac Chemical Company. The method of surface sulfonating these copolymer beads has been previously reported (Fricke et al., 1971).

#### Centrifugation

Five different materials were placed in glass tubes 1.7 cm in inside diameter by 4.7 cm in height. Each tube had a fritted disk sealed in the bottom. These tubes were placed on thick walled glass cylinders inside high impact polyethylene centrifuge tubes. The outer tubes were covered with Parafilm during centrifugation. The outer tubes were placed in a centrifuge supplied with test tube holders which swing into a horizontal position at sufficiently high speeds. When the samples, which were initially wetted with an excess of distilled water, were centrifuged, the water went through the fritted disk and was collected in the bottom of the outer centrifuge tube.

The materials used in this research were studied from the normal gravitational force (1 G) to approximately 1200 G. Forces vary over the length of the centrifuge tube. The forces reported in the paper are G forces at the middle of the column of liquid remaining on the sample.

To obtain reproducible results, the samples were centrifuged a number of times with water on them prior to determination of the amount of water retained. Once the beads were wetted they were not shaken between runs at different forces. Presumably, the beads had settled and were in a similar packing arrangement for all measurements. The samples were centrifuged in no particular order of force and were rewetted with an excess of water between runs.

All weights reported in this research are equilibrium weights, that is, the sample was centrifuged long enough for the weight to remain essentially constant. For the 50-60 mesh beads, it was determined that a maximum of 10 minutes was necessary for constant minimum weights of the samples to be attained at forces above 100 G. As much as 30 minutes was required at the same low forces for the 230-325 mesh samples.

#### Size Distribution

The particles used in this research were photographed with a Nikon Model S microscope using Kodak Panatomic-X film. Enlargements were made on either Kodak Polycontract-N single weight paper using Contrast Filter No. 4 or on single weight Medalist F-4 paper. High contrast between the black and white features on the film is achieved by this procedure. A micrometer scale was photographed on the film at irregular intervals. The exact magnification was determined by measuring the micrometer prints which were enlarged at the same time as the 8  $\times$  10-in. prints of the beads.

A Carl Zeis Particle Size Analyzer TGZ-3 was used to determine the sizes of the particles from the enlargements. This instrument is particularly well suited for the determination of sizes of spherical or circular particles since it uses an adjustable circular light beam. The instrument has 48 categories of sizes into which the sizes of the particles on the photographs can be placed. The absolute sizes range from 1.22 to 27.71 mm with center intervals evenly spaced along the range. The largest particles on the prints cannot exceed 27.71 mm.

#### RESULTS AND DISCUSSION

Centrifugation profiles obtained for the five materials used in this research are presented in Figure 1. The ordinate is the weight of water in grams which remained

on the sample after it was centrifuged to a constant weight at each G force. A logarithmic plot of the force in G's has been used to accentuate the changes in the weight of liquid in the lower region of forces from 1 to about 400 G. The two figures have been placed together for easy comparison of the different forces at which the water drains from each sample.

#### **Upper Plateau of Centrifugation Profile**

At 1 G and over a range of centrifugal force, the amount of liquid retained remains constant (upper plateau, Figure 1). It is believed that on this upper plateau the liquid completely fills the pores between the beads. The observation that the volume on the upper plateau is proportional to the volume of the sample present is consistent with this conclusion. The effect of the different sample sizes from Table 1 is shown in Figure 1. The same shape symbol represents identical materials. The blackened symbol designates a larger sample weight than the corresponding clear symbol (refer to Table 1).

The maximum volume of liquid at 1 G and the dry weight of the sample were used to calculate the pore volume per gram (dry weight) of solid and per milliliter of solid. The results of this treatment are presented in Table 1. Mercury porosimeter measurements (Ritter and

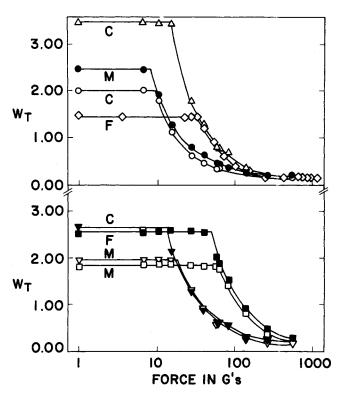


Fig. 1. Centrifugation profile of the weight of water  $W_T$  in grams on representative samples of surface sulfonated copolymer beads and glass beads vs. logarithm of the centrifugal force (from 1 G to 560 G):  $\bigcirc$ , 50-60 Mesh Resieved SSC Dow;  $\triangle$ , 100-200 Mesh SSC, Dow;  $\diamondsuit$ , 100-200 Mesh SSC, lonac;  $\bigtriangledown$ , 120-170 Mesh Glass;  $\Box$ , 230-325 Mesh Glass; F = fine porosity fritted Disk; M = medium porosity fritted Disk; and C = coarse porosity fritted Disk. Clear and blackened symbols are the same batch of material but different weights.

Material	No. particles sized	-, u	Size distributi $r^2 \times 10^{-3},$ $u^2$	on data $ \frac{r^3 \times 10^{-4}}{u^3}, $	Shap estimate $\sqrt{\beta_1}$		RSDre	Sample weight, g (plotting symbol)	Porosity of fritted disk	(Pore volume in ml) Bead weight in g)	ا	re volume in ml  d volume in ml  Porosimeter
50-60 mesh Surface sulfonated resieved Dow copolymer beads <sup>a</sup>	3503	111	12.7	148	-2.96	15.3	0.183	3.64 ( ○ ) 4.53 ( ● )	Coarse Medium	0.545 0.549	0.589 0.593	Ξ
120-170 mesh Glass beads <sup>b</sup>	2681	40.7	1.81	8.45	-0.819	3.35	0.303	10.8 (♥) 7.90 (♡)	Coarse Medium	0.249 0.247	0.600 0.595	0.597
100-200 mesh Surface sulfonated ionac copolymer beads <sup>b</sup>	6213	35,6	1.51	7.16	0.229	2.35	0.437	2.97 (♦) 2.89 3.57 3.58	Fine Fine Fine Fine	0.498 0.516 0.510 0.510	0.538 0.558 0.552 0.551	0.576
100-200 mesh Surface sulfonated Dow copolymer beads <sup>c</sup>	4345	24.4	0.854	3.77	0.994	3.69	0.662	4.14 (△)	Coarse	0.837	0.905	_
230-325 mesh glass beads <sup>b</sup>	4273	14.7	0.256	0.502	0.236	2.43	0.437	10.4 (■) 7.47 (□)	Fine Medium	0.245 0.246	0.590 0.592	

<sup>&</sup>lt;sup>4</sup> Monomodal size distribution.

Drake, 1945; Mayer and Stowe, 1966) of the pore volume of two of the materials were compared with the centrifugation results. The pore volumes for the glass beads obtained by the two methods are within the experimental error of each other (Table 1). This confirms the interpretation that the upper plateau is the total (or pore) volume between the beads.

The interstitial pore volume obtained for the surface sulfonated Ionac copolymer beads by the centrifugation procedure was smaller than the volume obtained by the mercury porosimeter method. This difference can be explained if it is assumed that the pores of the Ionac beads less than one micron in diameter, which were available to the mercury in the porosimeter method, were not accessible to the water during centrifugation.

#### Region Between the Upper and the Lower Plateaus

As the centrifugal force is increased beyond the region of the upper plateau, the force exceeds the surface tension which holds the liquid in the pores and the liquid is drained from the pores. In this region the amount of liquid retained decreases as the centrifugal force is increased (see Figure 1).

Glass tubes were used in this research and the sample could easily be seen. At forces between those corresponding to the upper and lower plateaus, a liquid boundary was formed perpendicular to the radial axis of the centrifuge during centrifugation. This boundary was observed to be between the disk and the top of the sample when the tube was removed from the centrifuge. The height of the boundary above the fritted disk was found to depend upon the centrifugal force. The pore size distribution approach (Ksenzhek, 1967) which assumes that larger pores in the sample are emptied while smaller pores remain filled with liquid is incorrect for the studies in this research.

The top of the bulk liquid forms a boundary around the beads. The liquid in the sample above this bulk liquid (or above the boundary) is located mainly at the contacts of the beads. In addition, there is liquid adhering to the surface of the beads and in the pores of the sample. The amount of this liquid is presumed to be small and is not

distinguished from liquid at the contacts of the beads.

When the force becomes great enough to remove all of the bulk liquid from the sample, only that liquid at the contacts of the beads will remain. At sufficiently fast centrifugation speeds the forces will be great enough to overcome the interfacial surface tension and additional liquid will be removed from the contacts of the beads. This represents the end of the lower plateau.

The model presented in this paper to explain the retention of liquid by the spherical beads treats the centrifuge tube as a single capillary broken up by the beads. The model assumes that there is a liquid boundary the length of which is calculable from the heights of the liquid in the sample and the corresponding forces.

The definitions used for the model are given in the Notation. The liquid weights are illustrated in Figure 2. The upper plateau region is from G=1 to  $G_1$ . The lower plateau is from  $G_2$  to  $G_3$ . Beyond the lower plateau there will be a loss of liquid from the capillaries created by the contacts of the beads  $G_3$  to  $G_4$  and a loss of liquid from the capillaries in the fritted disks, at forces greater than  $G_4$ . Figure 2 does not necessarily imply that liquid will start to leave the capillaries at the bead contacts before the fritted disk capillaries.

The bulk liquid referred to as  $W_B$  is assumed to be interconnected in the model presented in this paper. The relationships between the weights given by the definitions are

$$W_E = W_T + W_D \tag{1}$$

$$W_T = W_S + W_C = W_B + W_{Ctot}$$
 (2)

$$W_{S} = W_{B} + W_{C}' \tag{3}$$

$$W_{Ctot} = W_C + W_{C'} \tag{4}$$

The value of  $W_{C\text{tot}}$  will be equal to  $W_{C\text{max}}$  from G=1 to  $G_3$ . At forces greater than those corresponding to  $G_3$ ,  $W_{C\text{tot}} < W_{C\text{max}}$ . In the calculations in this paper  $W_{C\text{max}} = W_{C\text{tot}}$ .

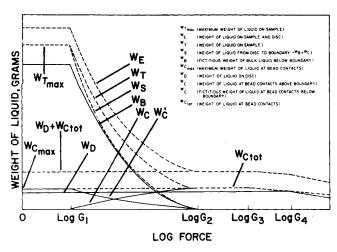
The sample is assumed to be homogeneously packed in the tube so that  $W_{C}'/W_{S}$  is constant. This is true for any height of liquid as long as there is bulk liquid above the

Bimodal size distribution.

<sup>&</sup>lt;sup>4</sup>√B<sub>1</sub> is the coefficient of skewness (m<sub>8</sub>/m<sub>8</sub>)<sup>2</sup> and β<sub>8</sub> is the coefficient of peakedness or Kurtosis (m<sub>8</sub>/m<sub>8</sub>) where m<sub>8</sub>, m<sub>8</sub> and m<sub>4</sub> refer to the second, third, and fourth moments about the mean \*RSDr is the relative standard deviation of the radius

 $RSDr = \frac{1}{r} \sqrt{\sum_{i} f_i (r_i - \hat{r})^2} = \left(\frac{\hat{r}^2}{(r)^2} - 1\right)^{1/2} = \frac{\sqrt{m^2}}{\hat{r}}$ 

f Mercury Porosimeter results were obtained by American Instruments Co., Inc., Silver Spring, Maryland



fritted disk. Thus,

$$\frac{W_{C'}}{W_{S}} = \frac{W_{C\text{max}}}{W_{T\text{max}}} \tag{5}$$

This is probably not exactly correct since some liquid will be drawn from the capillaries at the contacts of the beads as the force is increased, but the amount is assumed to be negligible.

Substituting Equation (5) into Equation (2) and the value of  $W_C$  in Equation (4) into the resulting equation and solving for  $W_C$ :

$$W_C = \frac{W_{C_{\text{max}}}(W_{T_{\text{max}}} - W_T)}{(W_{T_{\text{max}}} - W_{C_{\text{max}}})} \tag{6}$$

This equation may be used to calculate the weight of the liquid in the capillaries at the contacts of the beads above the bulk liquid  $W_C$  from experimental data.

The height of the bulk liquid above the fritted disk may be calculated as

$$h = h_T \frac{(W_T - W_{C_{\text{max}}})}{(W_{T_{\text{max}}} - W_{C_{\text{max}}})} \tag{7}$$

Equation (7) expresses the proportionality relationship between the height and the amount of liquid  $W_B$ .

The model presented in this paper assumes that all the liquid is interconnected and a linear boundary is formed which runs around the beads. At equilibrium the force due to the downward pull of the liquid mass is balanced by the upward pull of the surface tension. These two forces are equated and when the column of liquid is under normal gravitational acceleration  $g_0$ , the general form of the well-known capillary rise equation results

$$\left\{ \begin{array}{l} \text{Length of the Linear} \\ \text{Boundary of the} \\ \text{Wetted Surface} \end{array} \right\} \begin{array}{l} \gamma \cos \theta = \left\{ \begin{array}{l} \text{Total Volume} \\ \text{of Liquid on} \\ \text{the Sample} \end{array} \right\} \rho \, g_0 \end{array}$$
 (8)

where  $\gamma$  is the surface tension of the liquid (72 dynes cm<sup>-1</sup> for water),  $\rho$  is the density of the liquid (1.0 g cm<sup>-3</sup> for water), and  $\theta$  is the liquid-solid contact angle ( $\theta=0$  for a completely wetted surface). Equation (8) assumes that the force of any segment of the column of liquid is independent of the height of the segment in the column. When the column of liquid is centrifuged, the force at any point in the column of liquid will depend on the distance of the point from the center of the centrifuge R.

Equation (8) may be modified for centrifugal accelerations so that the force acting on the liquid is the sum of two terms, one for the liquid in the sample and a second term for the liquid in the disk:

$$L \gamma \cos \theta = A_S \rho \int_{R_1}^{R_2} g_S dR + A_D \rho \int_{R_2}^{R_3} g_D dR$$
 (9)

where  $R_1$ ,  $R_2$  and  $R_3$  are the distances from the center of the centrifuge to the top of the column of liquid, to the top of the fritted disk, and to the bottom of the fritted disk, respectively;  $g_S$  and  $g_D$  are the centrifugal accelerations for the liquid in the sample and the liquid in the fritted disk, respectively.

The centrifugal acceleration in cm  $\sec^{-2} g$  is a function of N, the speed of the centrifuge in rev./min. and R

$$g^2 = g_0^2 + [R^2 N^4 \pi^4 / (81 \times 10^4)] \tag{10}$$

where  $g_0$  is the acceleration of gravity. The horizontal (or centrifugal) and the vertical (or gravitational) components of force have been added vectorially in Equation (10). For convenience, let

$$a^2 = N^4 \pi^4 / (81 \times 10^4) \tag{11}$$

Then Equation (9) becomes

$$L \gamma \cos \theta = A_{\rm S} \rho \int_{R_1}^{R_2} (g_0^2 + a^2 R^2)^{\frac{1}{2}} dR$$
$$+ A_D \rho \int_{R_2}^{R_3} (g_0^2 + a^2 R^2)^{\frac{1}{2}} dR \quad (12)$$

Beyond  $G_1$  (see Figure 2) N is very high,  $g_0^2 \ll a^2R^2$ , and Equation (12) becomes

$$L \gamma \cos \theta = A_S \rho \frac{a}{2} (R_2^2 - R_1^2) + A_D \rho \frac{a}{2} (R_3^2 - R_2^2)$$
(13)

where "a" may be evaluated by Equation (11).

In the centrifuge used,  $R_2$  and  $R_3$  were constant. The height of the column of liquid above the fritted disk h is a function of  $R_1$ .

$$h = R_2 - R_1 \tag{14}$$

It is convenient to express the first term of Equation (13) in terms of the measured or calculated height of the column of liquid above the fritted disk h and the distance from the center of the centrifuge to the top of the fritted disk  $R_2$ . The distance to the center of the bulk liquid on the sample is

$$\overline{R_{\rm S}} = R_2 - \left(\frac{h}{2}\right) \tag{15}$$

A similar expression may be written for the distance to the center of the fritted disk  $\overline{R}_D$ . Substitution of Equations (14) and (15) into Equation (13) gives

$$L \gamma \cos \theta = (A_S \overline{R}_S h_S + A_D \overline{R}_D h_D) \rho \pi^2 N^2/900$$
(16)

In terms of the weights of liquid Equation (16) may be written

$$L \gamma \cos \theta = [(W_T - W_C) \overline{R}_S + W_D \overline{R}_D] \pi^2 N^2/900$$
(17)

The height of the liquid in the total capillary includes the height of the liquid in the sample h and in the disk. The value of h necessary for Equation (15) is obtained from Equation (7). In Equation (17) the value of  $W_T$  is experimental. The value of  $W_C$  is obtained from Equation

(6). The values of  $W_D$  and  $\overline{R}_D$ , determined in a separate experiment, are constant because only the case where the disk is filled with liquid is considered. It is assumed that the glass beads and the surface sulfonated copolymer beads are completely wetted by water. The value of  $\theta =$ 0 was used for all materials in this research.

The heights of liquid on a number of samples were observed and calculated from the weight of liquid remaining after centrifugation to a constant weight. The data are presented in Table 2 as are the calculations based on the model presented in this paper [Equation (17)]. The values of L reported are the results estimated from calculated values of h. The values of L were not much different when the observed values of h were used in the calculations. For example, the values of L for the first sample listed were 236, 255, 244, and 248 cm using the observed value of h. It is believed that most of the observed and calculated heights of liquid are identical to

Table 2.	TOTAL :	LENGTH OF	WETTED	BOUNDARY	FOR THE		
CENTRIFUGED SAMPLES AND DISKS							

GENTRIFUGED SAMPLES AND DISAS						
Sample 50-60 mesh surface sulfonated Dow copolymer beads	Rev./ min. 275 315 425 505	h (ob- served) cm 2.20 1.01 0.51 0.54	h (calculated) cm [Equation (7)] 1.45 1.12 0.53 0.35	L, cm [Equation (17)] 242 254 244 249		
	Rel. error	r of mean	(90% level)	2.49%		
	275 315 425 505	2.00 1.38 0.38 0.51	1.98 1.36 0.70 0.51 Mean	329 311 327 360		
	Rel. error	of mean (	90% level)	7.28%		
120-170 mesh glass beads	425 505 615 635	1.39 0.87 0.58 0.47	1.35 0.84 0.51 0.46 Mean	491 455 444 436 456		
	Rel. error	of mean (	90% level)	6.25%		
	425 505 615 635	1.34 0.79 0.63 0.55	1.42 0.94 0.56 0.52 Mean	541 539 520 529 532		
	Rel. error	of mean (	90% level)	2.09%		
100-120 mesh surface sulfonated ionac copolymer beads	500 590 670 800 980	1.50 1.00 0.70 0.35 0.20	1.54 1.07 0.74 0.39 0.21	752 760 713 613 596		

	Rel. erro	r of mean (	(90% level)	10.8%		
	500	1.50	1.41	719		
	590	1.00	0.96	726		
	670	0.70	0.62	655		
	800	0.35	0.33	588		
	980	0.20	0.17	596		
			Mean	657		
	Rel. error	r of mean (	90% level)	9.45%		
	500	1.50	1.60	746		
	590	1.00	1.07	743		
	670	0.70	0.72	693		
	800	0.35	0.37	605		
	980	0.33	0.19	615		
	000	0.20	0.19	013		
			Mean	680		
	Rel. erro	of mean (	90% level)	9.50%		
	500	1.50	1.61	760		
	590	1.00	1.02	723		
	670	0.70	0.70	698		
	800	0.35	0.36	624		
	980	0.20				
	900	0.20	0.17	614		
			Mean	684		
Rel. error of mean (90% level) 8.84%						
100-200 mesh surface	315	2.25	2.83	755		
sulfonated Dow	425	1.31	1.37	735		
copolymer beads	505	0.98	0.95	763		
	615	0.59	0.49	659		
	635	0.45	0.48	693		
	730					
	130	0.37	0.40	802		
			Mean	734		
	Rel. error	of mean (	90% level)	5.74%		
230-325 mesh	635	2.43	2.29	1667		
glass beads	730	1.76		1759		
9	940	0.99	0.00	1690		
		0.00	0.00	1000		
			Mean	1705		
	Rel. error of mean (90% level) 4.73%					
	635	2.27	2.34	1637		
	730	1.73		1748		
	940	0.94		1588		
	0.10	0.01	0.00	1000		
			Mean :	1658		
Rel. error of mean (90% level) 8.35%						
within experimental e A downward trend creased for the 120-1 sulfonated Ionac cope even for samples whi	1  in  L  is $10  mesh$ $10  olymer be$ $10  olymer$	observed glass bea eads. The these tree	ds and the average v nds.	e surface was used		
One objective of	the cal	culations	is to d	etermine		
One objective of the calculations is to determine whether the linear boundary of the samples $L_S$ is charac-						

One objective whether the linear boundary of the samples  $L_S$  is characteristic of each different size distribution of each material. To determine L<sub>S</sub>, the length of the boundary in the disk  $L_D$  must be known.

$$L_S = L - L_D \tag{18}$$

By a treatment analogous to that for the sample, the

Mean 687

TABLE 3. CALCULATION OF THE LENGTH OF THE WETTED BOUNDARY FOR CENTRIFUGED SAMPLES

Sample	Porosity of disk	Mean value of $L$ , cm (Table 2)	$L_{\mathcal{D}}$ , cm	$L_{ m S}$ , $^{ m d}$ cm	<i>J</i> , cm <sup>-1</sup> [Equation (20)]
50-60 mesh surface sulfonated resieved Dow copolymer beads	Coarse Medium	247 331	52ª 136	195	86
120-170 mesh glass beads 100-200 mesh surface	Coarse Medium Fine	456 532 687	55 <sup>a</sup> 131	401	177
sulfonated ionac copolymer beads	Fine Fine	657 680	(181)° (181)° (181)°		
100-200 mesh surface sulfonated Dow copolymer beads	Fine Coarse	684 734	(181)° 63°	496 671	219 297
230-325 mesh glass beads	Medium Fine	1658 1 <b>705</b>	(134) <sup>b</sup> 181	1524	675

These L<sub>D</sub> values were determined using Equation (19).
The L<sub>D</sub> value of 134 cm for the medium porosity frit is the average of 136 and 131 cm obtained from the two experiments summarized above.
The L<sub>D</sub> value of 181 cm for the fine porosity frit is the value obtained for the 230-325 mesh glass beads listed below.
L<sub>S</sub> values calculated using Equation (18).

value of  $L_D$  may be calculated from experimental data as

$$L = (W_D - W_{DC}) \ \overline{R}_D \ \pi^2 \ N^2 / (1800 \ \gamma \cos \theta) \quad (19)$$

where  $W_{DC}$  is the capillary liquid above the liquid boundary in the disk. This is determined by Equation (6) where the terms refer to the disk instead of the sample. A factor of 2 was introduced into the equation for the disk because the bottom of the disk is also exposed to air and contributes to the total length of the boundary of the disk.

The lengths of the boundaries of the various porosity disks will be different. In a separate experiment the various porosity disks were centrifuged with water on them. The coarse porosity disks could be centrifuged at forces sufficient to cause a loss of water from the disks and  $L_D$ was calculated at each acceleration using Equation (19). The value of  $L_D$  for the medium and fine porosity disks could not be determined by this type of experiment. Liquid was pulled from the medium porosity disks, but not all the bulk liquid could be removed by centrifugation. None of the interstitial liquid could be removed from the fine porosity disks even at the maximum forces applied (1200 G).

The three experimentally determined values of  $L_D$  for the coarse porosity disks given in Table 3 do not differ significantly from each other. Where the coarse disks were used, the Ls values for the beads were determined using Equation (18). The  $L_D$  value for the medium porosity disks was determined from the difference between the L and Ls values for the 50 to 60 mesh surface sulfonated beads and the 120 to 170 mesh glass beads. The data are presented in Table 3. The  $L_D$  value for fine porosity disks was determined from the 230 to 325 mesh glass beads

The length of the wetted sample boundary is dependent upon the size of the particles and the cross-sectional area of the container in which the beads are placed. A value J which is presumably independent of the size of the container is calculated

$$J = \frac{L_{\rm S}}{A_{\rm tube}} \tag{20}$$

where A<sub>tube</sub> is the cross-sectional area of the tube in which the sample is centrifuged. In this research  $A_{\text{tube}} = 2.26$ cm<sup>2</sup>. The calculated values of J are given in Table 3.

The total length of the wetted boundary is probably related to the circumference of the beads. The smaller the beads, the more of them that can be packed into a given space and the longer the boundary or cumulative circumference of the beads at the water-air interface. If it is assumed that

$$A_{\text{tube}} = N \pi \overline{r^2} k \tag{21}$$

where N is the number of beads in a cross section of the tube and k is a characteristic of the way the beads pack,

$$L_{\rm S} = 2N \ \pi \ \overline{r} \ k' \tag{22}$$

where k' is a characteristic of the way the beads pack, then from Equation (20) it follows that

$$J = 2 \frac{\overline{r} \, k'}{\overline{r^2} \, k} \tag{23}$$

In Equations (21) to (23)

$$\overline{r^k} = \sum f_i r_i^k \tag{24}$$

where k = 1 or 2 and  $f_i$  is the fraction of the number of beads which have a radius  $r_i$  (from the size distribution data—actually  $r_i - \Delta$  to  $r_i + \Delta$  where  $\Delta$  is one half the interval between  $r_i$  and  $r_{i+1}$ ). The  $\overline{r^k}$  data are presented in Table 1.

If (k'/k) is a constant, then a plot of J versus  $(r/r^2)$ would give a straight line passing through the origin. J is plotted versus  $(\overline{r}/\overline{r^2})$  in Figure 3. J is also plotted versus  $(1/\overline{r})$  and  $1/\overline{r^2}$  in the same figure.

The absence of a simple linear relationship for any of the plots in Figure 3 suggests that the length of the boundary in addition to being related to  $(\overline{r}/\overline{r^2})$ ,  $\overline{r}$ , or  $\overline{r^2}$  depends upon the size distribution for each sample. The size distribution will determine how the beads pack. The failure of Equation (23) may mean that k and k' vary with the size distribution instead of being constant.

#### Lower Plateau of the Centrifugation Profile

The detailed results for the lower plateau (high forces) are presented in a previous paper (Fricke et al., 1971). A series of solutions which had different densities, viscosities, and surface tensions were investigated. It was shown that the volume of liquid on the lower plateau remained

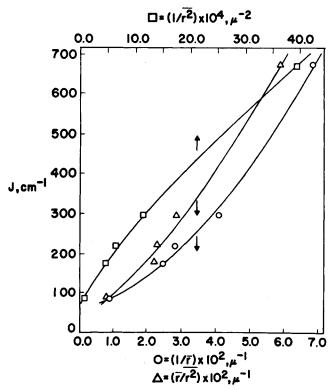


Fig. 3. Length of wetted boundary of centrifuged samples per crosssectional area of tube J vs. functions of the mean radius and the mean squared radius.

constant from about 400 to 1200 G.

A quantitative linear relationship was presented which correlated the volume percent of liquid in the capillaries, created by the contacts of the beads, with the spread of the size distribution of the beads.

#### **ACKNOWLEDGMENT**

The authors wish to thank Dow Chemical Company, Inc. for supplying poly(styrene-8%-divinyl-benzene) copolymer beads and the American Instrument Company, Inc. for the mercury porosimeter measurements.

The U. S. Atomic Energy Commission, Health and Safety Laboratory, provided a fellowship for G. H. Fricke and partially supported the research. This work is taken in part from the Ph.D. research of Gordon H. Fricke.

#### NOTATION

= contribution to the total centrifugal acceleration g а due to rotation of the tube with the fritted disk divided by the distance from the center of the centrifuge R

= cross-sectional area of the liquid in the fritted disk  $A_D$  $A_{S}$ = cross-sectional area of the liquid in the sample

Atube = cross-sectional area of the tube in which the sample is centrifuged

= fraction of the number of beads with a radius  $r_i$ fi

= centrifugal acceleration g gravitational acceleration

= ratio of the centrifugal to the gravitational force or acceleration, (that is,  $g/g_0$ )

hheight of the linear boundary above the disk

= height of the sample in the centrifuge tube. This  $h_T$ is equal to the maximum height of the liquid in the sample

= ratio of length of the linear boundary of the wetted sample to the cross-sectional area of the tube k and k' = constants characteristic of how the beads pack in the tube

= total length of the wetted boundary of the sample Land the fritted disk  $(= L_S + L_D)$ 

 $L_{D}$ = length of the linear boundary in the wetted frit-

= length of the linear boundary of the wetted sam- $L_{S}$ ple

N = speed of the centrifuge in rev./min.

R = distance of the liquid at any point in the tube from the center of the centrifuge

 $R_1$ = distance from the center of the centrifuge to the top of the continuous column of liquid

 $R_2$ = distance from the center of the centrifuge to the top of the fritted disk

= distance from the center of the centrifuge to the  $R_3$ bottom of the fritted disk

 $\overline{R}_{D}$ = distance from the center of the centrifuge to the center of the fritted disk

 $\overline{R}_S$ = distance from the center of the centrifuge to the center of the continuous column of liquid

= radius of the ith category of beads  $r_i$  $r^k$ = average value of  $r^k$  where  $k \equiv 1$  or 2

 $W_E$ = total experimental weight of liquid including the liquid on the sample and on the fritted disk

 $W_T$ = weight of liquid above the fritted disk = weight of liquid on the fritted disk

= weight of liquid from the top of the disk to the linear boundary

 $W_C$ = weight of capillary liquid remaining at the contacts of the beads above the linear boundary

 $W_{c'}$  = weight of capillary liquid in  $W_s$  created by a fictitious separation of Ws into bulk liquid WB and the capillary liquid at the contacts of the beads  $W_{c'}$ 

 $W_B$  = weight of the bulk liquid in  $W_S$  referred to above  $W_{DC}$  = weight of capillary liquid in the disk above the linear boundary, like  $W_c$  but for the disk

 $W_{Tmax}$  = maximum weight of liquid on the sample obtained from the upper plateau (pore volume liq-

 $W_{C \text{max}} = \text{maximum}$  weight of liquid remaining at the contacts of the beads when all the bulk liquid has been centrifuged away. This weight is obtained from the lower plateau

 $W_{Ctot}$  = weight of liquid at the contacts of the beads  $(=W_C+W_{C'})$ 

#### **Greek Letters**

= surface tension of the liquid

= density of the liquid

= liquid-solid contact angle

#### LITERATURE CITED

Batel, W., "Menge und Verhalten der Zwischenraumflässigkeit in körnigen Stoffen," Chem. Ing. Tech. Z., 33, 541 (1961).

Fricke, G. H., D. Rosenthal, and G. A. Welford, "Wet Weights of Ion Exchange Resin Beads by Centrifugation," Anal. Chem., 43, 648 (1971).

Haruni, H. H., and J. A. Storrow, "Hydroextraction. V. Radial Distribution of Pressure in Homogeneous and Banded Cakes," Chem. Eng. Sci., 2, 108 (1953a).
—————, "Hydroextraction. VII. Residual Moisture in

Whizzed Cakes," ibid., 203 (1953b).

Hassler, G. L., and E. Brunner, "Measurement of Capillary Pressures in Small Core Samples," *Trans. A.I.M.E.*, 160, 114

Ksenzhek, O. S., E. A. Kalinovskii, S. A. Petrova, and V. I. Litvinova, "Centrifugal Method of Finding Pore-size Distribution Function in Porous Media," Russ. J. Phys. Chem., 41, 856 (1967).

Mayer, R. P., and R. A. Stowe, "Mercury Porosimetry: Filling of Toroidal Void Volume Following Breakthrough between Packed Spheres," J. Phys. Chem., 70, 3867 (1966). Nenninger, E., Jr., and J. A. Storrow, "Drainage of Packed

Beds in Gravitational and Centrifugal-Force Fields," AIChE J, 4, 305 (1958).

Princen, H. M., "Capillary Pheonomena in Assemblies of Parallel Cylinders. I. Capillary Rise between Two Cylinders," J. Colloid Interface Sci., 30, 69 (1969a).

-, "Capillary Phenomena in Assemblies of Parallel Cylin-

ders. II. Capillary Rise between Systems with More than

Two Cylinders," ibid., 359 (1969b).
Ritter, H. L., and L. C. Drake, "Pore-Size Distribution in Porous Media: Pressure Porosimeter and Determination of Complete Macropore-Size Distributions," Ind. Eng. Chem.

Anal. Ed., 17, 782 (1945).
Storrow, J. A., "Hydroextraction: Flow in Submerged Cakes,"
AIChE J., 3, 528 (1957).

Manuscript received August 10, 1971; revision received May 3, 1973, and accepted May 4, 1973.

## Combined Forced and Free Convection Flow Past a Horizontal Flat Plate

The problem of simultaneous forced and free convection flow of a Newtonian fluid past a hot or cold horizontal flat plate is investigated by means of numerical solutions of the full equations of motion and thermal energy subject only to the Boussinesq approximation. These solutions span the parameter ranges  $10 \le Re \le 100$ ,  $0.1 \le Pr \le 10$ , and  $-2.215 \le Gr/Re^{5/2} \le$ 2.215 where Re, Pr, and Gr are based on the ambient free stream fluid properties and the overall plate length l. When Gr > 0, the boundary flow near the plate surface is accelerated relative to the corresponding forced convection flow, with a resulting increase in both the local skin friction and heat transfer coefficients. When Gr < 0, the boundary flow is decelerated, the local skin friction and heat transfer are decreased, and the flow actually separates for  $Gr/Re^{5/2} < -0.8$  when Pr = 0.7. In the latter circumstance, an increasing degree of upstream influence is observed as  $Gr/Re^{5/2}$  is further decreased.

G. E. ROBERTSON J. H. SEINFELD and L. G. LEAL

**Department of Chemical Engineering** California Institute of Technology Pasadena, California 91109

#### **SCOPE**

The buoyancy effects induced by a hot or cold body can cause considerable deviations from the basic forced convection flow which would exist when the body and free stream fluid are at the same temperature. In some circumstances, such deviations may be of significance primarily because of the accompanying changes in the overall heat transfer rate; however, in general, one would be interested in a detailed understanding of the changes in flow structure, and a considerable body of literature has grown up in an attempt to achieve this goal. To date, the majority of this work has been concerned with the case in which a significant component of the buoyancy-induced body

Correspondence concerning this paper should be addressed to L. G.

force is either parallel or antiparallel with the direction of the undisturbed fluid motion [compare the work of Acrivos (1966), Merkin (1969), and others on the combined forced and free convection flow past a vertical flat plate].

In this work, we utilize numerical solutions of the full equations of motion and thermal energy, subject to the Boussinesq approximation, to consider the laminar, twodimensional flow of a Newtonian fluid past the upper surface of a hot or cold horizontal flat plate. The most significant previous investigations of this problem are the boundary-laver analyses of Sparrow and Minkowycz (1962) and Leal (1973a). In these papers, it is shown that the cross-stream buoyancy-induced body force acts effectively to produce a streamwise pressure gradient in the fluid adjacent to the plate surface: favorable, in the usual