Viscoelastic Behavior of Molten Polymers in Porous Media

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The modification of the Blake-Kozeny equation for porous media flow using the power law has been shown to hold for molten polymers as well as for the previous cases for polymer solutions. The present work extended the correlation of friction factor with Reynolds number an additional three decades.

It was also shown, however, that the modified Blake-Kozeny equation broke down when bed shear rates were in the range of excessive curvature on the polymer flow curves (shear stress-shear rate). In such cases it is suggested that the Newtonian Blake-Kozeny equation, together with apparent viscosity data, could be used to correlate such porous media flow of non-Newtonians.

Appearance of viscoelastic effects at the critical Deborah number value of 0.05 predicted earlier were not found to hold. The data of the present investigation show that such a critical value must be at least 0.19 or even higher. This result helps to resolve partially the anomalous results obtained by previous investigators.

The flow of non-Newtonian fluids through porous media constitutes an important segment of many industrial processes. For example, such flows are encountered in secondary oil well recovery systems. In addition, they can also be found in actual and proposed mineral in situ recovery processes for oil shale, tar sands, and various ores. One other important situation is that present in most polymer processing operations: the flow of molten polymers through screen or sand packs.

The open literature was essentially devoid of any studies on the flow of non-Newtonians in porous media until recently. During the past few years a number of such investigations have appeared. These have included the work of Bird and Sadowski (*1*), Sadowski (*2, 3*), Middleman (*4, 5*), McKinley and co-workers (*6*), Griskey and Gregory (*7*), Gheorghitza (*8*), List (*9*), Dauben (*10, 11*), Slattery (*12, 18*), Gogarty (*13, 14*), Jones and Maddock (*15*), Pye (*16*), Marshall and Metzner (*17*), Hermes (*19*), and Gregory (*20*). These studies were divided between research that included experimental and theoretical work (*1* to *7, 10, 11, 13, 14, 16, 17, 19, 20*) and research that was entirely theoretical (*8, 9, 12, 15, 18*). All of the experimental work, with the exception of that of Griskey and Gregory (*7*) and Gregory (*20*), only considered flows of polymer solutions. The work of Griskey and Gregory treated the flows of molten polymers through porous media.

A number of different approaches were taken to treat the experimental flow data. Bird and Sadowski (*1*) and Sadowski (*2, 3*) correlated a friction factor with a modified Reynolds number. The correlation was based on Darcy's law and the Ellis equation for non-Newtonian fluids. Christopher and Middleman (*4*) and Marshall and Metzner (*17*) used a similar approach except that they used the power law model for non-Newtonian fluids.

Gregory and Griskey (*7*) developed a friction factor modified Reynolds number correlation based on the Mooney-Rabinowitsch equation. McKinley, Johns, and Greenkorn (*6*) used a superposition principle rather than development of a modification of the Darcy equation, and Dauben and Menzie (*11*) correlated their data on the basis of an apparent viscosity calculated using a Newtonian flow permeability value.

In the course of experimental research on non-Newtonian flow in porous media anomalies have occurred, Metzner and Marshall (*17*), for example, found that serious departures from their modified friction factor-modified Reynolds number correlation occurred as viscoelastic effects increased. Dauben (*10, 11*) also noted a similar happening. The measure of viscoelasticity used by Metzner was N_{Deb}, the Deborah number

$$N_{Deb} = \frac{V\theta}{D_p} \qquad (1)$$

where V was average velocity through the bed (V_0/ϵ), D_p the particle diameter, and θ the relaxation time

$$\theta = \frac{\eta}{G} \qquad (2)$$

According to Metzner (*17*) at Deborah numbers from 0.05 to 0.06 the friction factor and Reynolds number product deviated greatly from the horizontal line that would be expected. However, Christopher and Middleman (*4*) carried out a similar analysis and found no evidence of such a departure even at values of Deborah number of a higher order of magnitude (1.0 to 1.6). The present work was undertaken to resolve this disagreement in the role of viscoelasticity on non-Newtonian flow in porous media. The use of molten polymers was felt to be especially meaningful since their relaxation times should be several orders of magnitude higher than those of the fluids used by Metzner (*17*) and Middleman (*4*).

EXPERIMENTAL PROCEDURE

The polymer used in the present study was a polyethylene, Alathon 10. Figure 1 represents the experimental flow apparatus. Polyethylene pellets were fed to a 1-in. laboratory extruder where they were melted and pumped to a helical gear pump driven by a Reeves varispeed drive. The gear pump metered a constant flow of polymer to the test section.

Figure 2 is a detail drawing of the test section. Two stainless steel screens (16 × 16 and 200 × 200 mesh) were placed immediately over the holes in the bottom of the test section. The screens prevented the escape of any of the porous media through the holes.

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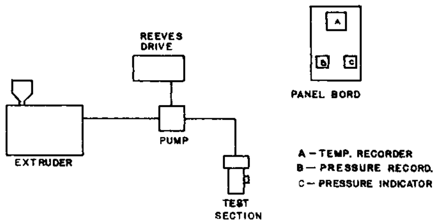

Fig. 1. Schematic diagram of apparatus.

The test section was filled to a given depth with stainless steel or glass beads. These were poured from a height of 6 in., while the test section was continuously rotated to provide a random bed packing. At ½-in. bed height intervals the bed was tamped ten times with a special device dropped from a height of about 6 in. Packed section bed depth was carefully measured with an architect's scale. This made possible the precise determination of bed porosity.

Experiments were performed at constant temperatures and flow rates. Temperatures of 375°, 400°, and 425°F., flow rates from 12 to 60 g./min., and particle sizes of 0.054 and 0.125 in. and 3, 4, 5, and 6 mm. were studied.

Pressures were measured with a Taylor pressure bulb and temperatures with Aminco high-pressure thermocouples.

Data were taken for both a given bed and test section and also for the test section under the same conditions without the bed. The pressure drop obtained in the latter case was subtracted from the overall pressure drop with the bed present to give the pressure drop for the bed alone.

The rheological behavior of the polymer was characterized using a Model R18 Weissenberg Rheogoniometer. Shear stress-shear rate data, normal stress data, and relaxation time shear rate behavior were all determined. Those are presented in Figures 3 to 6.

RESULTS AND DISCUSSION

The experimental flow data and the rheological data were then treated in a manner similar to that used by Christopher and Middleman (*5*) and Marshall and Metzner (*17*). This consisted of fitting a modified Blake-Kozeny equation (*5, 17*) to the experimental data. Power law behavior

$$\tau = K\left(\frac{d\gamma}{dt}\right)^n \tag{3}$$

was assumed to hold for the capillary flow.

In the Blake-Kozeny equation the following relations held:

$$v_0 = \frac{n\epsilon}{3n+1}\left(\frac{D_p\epsilon}{3(1-\epsilon)}\right)^{\frac{n+1}{n}}\left(\frac{6\Delta P}{25KL}\right)^{1/n} \tag{4}$$

$$v_0 = \left(\frac{k}{H}\,\frac{\Delta P}{L}\right)^{1/n} \tag{5}$$

$$H = \frac{K}{12}\left(9+\frac{3}{n}\right)^n (150\,k\epsilon)\,\frac{1-n}{2} \tag{6}$$

$$f^* = \frac{\Delta P\, D_p\, \epsilon^3\, \rho}{L G_0^2\,(1-\epsilon)} \tag{7}$$

$$N_{Re}{}^* = \frac{D_p\, G_0^{2-n}\, \rho^{n-1}}{150\, H\,(1-\epsilon)} \tag{8}$$

Application of Equations (3) to (8) yielded the relation

$$f^* = \frac{1}{N_{Re}{}^*} \tag{9}$$

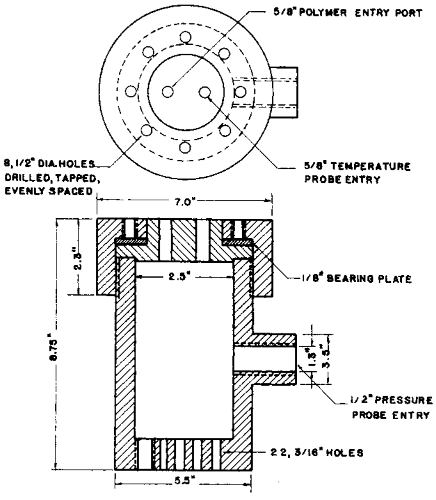

Fig. 2. Detail of test section.

This expression held for all of the data of Christopher and Middleman (*5*), Bird and Sadowski (*1* to *3*), and for certain of the data of Marshall and Metzner (*17*), the exception being those data which appeared to show viscoelastic effects.

When Equations (3) to (8) were applied to the present work, it was found that the relation of Equation (9) held for all of the particle sizes (3, 4, 5, and 6 mm.) except the smallest (1.37 mm.). Figure 7 shows the friction factor-Reynolds number correlation for the larger particle sizes (3, 4, 5, and 6 mm.). As can be seen, the agreement is excellent. The data of Figure 7 extend this friction factor-Reynolds number correlation almost three more decades past that reported earlier (*4, 17*).

The deviation of the 1.37-mm. data was considerable. There were a number of possible explanations for this behavior. These included end effects, particle surface effects, and of course viscoelastic effects. A careful consideration of all of these showed that none could actually account for the deviation.

For example, end effects could not have been a possibility since bed depths were varied over a threefold range without noticeable results. A particle surface effect (including the possibility of adsorption of polymer) was checked by comparing similar beds of stainless steel and glass particles. Similar pressure drops in both beds indicated that a surface effect did not occur.

The third possibility, viscoelastic effects, seemed prom-

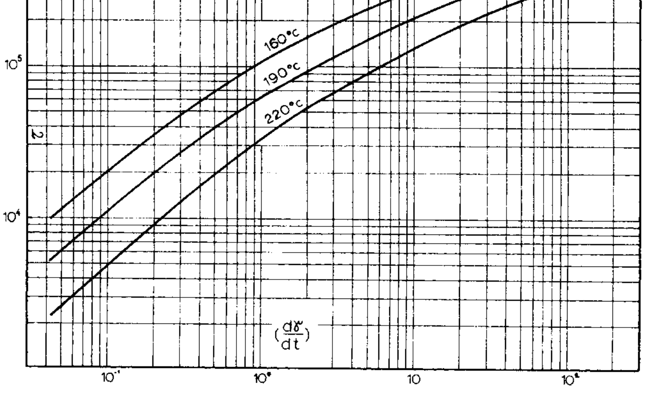

Fig. 3. Shear stress versus shear rate for Alathon 10.

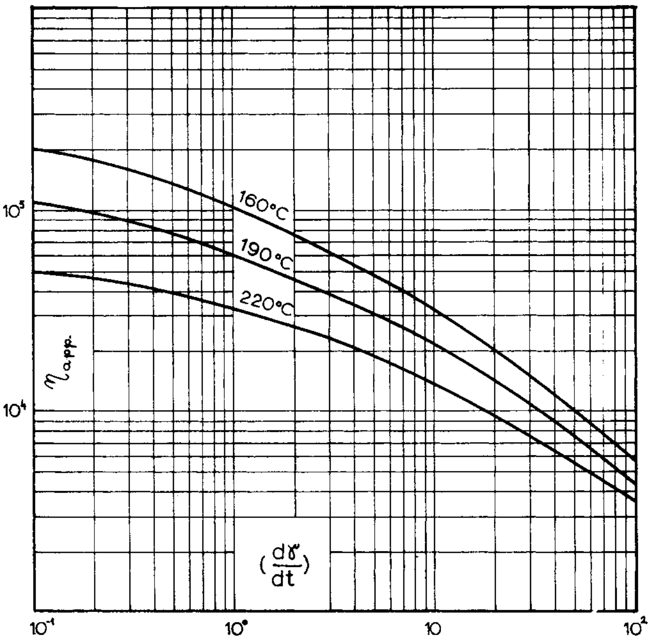

Fig. 4. Apparent viscosity versus shear rate for Alathon 10.

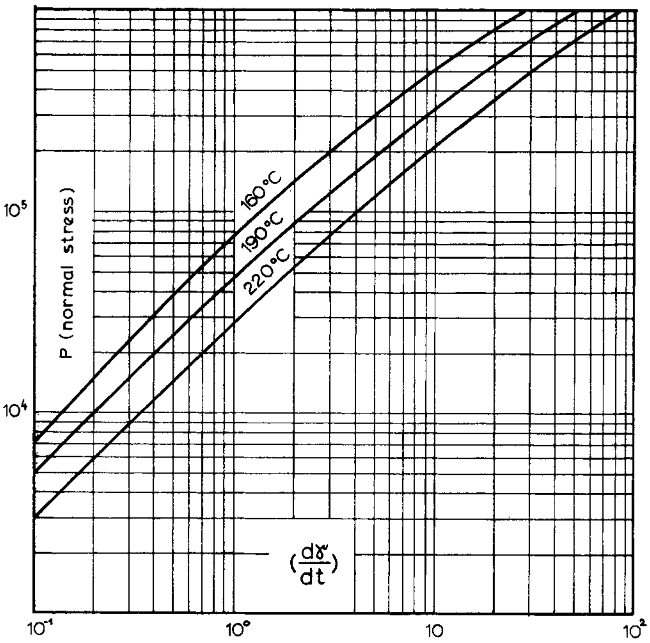

Fig. 5. Normal stress versus shear rate for Alathon 10.

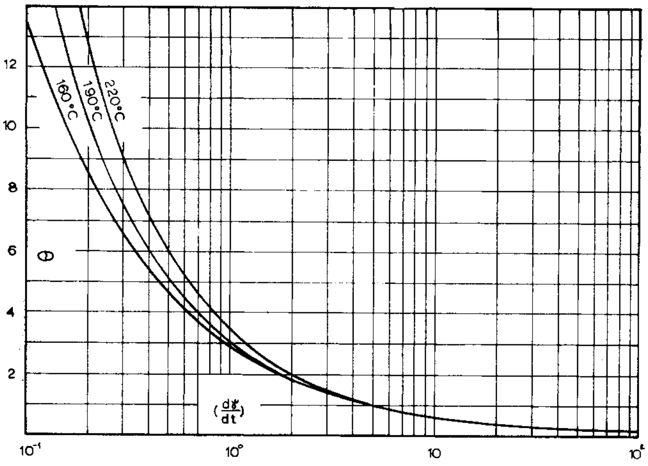

Fig. 6. Relaxation time versus shear rate for Alathon 10.

ising. However, this too proved unsatisfactory. Consider Figure 8, a plot of pressure drop versus particle size with temperature as a parameter. As particle size decreases from 3 to 1.37 mm. there is a sizable increase in pressure drop. This shows that there must correspondingly be a large increase in shear rate. It was found that the shear rates in the 1.37-mm. bed ranged from 60 to 150 sec.$^{-1}$, while those in the larger particle size beds were two to three orders of a magnitude lower.

The difference in shear rate is important. If Figure 6 is consulted it is seen that much lower relaxation times are obtained for the 1.37-mm bed. These lower relaxation times made the Deborah numbers for the small particle size data about one-third of the Deborah numbers for the larger particle sizes. In addition, the Deborah numbers were far below the critical value of 0.05 cited by Metzner (*17*). The combination of these factors eliminates viscoelastic effects as a possible reason for the deviation of the small particle data.

There is, however, one additional factor which should be cited. This is the flow curve behavior (shear stress-shear rate) for the molten polymer. These data are given in Figure 3. As can be seen in the shear rate range for the small particle data the flow curves experience considerable curvature. It is known that in such regions the power law is not applicable. If this is the case then Equations (1) to (6) would not apply and hence the small particle data could not be expected to follow Equation (7).

Indications show that the small particle data may be fitted by the original Blake-Kozeny relations.

$$f = \frac{\Delta P \, D_p \, \epsilon^3 \, \rho}{L G_0^2 \, (1 - \epsilon)} \tag{10}$$

$$N_{Re} = \frac{D_p \, G_0}{\mu} \, \frac{1}{(1 - \epsilon)} \tag{11}$$

if an apparent viscosity is used instead of the Newtonian viscosity.

As was noted earlier one of the express points of interest of the present work was to attempt to resolve the apparent anomaly between the data of Gaitonde and Middleman (*5*) and of Marshall and Metzner (*17*). It was also indicated that the molten polymer used in the present work should have much higher relaxation times than those used in the earlier studies. This was found to be the case; see Table 1.

A plot of the product of f^* and N_{Re}^* versus Deborah number (Figure 9) failed to show any deviation from the correlation value (1.0) and hence no noticeable viscoelastic effects were noted. The data cluster of Figure 9 covers not only the critical Deborah number (0.05) cited by Metzner but also a portion of the region where the friction factor-Reynolds number product was almost twice the correlation value of unity (*17*). The results of Figure 9 clearly show that the assumption of a critical Deborah number of 0.05 is not valid. The data of Marshall and Metzner (*17*), in fact, help to corroborate this finding. In their article they present only one data point between

TABLE 1. COMPARISON RELAXATION TIMES

Range of relaxation times, sec.	Source
0.2 to 4	Present work
5×10^{-6} to 3.4×10^{-2}	Marshall and Metzner (*17*)
8×10^{-3} to 1×10^{-2}	Gaitonde and Middleman (*4*)

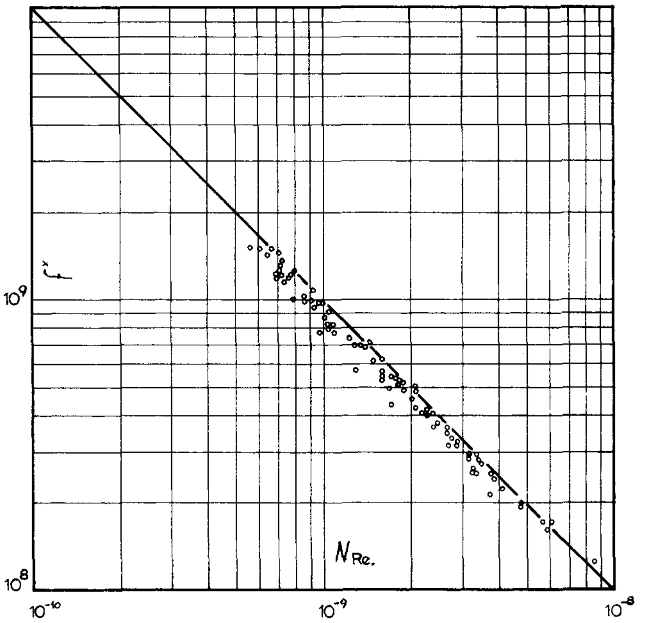

Fig. 7. Friction factor versus Reynolds number using modified Blake-Kozeny equation.

Deborah numbers of 0.04 and 0.19. This one point (at $N_{Deb} = 0.08$) shows comparatively slight deviation from $f^* \cdot N_{Re}^* = 1.0$. This behavior and the data of Figure 9 cast severe doubt on the possibility of any viscoelastic effect occurring prior to a Deborah number of at least 0.19. It would seem that the critical value might even be higher since the data of Figure 9 show no viscoelastic effect even up to $N_{Deb} = 0.3$.

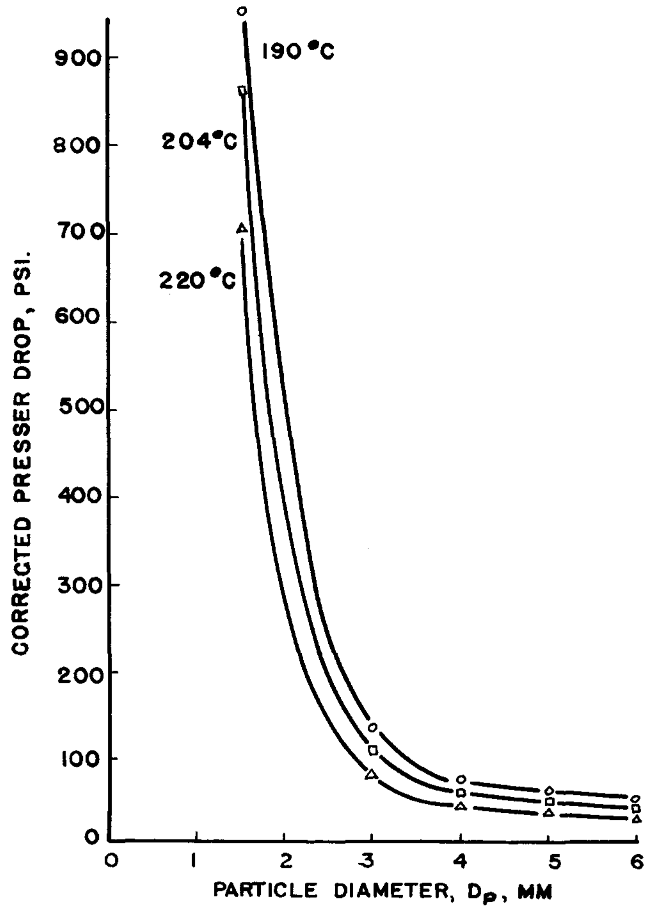

Fig. 8. Pressure drop versus particle size.

As an additional point of interest, it should be noted that a plot of the product of $f^* \cdot N_{Re}^{**}$ [the friction factor and Reynolds number derived by Griskey and Gregory (7) from the Mooney-Rabinowitsch relation] was also constant for all Deborah numbers of the present work. This is shown in Figure 10.

CONCLUSIONS

The present investigation has yielded a number of results:

1. The modified Blake-Kozeny equation for non-Newtonian flow in porous media holds for molten polymers as well as for polymer solutions demonstrated earlier. The correlation (friction factor with Reynolds number based on a modified Blake-Kozeny equation) with the power law was extended almost three decades lower than that previously reported.
2. The modified Blake-Kozeny result based on power law was shown not to hold when bed shear rates were in the range of excessive curvature in the flow (shear stress-shear rate) curves. However, the Newtonian Blake-Kozeny equations, together with apparent viscosity data, appear to be able to describe porous media flow for molten polymers when power law is not applicable.
3. The critical Deborah number value where viscoelastic effects begin to become significant is not 0.05 as previously reported but possibly at $N_{Deb} = 0.19$ or even higher.

NOTATION

D_p = particle diameter, cm.
$\left(\frac{d\gamma}{dt}\right)$ = shear rate, sec.^{-1}
f^* = modified friction factor, Equation (5)
G = elastic modulus, dynes/sq.cm.
G_0 = superficial mass velocity, g./(sq.cm.)(sec.)

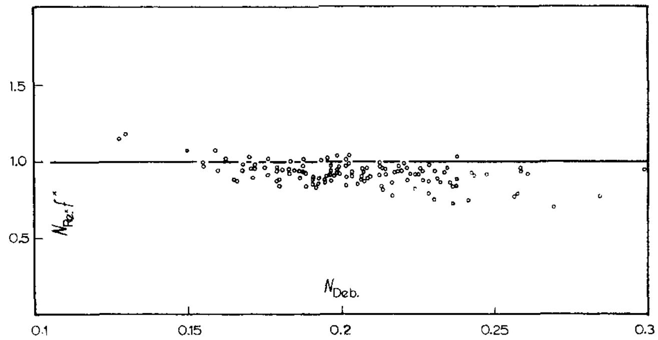

Fig. 9. Test of viscoelastic effects in porous media flow.

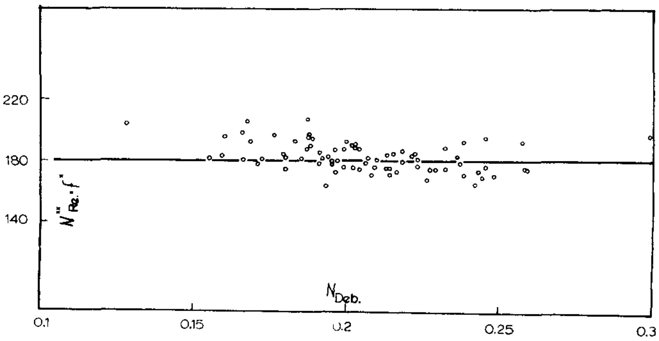

Fig. 10. Test of viscoelastic effects in porous media flow.

H = non-Newtonian bed factor, (dynes)(sec.^{n})/cm.$^{-1-n}$

k = bed permeability, sq. cm.

K = power law parameter, (dynes) (sec.^{n}) /sq.cm.

K' = from $\frac{D\Delta P}{4L} = K'\left(\frac{8V}{D}\right)^{n'}$; (dynes)(sec.^{n})/sq.cm.

L = length, cm.

n = flow behavior index

n' = from $\frac{D\Delta P}{4L} = K'\left(\frac{8V}{D}\right)^{n'}$

N_{Deb} = Deborah number, $\frac{v\theta}{D_p}$

$N_{Re}{}^*$ = Reynolds number, as per Equation (6)

$N_{Re}{}^{**}$ = Reynolds number, $\frac{D_p\,G_0}{(1-\epsilon)\,\eta_{\text{mod}}}$

ΔP = pressure drop, dynes/sq.cm.

v_0 = superficial velocity, cm./sec.

v = average velocity, v_0/ϵ, cm./sec.

Greek Letters

ϵ = bed porosity

ρ = density, g./cu.cm.

η_{app} = apparent viscosity, (dynes) (sec.) /sq.cm.

$\eta_{\text{mod}} = 15\left(\frac{2}{25K'}\right)^{1/n'}\left(\frac{D_p\,P}{L(1-e)}\right)^{1/n'-1}$

θ = relaxation time, sec.

τ = shear stress, dynes/sq.cm.

μ = viscosity, (dynes) (sec.) /sq.cm.

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Crystallization: Kinetics and Design Considerations

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The following nucleation rate and growth rate relationships for the aqueous, continuous, cooling crystallization of potassium dichromate were determined from experimental crystal size distributions: $J = 3.9 \times 10^{10}\,(C - C_{eq})^{0.9}$; $r = 3.0 \times 10^{3}\,(C - C_{eq})^{1.7}$. Since nucleation rate is of lower kinetic order than growth rate, higher levels of supersaturation will yield crystal distributions with a larger mean size. Therefore for this system, batch or plug-flow reactors are preferred to continuous-stirred tanks.

In crystallization, nucleation and growth compete to relieve the level of supersaturation of the metastable state. Their relative kinetics primarily determine resulting size distributions. The objectives of this research were to analyze crystal size distribution data for the aqueous, cooling crystallization of potassium dichromate and to define growth and nucleation kinetics as functions of supersaturation. Using these results and previously published kinetic findings, we discuss the fundamental importance of kinetics on crystallizer design.

CRYSTALLIZATION KINETICS

Volmer's homogeneous nucleation model (*8, 16, 17*) is given by

$$J = K_1 \exp\{-K_2/[T^3 \ln^2 (C/C_{eq})]\} \qquad (1)$$

where the equilibrium dissolved solute concentration C_{eq} is defined as the lower limit of Mier's metastable crystallization region. Nielsen (*8*) graphically demonstrates that Volmer's model may be approximated as a power function of C/C_{eq} for several orders of magnitude in concentration.

The application of Volmer's nucleation model to high magma suspension crystallization may be questioned in light of known secondary nucleation phenomena: foreign particles act as catalysts (*9*); crystals act as autocatalysts (*10, 15*). The autocatalytic effect has been called nuclei breeding (*14*) or secondary nucleation (*2*). In high magma suspension nucleation rate can be correlated with crystal growth rate (or supersaturation) and suspended magma concentration (*1, 6, 10, 15*):

$$J = K_N{}'\, r^i\, M^j = K_N\, s^b\, M^j \qquad (2)$$

Crystal growth kinetics are generally defined as power functions of supersaturation

$$r = K_g\, s^a \qquad (3)$$

where the kinetic dependency a may be close to unity (*5*) or may be significantly different from unity (*3, 13*).