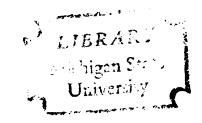
FLOW OF POLYVINYLPYRROLIDONE SOLUTIONS THROUGH PACKED BEDS

Thesis for the Degree of M. S. MICHIGAN STATE UNIVERSITY RAMADAS U. ACHARYA 1974





ABSTRACT

FLOW OF POLYVINYLPYRROLIDONE SOLUTIONS THROUGH PACKED BEDS

By

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The semi-theoretical Ergun equation is well established for flow of Newtonian fluids through packed beds. This definitive study provides a basis for analysis of effects of non-Newtonian fluid flow through packed beds and is based on data for aqueous solutions of Polyvinylpyrrolidone (PVP), which are viscous non-Newtonian fluids. A number of equations describing flow phenomena in packed beds are derivable for purely viscous non-Newtonian fluids; all of which reduce to the Blake-Kozeny form in the case of Newtonian fluids.

Meter's four parameter model was assumed to characterize the rheological behaviour of aqueous PVP solutions. The Meter's model analog of the Ergun equation was employed to correlate the pressure drop-flow rate data. Both numerical and analytical techniques were employed in this analysis. Packed bed pressure drop versus flow rate data were obtained for aqueous PVP solutions of concentration 0.5, 1.0, 3.0 and 4.0 percent by weight. It was concluded that the modified Ergun equation may be used to describe results for the 0.5 and 1.0 percent by weight PVP solutions. However, wide deviations between the experimental friction factor and those from the Ergun equation were observed for 3.0 and 4.0 percent solutions. It is speculated that this departure from the modified Ergun equation is a result of surface and viscoelastic effects. Modification in the capillary model may be needed to account for such effects. A comparative study between constant flow rate and constant pressure drop experiments is suggested in order to further resolve this matter.

FLOW OF POLYVINYLPYRROLIDONE SOLUTIONS

THROUGH PACKED BEDS

Βv

Ramadas U.dy Acharya

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NOMENCLATURE

= Column diameter = Particle diameter f expt = Experimental friction factor fcalc = Calculated friction factor G_{Ω} = Mass flow rate based on superficial velocity L = Bed length = Correction factor for wall effects $(N_{Re})_{eff}$ = Effective Reynolds number Q = Flow rate R = Radius = Hydraulic radius Rh = Shear stress when η drops down to $1/2(\eta_0 + \eta_{\infty})$ Tm = Shear stress = Wall shear stress v_z = Velocity = Average velocity ΔΡ = Pressure drop = Viscosity η = Viscosity at zero shear stress η_0 $\eta_{_{\boldsymbol{\varpi}}}$ = Viscosity at infinite shear stress = Porosity = Density = Wall shear rate

INTRODUCTION

A study of non-Newtonian fluid flow through porous media has wide applications in engineering science. Packed bed equations are very useful in individual problems such as industrial filtration of polymer solutions and slurries, movement of aqueous solutions through sand in secondary oil recovery, and design of packed bed reactors and towers. Furthermore, models proposed in the literature to describe non-Newtonian fluid behaviour have been tested in most cases only in relatively simple flow geometry. A test of these models for highly complex geometry of packed beds, for example, enhances the reliability and confidence in their application.

The most definitive study of flow of Newtonian fluids through porous medium appears to be that of Ergun [1]. Ergun's study provides a basis for similar analysis of non-Newtonian fluid flow. Good discussions of this analysis and extension of Ergun equation to viscous non-Newtonian fluids are provided by Bird et al.[2], Gaitonde et al.[3], Marshall et al.[4], Christopher et al.[5], Sadowski et al.[6], and Park et al.[7]. Different types of generalized methods to study this problem have been proposed. Aside from dimensional analysis, the main approach to this problem may be categorized as (1) generalized Darcy's law approach, (2) the capillary model combined with a particular rheological equation, or (3) the use of Newtonian equations containing an apparent viscosity evaluated at some appropriate average bed shear rate. So far,

the second approach has been most preferred. Bird, Sadowski, Marshall, Gaitonde, and Park are a few among those who used this approach selecting Ellis, Power law, Hershel Bulkley, Spriggs and Meter's rheological equations for a variety of polymer solutions.

The capillary model equation for flow in packed bed is a simplification since the actual flow involves fluids passing through irregular interstices between the particles. Deviations might be expected for non-Newtonian fluid flow through packed beds, due to frequent acceleration and deceleration. A literature survey indicated some evidence of viscoelastic effects and surface adsorption phenomena. Sadowski pointed this out and claimed to have observed viscoelastic and surface adsorption effects for aqueous polymer solutions. Marshall and Metzner also observed similar deviations and argued that the viscoelastic effect is the single cause of deviations. On the contrary, Christopher, Middleman, and Gaitonde, in similar studies of polymeric fluids, observed no such deviations, hence reported absence of viscoelastic effects. Christopher correlated Sadowski's data successfully with capillary model equation combined with Power law and surmised that Sadowski's conclusion is an artifact of his modification of Blake-Kozeny equation.

More recently Park et al. reported occurrence of viscoelastic effects for dilute polymeric solutions. In particular for PVP solutions departure from Ergun equation occurred at effective Reynolds number greater than one. It was noted that the deviations were larger for most dilute solution in contrast to the other polymeric solutions. The deviations decreased with an increase in concentration. Thus it was decided to investigate PVP solutions further and extend the data to higher Reynolds numbers.

The following assumptions were made in developing the capillary model equations for packed beds in this analysis:

- (1) The fluid is incompressible.
- (2) The porous medium is isotropic and of regular geometry.
- (3) Inertial terms from the equation of motion are deleted.
- (4) The fluid is homogeneous.

PACKED BED THEORY AND EQUATIONS

Analyses of non-Newtonian fluid flow through packed bed generally fall into three categories: (1) generalized scaleup, (2) the capillary model combined with a particular rheological equation, and (3) the use of Newtonian equation containing an apparent viscosity evaluated at some average bed shear rate. Approach (1) is an extension of Darcy's law and does not require a rheological model. Darcy's law simply states that for a given bed and Newtonian fluid, flow rate is proportional to the pressure drop. As discussed by Park et al.[7], the inherent complexities involved in the solution are quite cumbersome. The use of Newtonian equations containing an apparent viscosity evaluated at some appropriate average bed shear rate is not generally an acceptable solution, although it may turn out to be reliable for a particular solution. The second method as the choice made by the earlier workers, is both reasonable and supported by extensive experimental measurements. It is chosen as the basis for analyzing measurements of this study.

In the second method, the packed bed is regarded as a bundle of capillary tubes of complex cross sections and shape. The theory is then developed by applying the results of hydrodynamic analysis of straight tube to the collection of crooked capillaries. The tortuous shape of the capillaries is accommodated by making an appropriate correction to the length by a factor 25/12, as in the Newtonian case. Of course, it becomes necessary to make a suitable choice of rheological equation.

Apparently the choice is between a constitutive equation which describes viscoelastic or normal stress effects and equations describing purely viscous flow behaviour. An appropriate choice would be that one which fits the experimental viscometric data for all ranges of shear rate; at least in the range of average bed shear rate.

It has been shown that Meter's[8] model given below may be used to predict the non-Newtonian properties of the PVP solutions.

$$\eta = \eta_{\infty} + \frac{\eta_0 - \eta_{\infty}}{1 + \left| \frac{T}{T_{m}} \right|^{\alpha - 1}} \tag{1}$$

where $\eta = viscosity$,

 η_0, η_∞ = viscosities at shear rates approaching zero and infinity, T_m = shear rate when viscosity drops down to 1/2, and

 α = constant exponent.

Park[9] investigated this model for PVP solutions and determined the parameters η_{∞} , η_{0} , T_{m} and α . Table 6 contains the parameters for the relevant solutions. Equation (1) can be rewritten as:

$$\frac{\eta_0}{\eta} = \left[1 + \left|\frac{T}{T_m}\right|^{\alpha - 1}\right] \sum_{J=0}^{\infty} \left[-\left|\frac{T}{T_m}\right|^{\alpha - 1} \frac{\eta_{\infty}}{\eta_0}\right]^{J}$$
(2)

The equations derived in Appendix A based on the hydrodynamic analysis of the capillary model of the packed bed for Meter's model may be summarized as follows. The average velocity $V_{\mathbf{z}}$ through the available cross section for flow of the capillary is

$$\langle v_z \rangle = \frac{2R_h}{\eta_0 T_w^3} \int_0^w T_{rz} \left[\frac{1 + \left[\frac{T_{rz}}{T_m} \right]^{\alpha - 1}}{1 + \frac{\eta_\infty}{\eta_0} \left[\frac{T_{rz}}{T_m} \right]^{\alpha - 1}} \right] dT_{rz}$$
(3)

where $T_w = 2R_h \Delta P/2L$, shear stress at the wall of the capillary, $\Delta P = \text{pressure drop}$, and L = length of the bed.

The effective viscosity η_{eff} is:

$$\frac{1}{\eta_{eff}} = \frac{1}{\eta_{0}} \left[1 + \frac{2}{\alpha+1} \left(\frac{T_{w}^{*}}{T_{m}} \right)^{\alpha-1} - \frac{\eta_{\infty}}{\eta_{0}} \left(\frac{T_{w}^{*}}{T_{m}} \right)^{\alpha-1} \left\{ \frac{4}{\alpha+3} + \frac{2}{\alpha+1} \left(\frac{T_{w}^{*}}{T_{m}} \right)^{\alpha-1} \right\} + \left(\frac{\eta_{\infty}}{\eta_{0}} \right)^{2} \left(\frac{T_{w}^{*}}{T_{m}} \right)^{2\alpha-2} \left\{ \frac{2}{\alpha+1} + \frac{4}{3\alpha+1} \left(\frac{T_{w}^{*}}{T_{m}} \right)^{\alpha-1} \right\} + - + - - - \right]$$
(4)

where $T_w^* = 12 \text{ D}_p \Delta P / 25 \text{ 6M}(1-\varepsilon)L$, is a measure of wall shear stress in the bed. The effective viscosity so defined is useful only when $(\Pi_\omega/\Pi_0)^2 (T_w^*/T_m)^2 < 1$. When $(\Pi_\omega/\Pi_0)^2 (T_w^*/T_m)^2 \geq 1$, superficial velocity V_0 based on the column diameter, expressed as a product of average velocity and porosity ε ,

$$v_{0} = \varepsilon \langle v_{z} \rangle = \frac{\varepsilon^{2} R_{h}}{\eta_{0} T_{w}^{*3}} \int_{0}^{T_{w}} T_{rz}^{*} \left[\frac{1 + \left(\frac{T_{rz}}{T_{m}} \right)^{\alpha - 1}}{1 + \frac{\eta_{\infty}}{\eta_{0}} \left(\frac{T_{rz}}{T_{m}} \right)^{\alpha - 1}} \right] dT_{rz}$$
(5)

$$\eta_{\text{eff}} = \frac{\varepsilon^3 D_p^2 \Delta P}{150 M^2 (1-\varepsilon)^2 V_0}$$
 (6)

and

$$f = \frac{150(1-\epsilon)M\eta_{eff}}{D_pG_0}$$
 (7)

This result is good when the void fraction is less than 0.5 and is valid only in the region given by $D_pG_0/(1-\varepsilon)MN_{eff} < 10$, where $G_0 = \rho V_0$. For highly turbulent flow in packed beds the friction factor is a function of roughness only, and remains fairly constant and is,

$$f = 1.75 \tag{8}$$

Hence the modified Ergun equation as in Appendix A is:

$$\left[\frac{\rho \Delta P}{G_0^2 M}\right] \left[\frac{D_p}{L}\right] \left[\frac{\varepsilon^3}{1-\varepsilon}\right] = \frac{150}{\frac{D_p G_0}{(1-\varepsilon)M_{eff}}} + 1.75 \tag{9}$$

If we define

$$f_{expt} = \begin{bmatrix} \frac{\rho \triangle P}{G_0^2 M} \end{bmatrix} \begin{bmatrix} \frac{D_p}{L} \end{bmatrix} \begin{bmatrix} \frac{\epsilon^3}{1-\epsilon} \end{bmatrix}$$

and

f calc = 150 /
$$\frac{{}^{D}_{p}{}^{G}_{0}}{(1-\epsilon)M}$$
 + 1.75

it can be seen that in the low flow regions the logarithmic plot of $f_{\rm expt}$ vs. $(N_{\rm Re})_{\rm eff}$ will be a straight line with a slope of -1.

Equation (5) is numerically solved to obtain effective viscosity.

Appendix A contains the details and the techniques involved in the analysis. Hence in principle one can modify the capillary tube approach to account for departure from Newtonian flow. In this study the Meter's model equation for flow through a tube packed with spherical particles was applied.

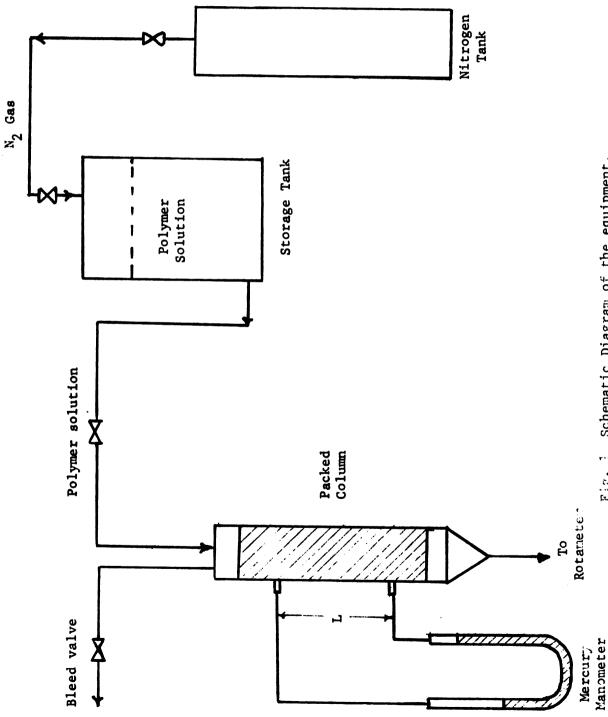
EXPERIMENTAL PROCEDURE

The schematic diagram (Figure 1) depicts the experimental set up. The equipment consisted of two glass columns of inner diameter 1 inch and 1/2 inch and spherical glass beads of average diameter 0.1621, 0.0597 and 0.0432 centimeters. Segments of glass columns are assembled together with aluminum flanges. Two stainless steel screens at either end contained the glass beads in the column. Extensive care is needed while packing to avoid any possible air entrapment. On either end, at least 6 inches of extra packing above the test section were provided to avoid end effects and foreign particles influencing the flow pattern in the test section. Two pre-calibrated rotameters for low and high flow rates respectively were used. "U" tube mercury manometers served to measure the pressure drop. The packed glass column and the tank containing the solution were immersed in constant temperature water jacket and bath respectively. Extreme care was taken to maintain the temperature at 21 + 0.5°C in the baths. Water was recirculated for the entire period in the bath and the jacket.

The average molecular weight of PVP (k-90) used was 360000.

Aqueous solutions of PVP of 0.5, 1.0, 3.0, 4.0 percent by weight were prepared in distilled water and filtered to avoid gel.

The solution was forced to flow through the bed by a constant nitrogen pressure in the tank. Prior to recording any data the solution was allowed to flow for some time until the refractive index of the



Schematic Diagram of the equipment.

solution matched with that of the sample. Constant flow rate and pressure drop were the indicators of steady state flow. Pressure drop and flow rate were measured simultaneously under steady state conditions.

The bed porosity was calculated from the packed bed data for distilled water by employing Ergun equation and known particle diameter before each run of solution. Only data for which $(N_{Re})_{eff}$ less than 10 have been used for such bed calibrations. Experimental data were obtained for water in the same range as that of the solutions.

RESULTS AND DISCUSSION

Results of the experiments are summarized in Figures 2 through 6 as a set of plots depicting the $f_{\rm expt}$ and $f_{\rm calc}$ vs. $(N_{\rm Re})_{\rm eff}$ for each aqueous solution. Effective viscosity vs. wall shear rate plots (Figure 7 and Figure 8) are presented to make further comparison and to gauge the usefulness of Ergun equation to predict viscosity of non-Newtonian fluids.

The Newtonian data presented in Figure 6 serves to calibrate the bed and technique. Figures 2 and 3 show the general agreement of 0.5 and 1.0 percent solutions and water with Ergun equation. This agreement is an indication of accuracy and consistency of sets of data. This was felt especially important in view of Park's[9] contrasting conclusions. Having observed greater deviations for 0.5 and 1.0 percent solutions, he concluded that the viscoelastic effects are significant above $(N_{Re})_{eff}$ equal to 1. The check between the Newtonian fluid and PVP solutions confirm no such viscoelastic effects. These results are consistent with those reported by Gaitonde et al. and Christopher et al. even though the flow regions are of considerably higher Reynolds number.

The data for 3.0 and 4.0 percent solutions when plotted (Figure 4 and Figure 5) fall well above the theoretical curve. In fact, the data fall on a line somewhat parallel to the theoretical curve. The ratio of the experimental values of friction factor and those given by the Ergun

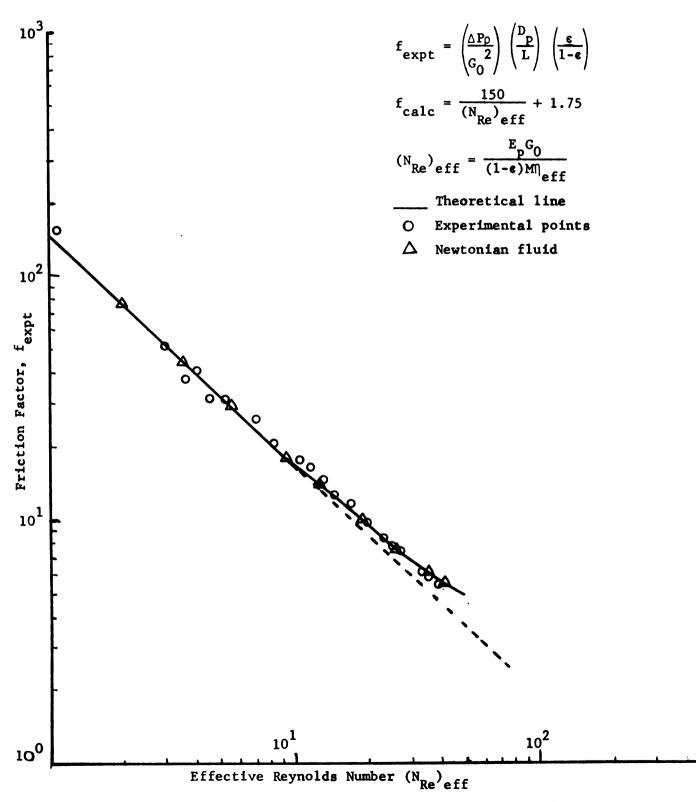


Figure 2. Pressure drop-flow rate correlation for flow of 0.5% PVP solutions Through packed beds.

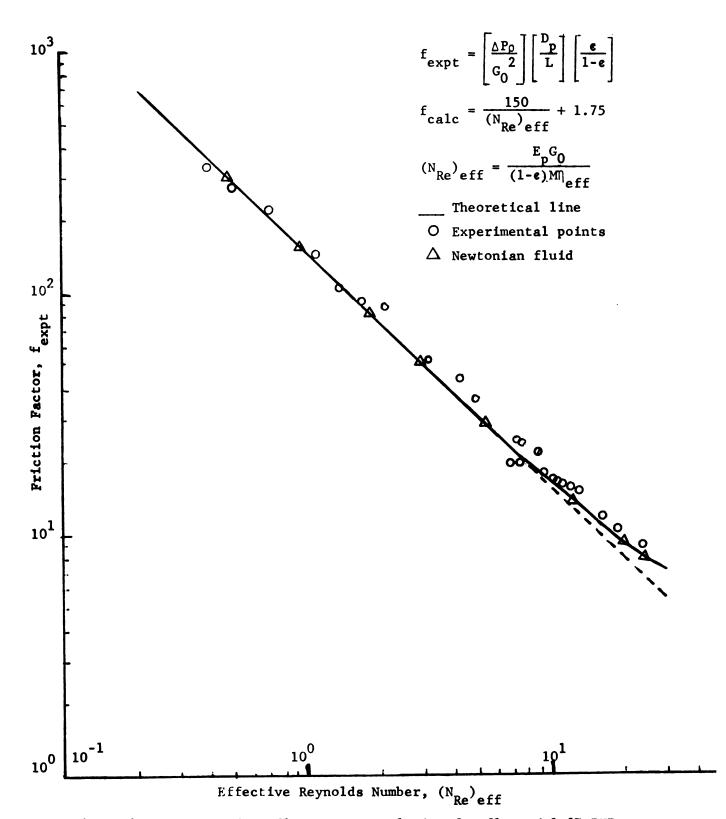


Figure 3. Pressure drop-flow rate correlation for flow of 1.0% PVP solution through packed beds.

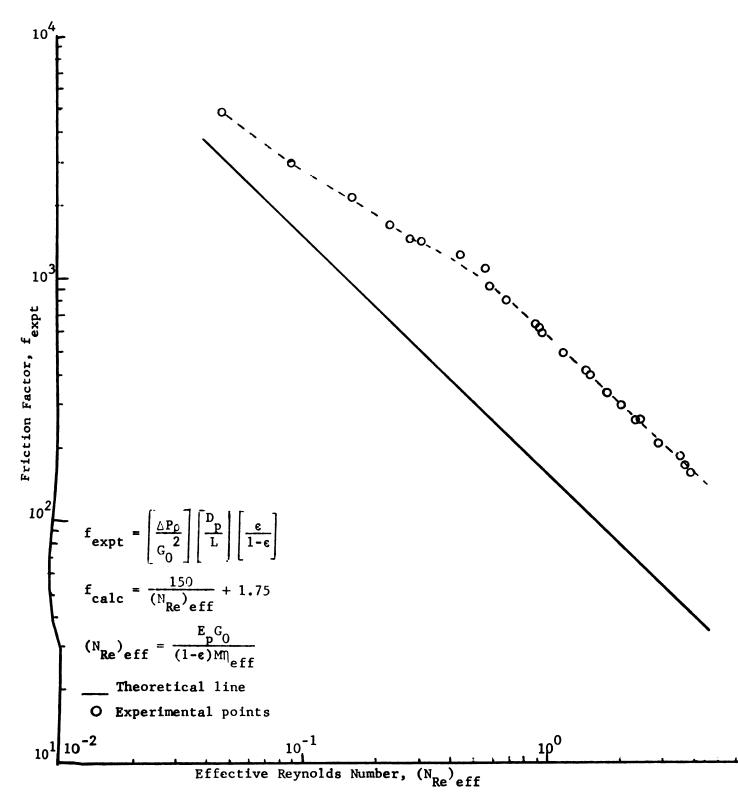


Figure 4. Pressure drop-flow rate correlation for flow of 3.01 PVP solutions through packed beds.

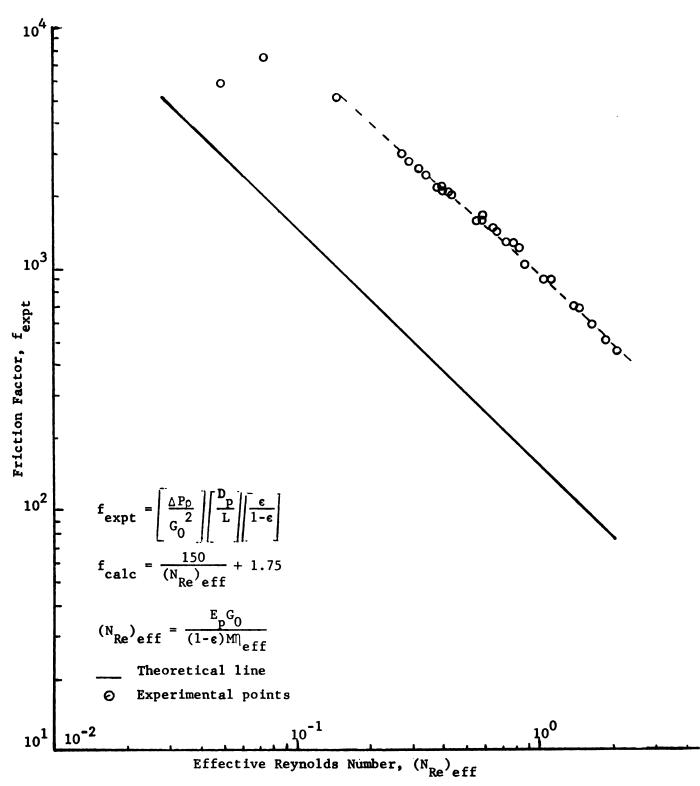


Figure 5. Pressure drop-flow rate correlation for flow of 4.0% PVP solution through packed beds.

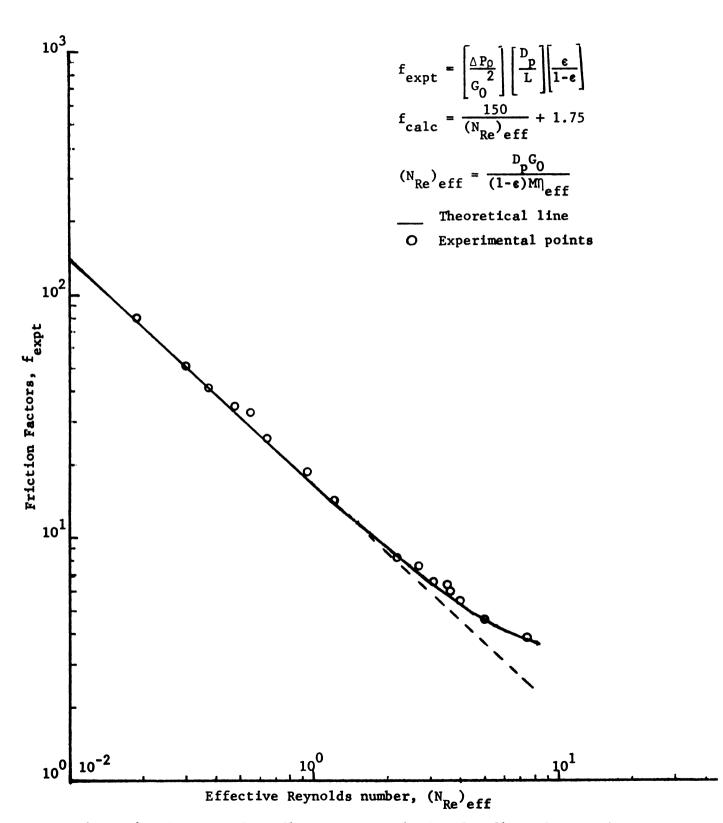
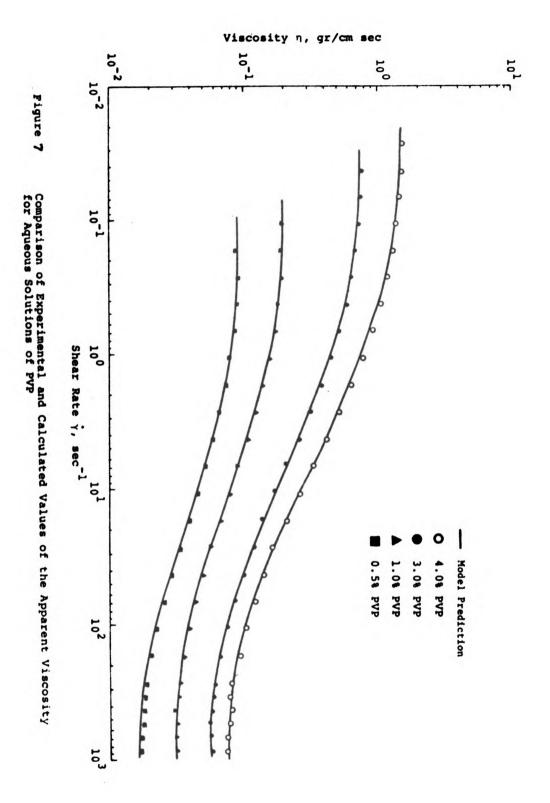


Figure 6. Pressure drop-flow rate correlation for flow of Newtonian fluid (water) through packed beds.



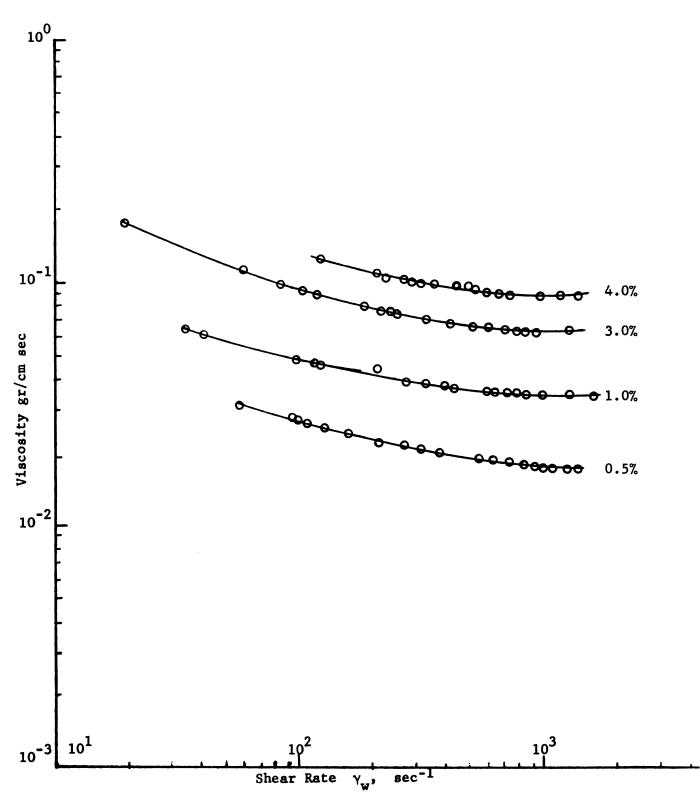


Figure 8. Model predicted values of viscosity and wall shear rate for aqueous solutions of PVP.

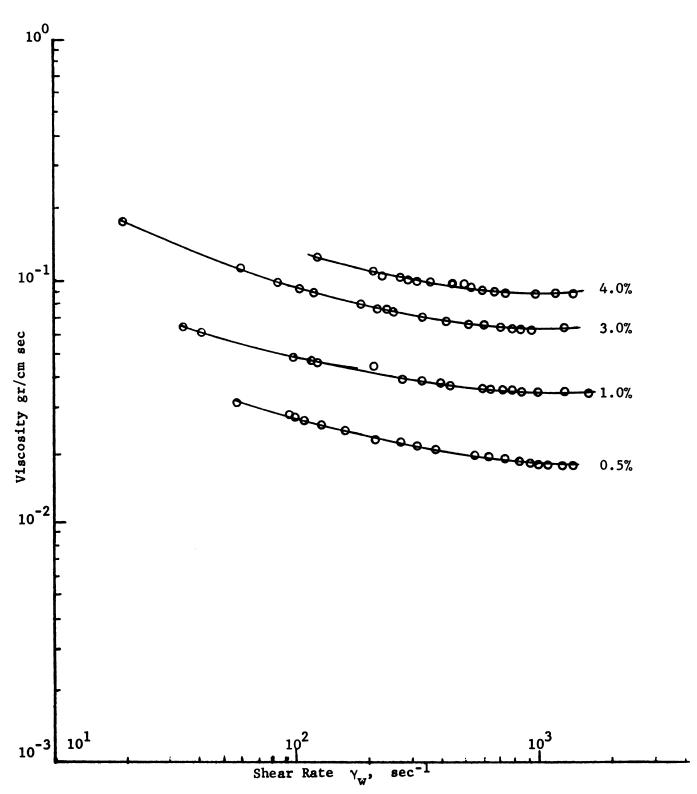


Figure 8. Model predicted values of viscosity and wall shear rate for aqueous solutions of PVP.

equation is as high as 4 for 3.0 percent solution and 6.5 for 4.0 percent solution. Sadowski, Marshall and Metzner also observed major departures from purely viscous fluid flow similar to those reported in Figures 4 and 5 for polymeric solutions. Sadowski, in his analysis of natrasol solutions, contended that the cause of such deviations are viscoelastic and surface adsorption phenomena. However, Christopher et al. correlated Sadowski's original data successfully with power law model equation in place of Ellis model equation used by the latter. Marshal and Metzner argued that the deviation in their case is only due to viscoelastic effect and ruled out surface adsorption.

The characteristic parameters for a fluid, Ellis and Deborah numbers only indicate the threshold value of the friction factor beyond which deviations appear. As compared to the prior investigations, the present study differs in the fact that the range of Reynolds number is very high. Marshall and Metzner showed that above Deborah numbers 0.1 to 1.0 the deviations might appear. The utility of such a number in this range of Reynolds number is not meaningful since either Ellis or Deborah number would be well above 1.

A qualitative discussion is presented below in an attempt to explain the deviations.

The theoretical analysis is based on the solution of viscometric flow problem (i.e., flow in a long straight circular tube). In such a flow no time dependent elastic effects are included or expected. In a porous medium the fluid moves through a tortuous path and it encounters constantly changing cross sections. The complexities in the bed subjects an elemental volume of a solution to continual acceleration and deceleration as it flows through the interstices. If the fluid relaxation time

 η/T_m is small with respect to the time required to go through a contraction or expansion V_0/D_p , the fluid will accommodate and no elastic effects would be observed. For example, Newtonian fluids accommodate quickly. On the other hand, if the relaxation time is large with respect to the time to go through a contraction or expansion, the fluid will not accommodate. As a result, the elastic effects cause deviation from the theoretical analysis.

Secondly, the surface effects arise as polymer molecules get adsorbed on a solid surface at multiple points of attachment. The remainder of the molecules extend more or less freely into the solvent and serve as additional points of attachment for an eventual gel formation. In a flow system, at the points of contact between the bed particles, a network of molecules may be formed. At the same time the flowing fluid constantly tends to remove adsorbed molecules from the surface. The cumulative effect is to decrease the bed permeability and a rise in pressure drop would be observed. The experimental friction factor values would be greater than the model predicted values.

Thus the viscoelastic and surface effects are the causes of deviations observed for 3.0 and 4.0 percent PVP solutions. From Figures 4 and 5 it appears as though the adsorption builds up as the flow rate increases (indicated by the increase in the observed friction factor) to a certain extent and tends to remain constant (indicated by the portion of the curve which is fairly parallel to the theoretical line). It is possible that this phenomena is due to constant flow rates. Although Marshall and Metzner ruled out adsorption, the implication to be drawn here is that neither one of the effects should be discarded from use in analysis. Two of the reasons sighted in discarding adsorption are that

the flows through the capillary tubes of comparable size revealed no such problems (Ueber 1964), and solution concentrations employed were chosen partly on considerations of optical clarity. The capillaries formed in the bed probably do not compare in the surface adsorption property with the straight capillary tubes of the same size, and the absence of adsorption on the straight capillary tubes for PVP solutions needs to be verified. The optical clarity of the solutions does not have much weight on surface adsorption.

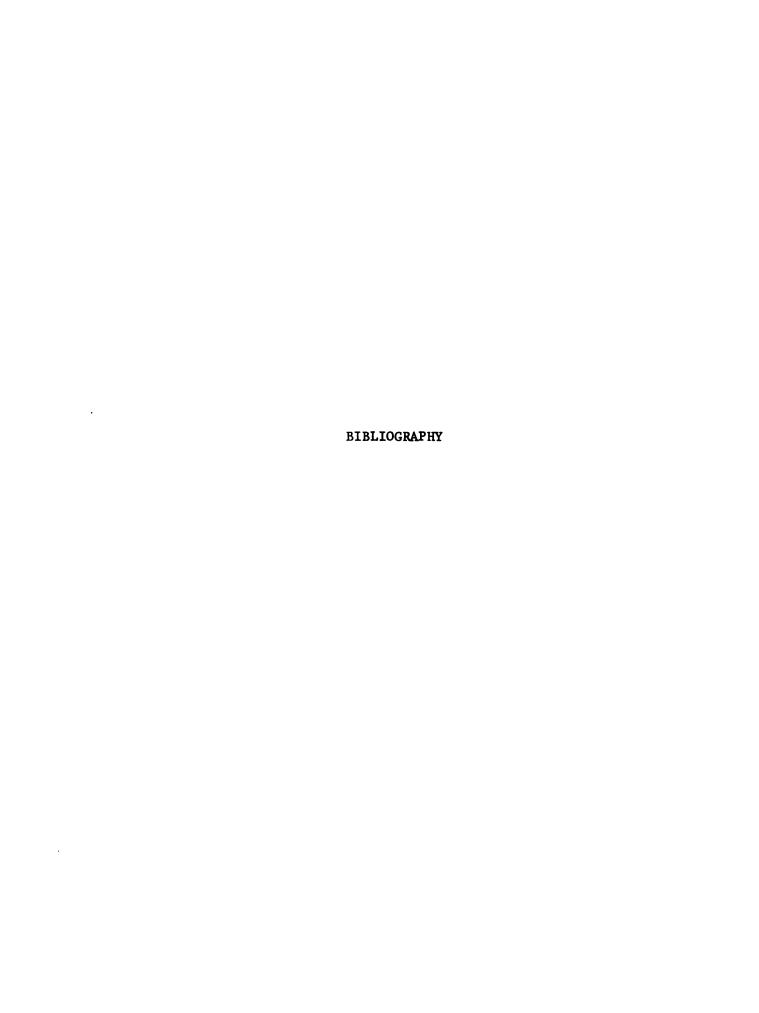
It is hardly possible to distinguish quantitatively the two effects separately. A test for this would be a comparison of constant flow rate experiments with the constant pressure drop experiments. In the constant pressure drop experiments, the formation of gel or adsorption decrease the flow rate. This decrease in flow rate further increases adsorption. In the absence of this phenomena the experiments are identical.

No attempt has been made to conduct constant pressure drop experiments and to correlate the surface effects quantitatively to Ergun equation. Present theoretical analysis does not include such effects and hence the equation fails to explain the data for 3.0 and 4.0 percent solutions. A thorough analysis supported by constant pressure drop and flow rate experiments is needed to accommodate the effects.

CONCLUSIONS

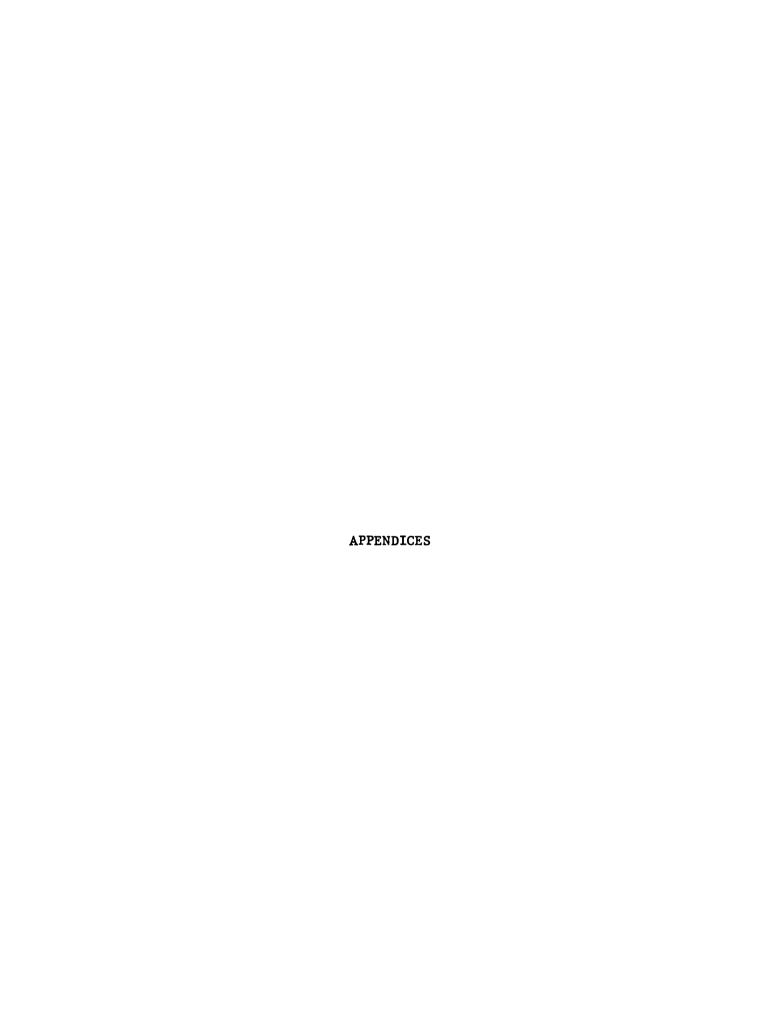
Results of the present investigation may be summarized as follows:

- 1. Modified Ergun equation may be used for 0.5 and 1.0 percent PVP solutions. No evidence of viscoelastic effects were observed.
- 2. For higher concentrations, i.e., 3.0 and 4.0 percent solutions, surface and viscoelastic effects were very significant. Large deviations between experimental values of friction factor and those from modified Ergun equation were observed.
- 3. Capillary model equation for packed bed needs further modification to account for viscoelastic and surface effects. A comparison between constant pressure drop and constant flow rate experiments is desired to account quantitatively the deviations.
- 4. A thorough investigation at low Reynolds number (below 0.5) may also be made for 3.0 and 4.0 percent solutions to determine the adsorption effects (viscoelastic effects are negligible in that range).



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APPENDIX A

PACKED BED THEORY AND EQUATIONS

1. Rheological equation for PVP solutions:

Polymers and polymer solutions exhibit the same general behaviour with regard to the non-Newtonian viscosity as a function of shear stress T. In the limit of very small shear stress the viscosity approaches a lower limiting viscosity η_0 . With increasing shear stress the viscosity η decreases, and if the shear stress can be increased sufficiently, the viscosity becomes constant at an upper limit η_∞ . Hence η_0 and η_∞ are measurable characteristic quantities of the fluid. Another measurable quantity is T_m , the shear stress when η drops down to $1/2(\eta_0 + \eta_\infty)$. Meter related these properties and suggested a model:

$$\eta = \tau_{|_{\infty}} + \frac{\tau_{|_{0}} - \eta_{|_{\infty}}}{1 + \left| \frac{T}{T_{m}} \right|^{\alpha - 1}}$$
(A-1)

where α = exponent (a constant). α indicates the abruptness of the transition from η_0 to η_∞ . η_0/T_m , η_∞/T_m are two characteristic times of the fluid. If η_∞ is much smaller than η_0 , Equation (A-1) can be rewritten as

$$\frac{1}{\eta} = \left[1 + \left|\frac{T}{T_{m}}\right|^{\alpha-1}\right] \sum_{J=0}^{\infty} \left[-\left|\frac{T}{T_{m}}\right|^{\alpha-1} (\eta_{\infty}/\eta_{0})\right]^{J}$$
(A-2)

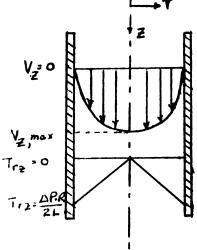
Park [9] studied extensively the rheological behavior of PVP solutions and determined the parameters conforming to Meter's model. The parameters are listed in Table 1.

2. Packed bed equations:

It will be shown that the packed bed equations for non-Newtonian fluids reduces to the Newtonian form of Blake - Kozney and Ergun equations. The following assumptions are made in the derivation of the relevent equations.

- 1. The fluid is incompressible.
- 2. The porous medium is isotropic and of regular geometry.
- 3. Inertial terms from the equation of motion are deleted.
- 4. Fluid is homogeneous.
- 5. Temperature is constant.

Consider the flow of non-Newtonian fluid through a circular tube of radius R.



Making a momentum balance over the shell of a thickness dr and length

L; the following differential equation is obtained.

$$\frac{d}{dr}(r T_{rz}) = (\frac{\Delta P}{L}) r \qquad (A-3)$$

where T_{rz} = shear stress, r = radius of the shell, and ΔP = pressure drop. Integrating,

$$T_{rz} = \frac{\Delta P}{2L} r + \frac{C}{r}$$
 (A-4)

The constant C must be zero if the momentum flux is not to be infinite at r=0. Hence

$$T_{rz} = \frac{\Delta P}{2L} r \qquad (A-5)$$

At the wall,

$$(T_{rz})_{r=R} = T_{w} = \frac{R\Delta P}{2L}$$
 (A-6)

$$T_{rz} = T_{w}(r/R) \tag{A-7}$$

It is assumed that (1) the fluid is in steady state laminar flow,

(2) the fluid is time independent, and (3) there is no slip between the fluid and the tube wall. The volumetric flow rate through the cylindrical shell of thickness dr and length L is

$$dQ = V_z 2\pi r dr (A-8)$$

where V_z = velocity at radius r.

$$Q = \pi \int_{0}^{R} V_{z} 2r dr$$

$$= \pi^{0} \int_{0}^{R} V_{z} d(r^{2})$$
(A-9)

Integrating by parts,

$$Q = \pi \left[V_z R^2 - \int_0^R r^2 dV_z \right]$$

 $v_{z_{r=R}} = 0$, hence

$$Q = -r \int_{0}^{R} r^{2} dV_{z}$$
 (A-10)

From equation (A-7)

$$r^{2} = \frac{R^{2}T_{rz}^{2}}{T_{w}^{2}} , dr = \frac{R}{T_{w}} dT_{rz}$$

Making these substitutions into equation (A-10),

$$Q = -\pi \int_{0}^{T_{w}} \frac{R^{2} T_{rz}^{2}}{T_{w}^{2}} \left(\frac{dV_{z}}{dr}\right) dT_{rz}$$

$$\langle V_{z} \rangle = \frac{Q}{\pi R^{2}} = -\frac{R}{T_{x}^{3}} \int_{0}^{T_{w}} T_{rz}^{2} \left(\frac{dV_{z}}{dr}\right) dT_{rz}$$
(A-11)

where $\langle V_z \rangle$ = average velocity. From Meter's equation,

$$-\frac{\mathrm{d}v_{z}}{\mathrm{d}r} = \frac{T_{rz}}{\eta_{\infty} + \frac{\eta_{0} - \eta_{\infty}}{1 + \left(\frac{T_{rz}}{T_{m}}\right)^{\alpha - 1}}} = T_{rz} \left[\frac{1 + \frac{T_{rz}}{T_{m}}}{1 + \frac{\eta_{\infty}}{\eta_{0}} \left(\frac{T_{rz}}{T_{m}}\right)^{\alpha - 1}} \right] \quad (A-12)$$

Hence

$$\langle V_{z} \rangle = \frac{\frac{R}{T_{w}^{3}}}{\frac{T}{W}} \int_{0}^{W} T_{rz}^{3} \left[\frac{1 + \left(\frac{T_{rz}}{T_{m}}\right)^{\alpha - 1}}{1 + \frac{\eta_{w}}{\eta_{0}} \left(\frac{T_{rz}}{T_{m}}\right)^{\alpha - 1}} \right] dT_{rz}$$
(A-13)

If $\eta_0 \gg \eta_\infty$, the denominator can be expressed in terms of powers of $(\eta_\infty/\eta_0)(T_{rz}/T_m)$. Equation (A-13) can be integrated analytically.

Analytical Technique:

$$\langle v_{z} \rangle = \frac{R}{T_{w}^{3}} \int_{0}^{w} T_{rz}^{3} \left[1 + \left(\frac{T_{rz}}{T_{m}} \right)^{\alpha - 1} \right] \left[\sum_{T=0}^{\infty} - \frac{\eta_{\infty}}{\eta_{0}} \left(\frac{T_{rz}}{T_{m}} \right)^{\alpha - 1} \right]^{J} dT_{rz} \quad (A-14)$$

Integrating term by term,

$$\langle v_{z} \rangle = \frac{R}{T_{w}^{3}} \left[\frac{T_{w}^{4}}{4} \left\{ 1 + \frac{4}{\alpha + 3} \left(\frac{T_{w}}{T_{m}} \right)^{\alpha - 1} - \frac{\eta_{\infty}}{\eta_{0}} \left(\frac{T_{w}}{T_{m}} \right)^{\alpha - 1} \right\} + \frac{2}{\alpha + 1} \left(\frac{T_{w}}{T_{m}} \right)^{\alpha - 1} \right\}$$

$$+ \left(\frac{\eta_{\infty}}{\eta_{0}} \right)^{2} \left(\frac{T_{w}}{T_{m}} \right)^{2\alpha - 2} \left\{ \frac{2}{\alpha + 1} + \frac{4}{3\alpha + 1} \left(\frac{T_{w}}{T_{m}} \right)^{\alpha - 1} \right\} + - + - + - \right\}$$

$$(A-15)$$

Imagine that the packed bed is a bundle of tubes of very complicated cross section with hydraulic radius R_h . The average velocity in the available cross section for flow in a single tube is:

$$\langle v_{z} \rangle = \frac{2R_{h}^{T}_{w}}{4\eta_{0}} \left[1 + \frac{4}{\alpha+3} \left(\frac{T_{w}}{T_{m}} \right)^{\alpha-1} - \frac{\eta_{\infty}}{\eta_{0}} \left(\frac{T_{w}}{T_{m}} \right)^{\alpha-1} \left\{ \frac{4}{\alpha+3} + \frac{2}{\alpha+1} \left(\frac{T_{w}}{T_{m}} \right)^{\alpha-1} \right\} + \left(\frac{\eta_{\infty}}{\eta_{0}} \right)^{2} \left(\frac{T_{w}}{T_{m}} \right)^{2\alpha-2} \left\{ \frac{2}{\alpha+1} + \frac{4}{3\alpha+1} \left(\frac{T_{w}}{T_{m}} \right)^{\alpha-1} \right\} + - + -$$
(A-16)

The hydraulic radius may be expressed in terms of the void fraction " ε " and the wetted surface "a" per unit volume of the bed in the following way.

where "a" is related to specific surface a_v (the total particle surface/the volume of the particle) by

$$a = a_v(1-\epsilon)$$

The quantity a defined in terms of the mean particle diameter D is

$$\mathbf{a}_{\mathbf{v}} = 6/\mathbf{p}$$

$$\mathbf{a} = \frac{6(1-\epsilon)}{\mathbf{p}}$$

$$\mathbf{a}_{\mathbf{h}} = \frac{\mathbf{p}_{\mathbf{p}}}{6(1-\epsilon)}$$
(A-17)

Mehta and Hawley [8] modified hydraulic radius for Newtonian fluid flow through packed bed as

$$R_{h} = \frac{\text{wetted surface of spheres + wetted surface of wall}}{\text{volume of bed}}$$

$$= \frac{\varepsilon}{\frac{6(1-\varepsilon)}{D_{p}} + \frac{4}{D_{c}}}$$

$$= \frac{\varepsilon}{\left[1 + \frac{4D_{p}}{6(1-\varepsilon)}\right]} 6(1-\varepsilon)$$

$$= \frac{\varepsilon D_{p}}{6(1-\varepsilon)M} \quad \text{where } M = \frac{4D_{p}}{6D_{c}(1-\varepsilon)} + 1$$

For packed beds the superficial velocity V_0 is given by

$$v_0 = \langle v_z \rangle \epsilon$$

substituting for R, T_w in (A-16),

A second assumption implicitly made in the foregoing development is that the path of the fluid going through in the bed is of length L; that is the same as the length of the bed. Actually, of course, the liquid traverses a very tortuous path, the length of which may be half again as long as the length L. For Newtonian fluids experimental measurements indicated the length be changed to 25/12 L. It is quite logical to assume the same value for non-Newtonian fluids. Insertion of this value into Equation (A-18) gives

$$V_{0} = \frac{\varepsilon^{3} D_{p}^{2} \Delta P}{150 \text{ m}^{2} (1 - \varepsilon)^{2} L \eta_{0}} \left[1 + \frac{4}{\alpha + 3} \left(\frac{T_{w}^{*}}{T_{m}} \right)^{\alpha - 1} - \frac{\eta_{\infty}}{\eta_{0}} \left(\frac{T_{w}^{*}}{T_{m}} \right)^{\alpha - 1} \right] \left\{ \frac{4}{\alpha + 3} + \frac{2}{\alpha + 1} \left(\frac{T_{w}^{*}}{T_{m}} \right)^{\alpha - 1} \right\} + \left(\frac{\eta_{\infty}}{\eta_{0}} \right)^{2} \left(\frac{T_{w}^{*}}{T_{m}} \right)^{2\alpha - 2} \left\{ \frac{2}{\alpha + 1} + \frac{4}{3\alpha + 1} \left(\frac{T_{w}^{*}}{T_{m}} \right)^{\alpha - 1} \right\} + - - \right]$$
(A-19)

where $T_{w}^{*} = 12 D_{p} \varepsilon \Delta P/25 6M(1-\varepsilon)L$. Equation (A-19) is Meter's model analog of Blake-Kozeny equation for Newtonian fluids; i.e.,

$$v_0 = \frac{\varepsilon^3 p_p^2 \Delta P}{150 \text{ M}^2 L (1-\varepsilon)^2 \eta_{eff}}$$
 (A-20)

where

$$\frac{1}{\eta_{eff}} = \frac{1}{\eta_{0}} \left[1 + \frac{4}{\alpha+3} \left(\frac{T_{w}^{*}}{T_{m}} \right)^{\alpha-1} - \frac{\eta_{\infty}}{\eta_{0}} \left(\frac{T_{w}^{*}}{T_{m}} \right)^{\alpha-1} \left\{ \frac{4}{\alpha+3} + \frac{2}{\alpha+1} \left(\frac{T_{w}^{*}}{T_{m}} \right)^{\alpha-1} \right\} + \left(\frac{\eta_{\infty}}{\eta_{0}} \right)^{2} \left(\frac{T_{w}^{*}}{T_{m}} \right)^{2\alpha-2} \left\{ \frac{2}{\alpha+1} + \frac{4}{3\alpha+1} \left(\frac{T_{w}^{*}}{T_{m}} \right)^{\alpha-1} \right\} + \dots - \dots \right] (A-21)$$

However Equation (A-19, (A-21) are applicable when

$$\left(\frac{\eta_{\infty}}{\eta_{0}}\right)^{2} \left(\frac{T_{w}^{*}}{T_{m}}\right)^{2} \leq 1$$

Numerical technique discussed later in this section solves this problem and has no bounds as above.

For highly turbulent flow, friction factor is only a function of roughness. For the flow of fluid through a bed of spheres, the pressure drop ΔP is given by

$$\Delta P = F/A \tag{A-22}$$

where F is the force exerted on the solid surface and A is the cross sectional area. The friction factor f, a dimensionless quantity, is also called a drag coefficient. It is approximately a constant at higher Reynolds numbers.

Consider the fluid flowing through a cylindrical tube as before.

The fluid will exert a force F on the solid surface which is equal to:

$$F = A' K f$$

where A' is the surface area of the column or the wetted surface, K is the kinetic energy per unit volume, and f is the friction factor; therefore,

$$K = \frac{1}{2} \varepsilon \left\langle V_z \right\rangle^2 ,$$

and
$$A^1 = 2\pi R L$$

$$F = (2\pi R L) \left(\frac{1}{2} \rho \left\langle V_z \right\rangle^2\right) f \qquad (A-23)$$

substituting for R in terms of hydraulic radius,

$$f = \frac{2R_h^{\Delta P}}{2L(\frac{1}{2} \rho \langle V_z^{\Delta} \rangle^2)}$$

Experimental data for Newtonian fluids indicated that:

$$6 f = 3.5$$

Hence

$$\frac{\Delta P}{L} = \frac{1.75 \rho (1-\epsilon) V_0^2}{\epsilon^3 D_p}$$
 (A-24)

Combining Equation (A-20 and Equation (A-24),

$$\frac{\Delta P}{L} = \frac{150 \, \eta_{eff} M^2 v_0 (1-\epsilon)^2}{D_p^2 \epsilon^3} + \frac{1.75 \, \rho (1-\epsilon) v_0^2 M}{\epsilon^3 D_p}$$
(A-25)

which is Ergun equation for non-Newtonian fluids. Rewriting in terms of G_0 , mass flow rate, and in the dimensionless groups:

$$\frac{\Delta P_0}{MG_0^2} \frac{D_p}{L} \frac{\epsilon^3}{1-\epsilon} = 150 \frac{M(1-\epsilon)}{\frac{D_p G_0}{\eta_{eff}}} + 1.75$$
(A-26)

and effective Reynolds number is:

$$(N_{Re})_{eff} = \frac{D_p G_0}{(1-\epsilon)M N_{eff}}$$
 (A-27)

Numerical Technique:

The Ergun equation so derived is only applicable when

$$(\eta_{\infty}/\eta_{0})^{2}(T_{w}^{*}/T_{m})^{2} \leq 1$$

A numerical integration of Equation (A-13) does not impose any such bounds on Ergun equation.

With proper substitution for R, T_w in Equation (A-13) gives

$$V_{z} = \frac{2\varepsilon D_{r}}{6M(1-\varepsilon)} T_{w}^{*3} \int_{0}^{T_{rz}} T_{rz}^{*3} \left[\frac{1 + \left(\frac{T_{rz}}{T_{m}}\right)^{\alpha-1}}{1 + \frac{\eta_{\infty}}{\eta_{0}} \left(\frac{T_{rz}}{T_{m}}\right)^{\alpha-1}} \right] dT_{rz}$$
 (A-28)

From Equation (A-20) and (A-28)

$$\eta_{\text{eff}} = \frac{\varepsilon^3 p_{\text{p}}^2 \Delta P}{150 \text{ M}^2 (1-\varepsilon)^2 [\langle V_{\rangle} \rangle \varepsilon]}$$
(A-29)

$$(N_{Re})_{eff} = \frac{D_p G_0}{M(1-\epsilon) \eta_{eff}}$$
 (A-30)

With these two definitions Ergun equation is versatile and is applicable at all ranges.

The method involves application of Simpson's three point integration formula. The salient feature of the computer program is the Subroutine Sizsimp which divides the intervals 'n' number of times and applies Simpson's rule over each interval. This is repeated until Abs. $(\langle V_z \rangle |_{n} - V_{z-n-1}) < 10^{-10}$.

APPENDIX B

FLOW RATE-PRESSURE DROP DATA FROM EXPERIMENTS AND COMPUTER PROGRAM

TABLE - 1 . CONSTANT FLOW PATE EXPERIMENTAL DATA FOR WATER AT 21°C

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.50 PERCENT PVP SOLUTIONS AT 21°C TABLE - 2 . CONSTART FLOW MATE EMPEMPENTAL DATA FOR

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CONSTANT FLOW MATE EXPERIMENTAL MATA FOR 1.40 PERCENT PVP SOLUTIONS AT 21 C

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TAMEN - A . CONSTANT FLOW MATE EXMEMIMENTAL DATA FOR 3.09 PERCENT PVM SULUTIONS AT 21 C

BED PROPERTIES AND MODEL PARAMETERS

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TABLE - 5 . CONSTANT FLUW RATE EXPERIMENTAL DATA FOR 4.00 PERCENT PVP SOLUTIONS AT 210 C

BED PROPERTIES AND MODEL PARAMETERS

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TABLE 6

METER MODEL PARAMETERS FOR PVP SOLUTIONS AS OBTAINED FROM A WEISSENBERG RHEOGONIOMETER AT 21°C

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                                                                                                                                                                                                                                                                                                                                10 503
                                                                                                                                # FURTAL (2F10.0) GO TO PIGHT = 0.00 GO TO PIGHT = 
HE 10 4. 17:13:00
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SUHROUTINE MNODEL (PD-EPS-DP-M-AL-E1-E0-A-TM-RH-DVZDR-ETA-TW-IPDEX+
                                                                                                                                                                    |NOLX = "
|E = {|2.6/25.0| * (DP/6./M) * (EPS/(1.-EPS)) * (PI)/AL)
| = E1/E|
                                                                                                                                                                                                                                                                                                                              عرا
                                                                                                                                                                                                                                                                                             STICK OUT THE SIZSIMP (S-SI-SZ-53-S4-55-A4S)
ACC = 1 * -10
SUCT = 3.0 * SIMZ=0.0 $ ANS=0.0 $ ANSI=0.0
N2 = (SI = S+ H2
N2 = 12 * N2
N0 4 K=1.8
N0 4 K=1.8
N0 5 I=1.3.2
X = $ + H* (I-1)
                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                    F (ABS (ANS-ANSI).LE.ACC) 60 TO 18
                                                                                                                                                                                                                                           = (14/14) + + (4-1.)

= (14+43+(1.+C))/EC/(1.+U+C)
                                                                        C = (TWZTM) **(A-1.)
DVZDR = FTU(TW.A.TM.D.E0)/TW**2
CD = C*D
                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                       COHOCONIONATION DE NOTATION DE
                                                                                                                                                                                                                                                                                                                                                                                                                                                                                               FX = FTW(X+52+S3+S4+55)
SUM2 = SUM2 + FX+(4-J+1)
CONTINUE
                                                                                                                                                                                                                                                                                                                                                                                                                       FX = F18 (X,52)
SC*1 = S*181 +
                   (NZV.0HH
                                                                                                                                                                                                                                                                                                                                             7
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