Non-Newtonian Flow in Porous Media

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This paper describes a preliminary study of the linear flow of a non-Newtonian fluid, a water solution of Dextran (a polysaccharide), in porous media. A modification of Darcy's law, which uses capillary rheology data, is developed to describe non-Newtonian flow in underground reservoirs. The generalization, in effect, replaces the porous media with a capillary of equivalent radius proportional to the square root of the ratio of permeability to porosity. The constant of proportionality α_0 should be independent of permeability and porosity for a given type of rock. This has been partially confirmed experimentally. In principle, a capillary rheogram and a single core test permit evaluation of α_0. Then non-Newtonian flow can be predicted in this type of rock regardless of porosity, permeability, or flow rate.

The flow of a Newtonian fluid (a fluid with a constant viscosity) through porous media is in good agreement with Darcy's law as expressed by Equation (1) with gravitational forces neglected.

$$V_o = -\frac{k}{\mu}\nabla p \qquad (1)$$

where V_o is the fluid superficial velocity vector, ∇p is the pressure gradient, μ is the fluid viscosity, and k, a property of the structure of the porous medium, is the permeability with consistent units of squared length. In the petroleum industry, it is customary to measure V_o in cm./sec., μ in centipoise, and ∇p in atm./cm. with the resulting units of k called the darcy. The conversion is 1 darcy = 9.87×10^{-9} sq. cm. This paper describes an extension of Darcy's equation (1) to the case in which the fluid does not follow Newton's law of a constant viscosity (ratio of shear stress to deformation rate); rather, the fluid belongs to a class called Stokesian fluids in the literature (*1*). Such fluids have the property that the nonhydrostatic components of the fluid stress are unique nonlinear functions of the deformation rate components with the result that the measured "viscosity" varies with the shear stress prevailing in the viscometer. The bulk of the paper develops a one-dimensional theory and compares it with preliminary experimental results for an aqueous solution of a sugar polymer available commercially under the trade name Dextran. The model is developed by direct analogy with the results obtained for flow of the fluid through a uniform capillary and utilizes the rheogram obtained from the latter. A two-dimensional analysis, not given here, showed that the dispersive or nonaxial component of the velocity enters the flow equation only as a product with an unknown normal coefficient of viscosity. It should also be pointed out that our choice of the model was guided by two restrictions: (1) The model must give good predictions over a wide shear stress range, and (2) the model must be in a form suitable for routine calculations. The first restriction eliminates some of the stress-deformation rate relations proposed in the literature for Stokesian fluids such as the power law model; the second eliminates others such as the Eyring model.

Finally, the flow of non-Newtonian fluids in porous media is important to the petroleum industry during drilling and secondary recovery operations.

THEORY

The shear stress $\sigma(r)$ resisting the steady motion of a fluid through a uniform capillary and at a radius r is given by a force balance as

$$\sigma(r) = -\frac{r}{2}\frac{\Delta p}{L} \qquad (2)$$

where $\Delta p/L$ is the pressure gradient over the length L of the capillary. The equation of momentum conservation for steady flow gives the result (2)

$$\sigma(r) = \psi_1 \frac{du}{dr} \qquad (3)$$

where u is the velocity at radius r and ψ_1 is an unknown function of the argument $\left(\frac{du}{dr}\right)^2$. From (2) and (3), we have for the velocity distribution

$$\psi_1 \left\{ \left(\frac{du}{dr}\right)^2 \right\} \frac{du}{dr} = -\frac{r}{2}\frac{\Delta p}{L} \qquad (4)$$

From Equation (4) with ψ_1 assumed to be a constant equal to the viscosity μ, we arrive after two integrations at Poiseuille's law for the volumetric flow rate Q of a Newtonian fluid through a capillary of uniform radius R

$$Q = \frac{\pi R^4}{8\mu}\frac{\Delta p}{L} \qquad (5)$$

For arbitrary ψ_1, we see from Equation (4) that du/dr and hence ψ_1 are unique functions of $\sigma(r) = \frac{r\Delta p}{2L}$. With this observation two integrations of equation (4) give with $x = \frac{r}{R}$

$$Q = \frac{\pi R^4}{8}\frac{\Delta p}{L}\int_0^1 \frac{4x^3}{\psi_1}dx = \frac{\pi R^4}{8\mu(\sigma_R)}\frac{\Delta p}{L} \qquad (6)$$

Here, $\mu(\sigma_R)$ is an "apparent" viscosity under the shear stress prevailing at the capillary wall, $\sigma_R = \frac{R\Delta p}{2L}$. If desired, the true shear viscosity may be determined from the apparent viscosity by means of the Mooney-Rabinowitsch equation. In its given form Equation (6) provides a well-known means of measuring $\mu(\sigma_R)$ from

$$\mu(\sigma_R) = (R\Delta p)(2L)/(4Q)(\pi R^3) \qquad (7)$$

It is convenient to introduce a dimensionless viscosity ratio $F(\sigma_R)$ as

$$F(\sigma_R) = \frac{\mu_o}{\mu(\sigma_R)} \tag{8}$$

where μ_o is the apparent viscosity at some convenient reference stress σ_o. Then Equation (6) becomes

$$Q = F(\sigma_R) \frac{\pi R^4}{8\mu_o} \frac{\Delta p}{L} \tag{9}$$

We now wish to point out an analogy between Darcy's law and Poiseuille's law. For steady flow in a uniform capillary, Equation (5) for a Newtonian fluid gives for the average velocity $V = Q/A$

$$V = \frac{1}{2}\left(\frac{R}{2}\right)^2 \frac{\Delta p}{\mu L} \tag{10}$$

while Darcy's law (1) gives the average pore velocity $V = \dfrac{V_o}{\varphi}$ in one-dimensional flow as

$$V = \frac{k}{\varphi} \frac{\Delta p}{\mu L} \tag{11}$$

where φ is the effective porosity of the medium. These two equations give the analogy

$$\frac{k}{\varphi} \sim \frac{1}{2}\left(\frac{R}{2}\right)^2 \text{ or } R \sim \sqrt{\frac{k}{\varphi}} \tag{12}$$

Progressing to non-Newtonian fluids, we see that Equation (9) for the capillary gives

$$V = F\left(\frac{R\Delta p}{2L}\right) \frac{1}{2}\left(\frac{R}{2}\right)^2 \frac{\Delta p}{\mu_o L} \tag{13}$$

If we apply the analogy (12) to the result (13), with $V_o = \varphi V$ it becomes

$$V_o = F\left(\frac{R_{EQ}\Delta p}{2TL}\right) k \frac{\Delta p}{\mu_o L} \tag{14}$$

where R_{EQ} is an equivalent pore radius for the porous material and T is the tortuosity of the media, that is, the ratio of the actual length of flow path to the length of the linear core L. By using the analogy of Equation (12), we can write

$$\frac{R_{EQ}}{2T} = \alpha_o \sqrt{\frac{k}{\varphi}} \tag{15}$$

where α_o is a constant for a particular type of porous material reflecting the pore size distribution and the tortuosity of the pores in the medium. If we define a shear stress for the porous medium σ_k as

$$\sigma_k = \alpha_o \sqrt{\frac{k}{\varphi}} \frac{\Delta p}{L} \tag{16}$$

then the modified form of Darcy's law for Stokesian fluids is

$$Q = F(\sigma_k) \frac{kA}{\mu_o} \frac{\Delta p}{L} \tag{17}$$

where $Q = VA$ is the volumetric flow rate across facial area A. In terms of an apparent viscosity, μ, Equation (17) is

$$Q = \frac{kA}{\mu(\sigma_k)} \frac{\Delta p}{L} \tag{18}$$

According to our model, which assumes that a porous media can be treated as a capillary of equivalent radius given by Equation (15), the function F is the same in both Equations (9) and (17) for the capillary and porous core, respectively. Consequently, if a Newtonian fluid is used to determine the permeability k of a core, that is, to calibrate the core, then the capillary equation (9) and the core equation (18) together afford two independent methods of determining rheograms of μ vs. σ for the non-Newtonian fluid which differ only in the scale of shear stress σ. Accordingly, a proper choice of the constant α_o should bring the two rheograms into superposition. This is the method which we use to test experimentally the modified Darcy equation (17) or Equation (18).

EXPERIMENTAL

The experimental program to verify the proposed rate equation (18) had the twofold objective of first demonstrating that a rheogram determined from a linear core of porous material can be superimposed upon the rheogram as determined from capillary measurements, and second of establishing that the constant α_o is independent of the permeability and the porosity for a particular type of porous material. We have carried out the first part of this program, but can only offer partial substantiation for our second claim.

The apparent viscosity $\mu(\sigma_R)$ was determined for a brine solution of Dextran (1.5 wt. % dissolved in the brine produced from a sandstone reservoir) with a capillary 255 cm. in length and with a nominal diameter of ½ mm. This capillary was calibrated with aqueous solutions of glycerine and was submerged in a water bath at 25°C. The averages of three replications are shown as the solid points in Figure 1 where the dimensionless viscosity ratio $F(\sigma_R)$ is plotted against wall shear stress $\sigma_R = \dfrac{R\Delta p}{2L}$ in lb.$_f$/sq. in. A reference viscosity of $\mu_o = 9.60$ cp. was used to plot Figure 1. An independent set of measurements at low shear stresses was made with an Ubbelohde viscometer. These are shown as open circles in the figure. The shear stress range is sufficient to show the asymptotic approach to Newtonian behavior at low and high shear stresses.

For the porous medium, a cylindrical core of sandstone from the same reservoir as the brine with a length of 15 cm., a porosity of $\varphi = 0.25$, and a permeability $k = 305$ millidarcies was sealed with Babbitt metal in a metal casing. The center 6-cm. section of this core served as our viscometer. By measuring the pressure drop across the section and the flow rate of Dextran through the core, we can use Equation (17) to calculate the product $kF(\sigma_k)$. The averages of three randomly performed replications determining this product are plotted as a function of the pressure gradient across the test section in Figure 2 where the functional similarity to the results of Figure 1 is immediately apparent. It is worth mentioning that the approach of the core to steady state conditions is slow indeed at the low pressure gradients with as long as 10 hr. being required before the pressures stabilize.

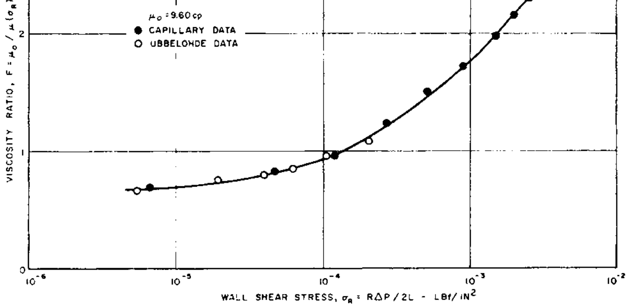

Fig. 1. Apparent viscosity shear stress capillary rheogram for 1.5% Dextran in brine.

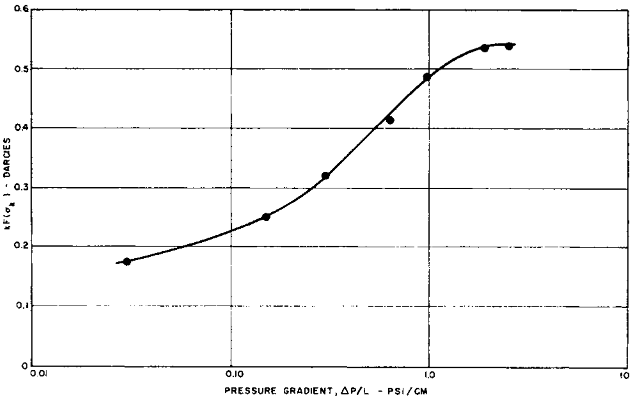

Fig. 2. Rheogram of a 1.5% (weight) solution of Dextran in brine as determined by a sandstone core.

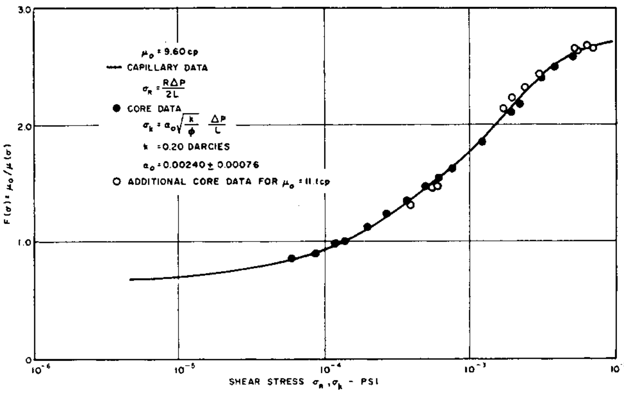

Fig. 3. Superposition of capillary and core rheograms.

Since Dextran is a polymer of reasonably large molecular weight, we had anticipated that the sandstone core would tend to filter the solution and in turn, to be plugged by the Dextran. For this reason, all the Dextran solution used in the entire program was prefiltered through a section of the same sandstone as the test section. Still, over the long period required to determine the data of Figure 2, a gradual buildup of pressure across the first section of the core indicated plugging. The initial permeability of the center test section to brine was 291 millidarcies. After the test program, this permeability had decreased to 142 millidarcies, presumably due to plugging. Consequently, the value of k to use in determining $F(\sigma_k)$ from the core data is not known precisely; rather, the range of k, 0.142 to 0.291 darcies, is all that is known. The following procedure was employed to superimpose the data of Figures 1 and 2. A value of k was assumed and numerical values of $F(\sigma_k)$ were calculated for points over the range covered by Figure 2. The shear stresses σ necessary to give these values of F could then be obtained from the capillary curve of Figure 1. From Equation (16) for σ_k, the respective value of α_o was calculated for each of the points.

A maximum range of superposition of the two curves with a minimum variation in α_o was used as a criterion of fit. This criterion was very sensitive to the choice of k as is shown in Table 1.

The range of superposition of the two curves increased twentyfold and the variation in α_o decreased seventyfold as k was increased from 0.100 to 0.200 darcies. Further increase in k left the range the same but increased the standard deviation in α_o. The values chosen as representing the best superposition were then $k_o = 0.2$ darcies, $\alpha_o = 0.00240 \pm 0.00076$ cm./darcy$^{1/2}$. The superposition is shown graphically in Figure 3 where the solid line is the capillary rheogram of Figure 1 and the solid points are from the core curve of Figure 2. Several months later, further measurements were made on the core with a Dextran solution whose reference viscosity (at standard laboratory conditions) was $\mu_o = 11.1$ cp. These data are shown in Figure 3 as open circles.

The experimental data given above demonstrate that the one-dimensional theory presented earlier is sufficient for one particular type of porous media and one type of Stokesian fluid at one permeability level. We have not conducted an extensive program to determine whether or not the numerical value of α_o is affected by the level of permeability. However, we do have available numerous results from routine flow measurements of 1.5% solutions of Dextran through sandstone from the same formation as that used in this study but with varying permeabilities. The permeabilities of these samples to brine range from 110 to 1,250 millidarcies. By using the same ratio of superposition permeability to initial permeability brine as determined in this study, namely $k_o/k = 0.20/0.291 = 0.687$, we have compared what our theory would predict for the flow rates with the observed flow rates in Figure 4. The dashed lines show the possible variation resulting from the probable error in α_o, although the assumption of a superposition permeability as indicated above is probably the cause of the major portion of the deviation.

The above program, both analytical and experimental, is incomplete to the extent that the theory is one-dimensional and that the experimental interpretation is clouded by plugging problems.

TABLE 1. SUPERPOSITION OF CAPILLARY AND CORE RHEOGRAMS

Selected value of k, darcies	Av. value of α_o, cm./darcy$^{1/2}$	Standard deviation, α_o	Shear stress range, lb./sq. in.
0.100	0.0468	0.07330	0.001 to 0.01
0.140	0.01160	0.01200	0.0002 to 0.01
0.180	0.00452	0.00498	0.0001 to 0.01
0.200	0.00238	0.00112	0.00005 to 0.01
0.205	0.00212	0.00235	0.00005 to 0.01

CONCLUSION

It is shown that a modified form of Darcy's law as given in Equation (19)

$$V = -F(\sigma)\,\frac{k\nabla p}{\mu_o} \tag{19}$$

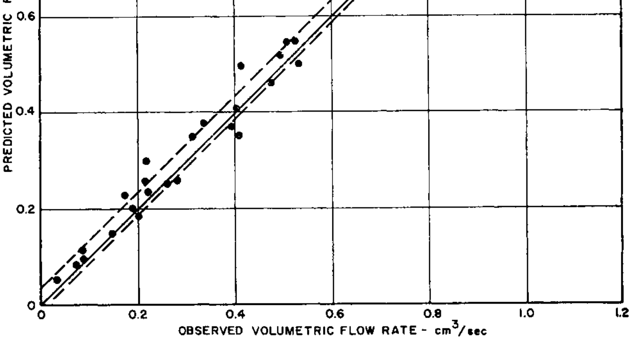

Fig. 4. Comparison of theory with routine measurements of the flow rate of 1.5 wt. % Dextran through sandstone cores of various permeabilities.

where

$$\sigma = \alpha_o \sqrt{\frac{k}{\varphi}}\,|\nabla p|$$

may be useful for calculating the flow of a non-Newtonian fluid through porous media. Here, the dimensionless viscosity ratio $F(\sigma)$ is determined from capillary measurements and the constant α_o from a few measurements on linear cores for each rock type. (In principle, a single measurement is sufficient.)

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Ideas similar to those presented here but not available at the time have been given by T. J. Sadowski (*3*) and Stanley Middleman (*4*) where specific rheological models are assumed for the non-Newtonian fluid.

NOTATION

k = permeability, millidarcies
k_o = superposition permeability, millidarcies
p = pressure, atm.
r = radius, cm.
v = velocity, cm./sec.
A = area, sq. cm.
F = dimensionless viscosity ratio
L = length, cm.
Q = volumetric flow rate, cc./sec.
R = capillary radius, cm.
V = average pore velocity, cm./sec.
V_o = fluid superficial velocity, cm./sec.
α_o = superposition constant, cm./millidarcies$^{1/2}$
φ = porosity
σ = shear stress, g./sq. cm., lb./sq. in.
μ = viscosity, cp.
$\mu(\sigma_R)$ = apparent or tube average viscosity, cp.
μ_o = apparent viscosity (cp.) at a given reference value of shear stress

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The Influence of Surface Coverage on Catalytic Effectiveness and Selectivity. The Isothermal and Nonisothermal Cases

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Both nonisothermal and isothermal catalytic effectiveness factors are computed for kinetic rate laws of the Langmuir-Hinshelwood, Hougen-Watson type, involving surface coverage by reactant and products. Selectivity taxation is also treated and the significant influence of interphase heat and mass gradients surrounding the catalyst is displayed. The complexities of these real kinetic systems suggest caution in the use of prior generalizations based upon simpler rate laws.

Many analytical and numerical solutions have been set forth to assess quantitatively the influence of intraparticle heat and mass diffusion upon catalytic activity (*1, 3, 5* to *18*) and selectivity (*1, 3, 4, 11, 16, 18*). While isothermal effectiveness and selectivity alteration are readily determined for linear kinetics by analytical means, nonlinear kinetic schemes and nonisothermality within the catalyst have required approximate solution or digital/analog simulation. It appears, however, that the most typical form of the catalytic rate law, that of Langmuir-Hinshelwood as elaborated, extended, and refined by Hougen and Watson, has not received attention commensurate with its prominence.

Implicit in the Langmuir-Hinshelwood, Hougen-Watson (L-H, H-W) model* is the notion of surface coverage by reactants and/or products, which coverage is essential to reaction. Clearly, simple first-order kinetics prevail for the reaction $C \rightarrow P$ when surface coverage by reactant and product is small, that is

$$\theta = \frac{K_1C}{[1 + K_1C + K_pP]} \rightarrow K_1C \text{ for } 1 >> K_1C + K_pP$$

then rate $= k\theta = kK_1C$.

Under these circumstances the isothermal effectiveness as well as the nonisothermal event is predictable in the light of prior work. However, while K_p may be large, yet

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* We are not defending the intrinsic reality of L-H, H-W implications, but merely recognizing its qualitative merit in the sense that Boudart has suggested.

James J. Carberry is at the University of Cambridge, Cambridge, England (1965-66).