Observations of Early Turbulence in the Pipe Flow of Drag Reducing Polymer Solutions

P. C. FORAME, R. J. HANSEN, and R. C. LITTLE

Naval Research Laboratory, Washington, D. C.

Early turbulence has for the first time been observed in the flow of very dilute polymer solutions in tubes larger than capillary size. Flow rate-wall shear stress measurements were conducted in 0.553 and 0.660 cm. diameter pipes. Polyethylene oxide samples of two molecular weights were employed, dissolved in water-glycerine mixtures with viscosities ranging from 0.0261 to 0.160 poise. The flow rate-wall shear stress relationship for these solutions corresponded to Poiseuille's Law below a well-defined onset wall shear stress, at which the Reynolds number was less than the transition value for Newtonian fluids. As the flow rate was increased from the onset condition, however, the wall shear stress became progessively larger than that predicted by the Poiseuille relationship. The onset wall shear stress for the phenomenon increased linearly with solvent viscosity. Its relationship to polymer concentration was dependent on the solvent viscosity. An explanation for early turbulence is suggested on the basis of these results, and the relationship of the phenomenon to turbulent flow drag reduction is discussed.

The non-Newtonian character of very dilute polymer solutions under turbulent flow conditions has been well documented in numerous experimental studies (*1*). Recently, the flow of dilute polymer solutions in capillary tubes has also been characterized by a marked departure from Newtonian behavior under conditions of steady laminar shear (*2*, *3*). This behavior, which shall be termed early turbulence in the present work, has the following characteristics: 1. it exists only above some well-defined critical wall shear stress characteristic of a given polymer solution; 2. this critical wall shear stress varies with polymer concentration and molecular weight (the effect of solvent viscosity has not been heretofore investigated); 3. at shear stresses above the critical wall shear stress, the drag exerted by the polymer solution exceeds that for the laminar flow of a Newtonian fluid at the same flow rate; 4. the familiar laminar-to-turbulent transition is replaced by a continuous change from early turbulence to turbulent flow with reduced drag as the flow rate increases. It has recently been suggested (through use of a simple relation involving Reynolds number, viscosity, density, and wall shear stress) that early turbulence will be observed in highly dilute drag-reducing aqueous polymer solutions if the pipe diameter used is of the order of 0.20 cm. or less (*2*). Apart from Hoyt's work (*4*)—done at a single flow rate—measurements of dilute Polyox polymer solutions (nominally of the same viscosity as water) have been done exclusively at larger pipe diameters. However, this same simple relation suggested that the early turbulence phenomenon could be observed in much larger pipes provided the solvent viscosity were increased to an appropriate degree. The present work explores the relationship of τ^*, the critical wall shear stress for early turbulence, to the solvent viscosity over a range of polymer concentrations and at two molecular weights in larger tubes. A possible explanation for the early turbulence phenomenon which qualitatively combines elements of both molecular and continuum views is briefly discussed.

EXPERIMENTAL APPARATUS AND PROCEDURES

Experimental runs were made at 24 ± 1°C. using solutions of Polyox WSR-205 or Coagulant (Union Carbide Co.) in water-glycerine mixtures of known concentration. The mean molecular weights of the two polymer additives, determined by intrinsic viscosity measurements (*5*), were 9.0×10^5 and 7.0×10^6, respectively. Stock solutions of each additive in distilled water were prepared and stored as described previously (*5*). In a typical flow experiment, distilled water was first thoroughly mixed with glycerine (U.S.P., Dow Chemical Company). Stock solution was then added in the amount necessary to give the desired solvent viscosity and polymer concentration. The mixture was then stirred very gently for an additional 20 to 30 min. This procedure not only produced a solution in which no inhomogeneities could be detected visually but also minimized degradation of the polymer molecules during solution preparation.

Both glycerine and Polyox molecules are expected to suc-

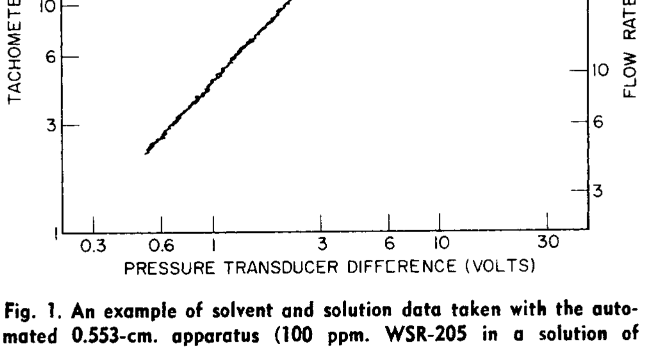

Fig. 1. An example of solvent and solution data taken with the automated 0.553-cm. apparatus (100 ppm. WSR-205 in a solution of viscosity 0.0786 poise).

Correspondence should be addressed to R. J. Hansen at Code 8441, Applied Mechanics Branch. P. C. Forame is at APO 96384, San Francisco, California.

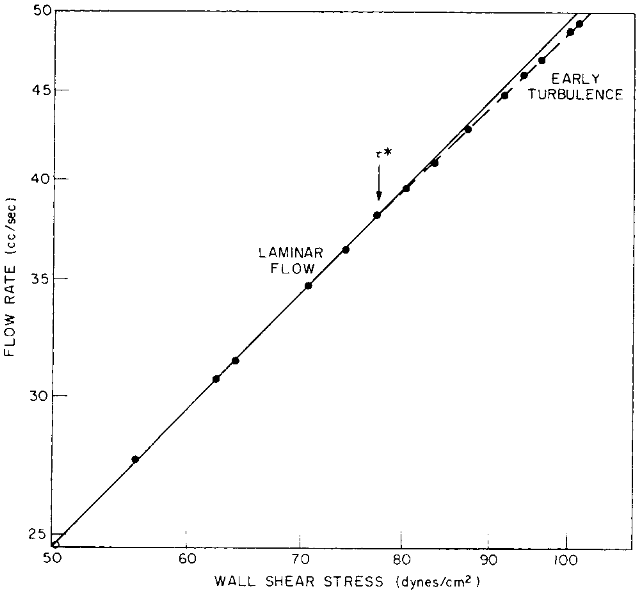

Fig. 2. An example of the data obtained with the 0.660 cm. apparatus (100 ppm. WSR-205 in a solution of viscosity 0.0580 poise).

cessfully compete for water molecules in these mixed solvent systems, the ether oxygens of the polymer having a particularly strong hydrogen bonding affinity. While Polyox is insoluble in fully anhydrous glycerine, hydration of the ether linkage by the water component can be expected to insure full compatibility of the polymer with the mixed solvent system. It can be appreciated that hydration of the ether linkages through hydrogen loading effects increases in the solubility parameter δ of the polymer from 9.6 (anhydrous state) to 17 in the fully hydrated state (assuming two water molecules bonded per ether linkage). The solubility parameter of the hydrated polymer then lies comfortably close to the range of solubility parameter values ranging from $\delta = 17.9$ for a 62% glycerine solvent upwards toward a $\delta = 24.0$ for pure water. Thus, compatibility of solvent mixtures with polymer over the experimental solvent compositions studied (up to 62% glycerine) seems quite reasonable on a solubility parameter basis alone, with additional benefits to be derived from H-bonding effects as the solvent composition approaches pure water.

Two pipe flow systems were employed, both of which are described in detail elsewhere (2, 5). The 0.553 cm. diameter pipe flow apparatus was automated, giving a continuous record of ln (flow rate) versus ln (shear stress). A typical record is shown in Figure 1. (Both transducer voltages and flow rate-wall shear stress scales are indicated.) With the 0.660 cm. diameter system, experiments were conducted at discrete flow rate values, and the wall shear stress was measured at 230 or 745 diameters from the entrance. Data from one set of experiments obtained with this system is shown in Figure 2. An onset condition was determined by visual inspection of one of these plots as the point at which the flow behavior began to deviate from Poiseuille's Law. Two to six experimental runs were made for each polymer concentration, molecular weight, solvent viscosity, and pipe diameter employed in order to fix the onset point. The average values of τ^* and the other flow parameters were computed from each set of experimental runs. The probable error in these average values is estimated to be ± 5%.

RESULTS

The early turbulence detected in water-glycerine solutions of Polyox flowing in a 0.553 cm. tube possessed all of the characteristics observed using aqueous solutions in smaller diameter tubes, that is, the absence of an abrupt laminar-to-turbulent transition, the increased drag compared to Poiseuille flow above the onset wall shear stress, and the reduction of drag in the turbulent regime (see Figure 1). The onset wall shear stress was found to depend on polymer molecular weight and concentration as shown in Table 1, where the critical wall shear stress τ^*, critical flow rate Q^*, tube diameter D, critical Reynolds number N^*, and critical wall shear rate S^* are tabulated. N^* and S^* were obtained from the expressions

$$N^* = \frac{4Q^*\rho}{\pi D\mu} \tag{1}$$

$$S^* = \frac{32Q^*}{\pi D^3} \tag{2}$$

where ρ, and μ denote solution density and viscosity respectively. The solutions used in this work were so dilute that no distinction was made between solvent and solution values for ρ and μ. Equation (1) follows from the definition of the Reynolds number, and Equation (2) is derived from Poiseuille's Law.

Table 1 shows that S^* increased but very slightly with increasing viscosity for a given additive concentration and molecular weight. An equivalent statement is that τ^* increased almost linearly with μ for constant concentration and molecular weight, since Poiseuille's Law may be written

$$\tau^* = \mu S^* \tag{3}$$

The variation in τ^* with μ is shown in Figures 3 and 4. The highest viscosity data points for 1 and 5 ppm. solutions of Polyox Coagulant are exceptions to these generalizations, for reasons discussed below.

A variation in τ^* with polymer concentration may be

TABLE 1. ONSET DATA

Polymer and concentration, wppm	Viscosity, poise	Diameter, cm.	τ^*, dynes/sq.cm.	Q^*, cc./sec.	S^*, sec.^{-1}	N^*
WSR-205						
100 ppm.	0.0261	0.553	29	19	1110	1770
100 ppm.	0.0531	0.553	70	22	1330	1070
100 ppm.	0.0786	0.553	104	22	1320	740
100 ppm.	0.106	0.553	144	23	1360	570
100 ppm.	0.0438	0.660	60	40	1400	1970
100 ppm.	0.0580	0.660	79	38	1360	1440
WSR-Coagulant						
1 ppm.	0.0261	0.553	35	22	1340	2120
1 ppm.	0.0532	0.553	70	22	1340	1090
1 ppm.	0.0786	0.553	113	24	1430	800
1 ppm.	0.106	0.553	178	28	1680	700
WSR-Coagulant						
3.1 ppm.	0.0261	0.553	31	20	1200	1890
3.1 ppm.	0.0531	0.553	69	22	1310	1060
3.1 ppm.	0.0786	0.553	102	22	1300	730
3.1 ppm.	0.106	0.553	150	24	1420	590
WSR-Coagulant						
5 ppm.	0.0261	0.553	32	21	1230	1960
5 ppm.	0.0531	0.553	70	22	1310	1060
5 ppm.	0.0786	0.553	104	22	1320	835
5 ppm.	0.106	0.553	143	22	1350	562
5 ppm.	0.160	0.553	289	30	1810	510
WSR-Coagulant						
25 ppm.	0.0261	0.553	29	19	1120	1770
25 ppm.	0.0531	0.553	70	22	1310	1060
25 ppm.	0.0786	0.553	107	23	1360	760
25 ppm.	0.106	0.553	158	25	1490	620

seen in Figure 3; and the relationship between these two quantities is further shown in Figure 5, where τ^* is plotted as a function of ln (polymer concentration). The pronounced minimum in τ^* with increasing concentration for the highest viscosity solution resembles that observed previously (2) in early turbulence studies of aqueous polymer solutions in a capillary tube. The fact that the minimum becomes progressively less evident with decreasing solvent viscosity in the present work probably indicates that its development is a strong function of solvent viscosity. Mechanical degradation of the polymer molecules may also account in part for the decrease in τ^* with increasing concentration observed for the 0.106 poise solution. It is not completely responsible for the dependence on viscosity of the τ^* — ln (concentration) relationship, however. Mechanical degradation does not provide a rationale for the increase in τ^* with concentration above 3 to 5 ppm., nor for the fact that the increase becomes more apparent with increasing viscosity.

A comparison of the onset behavior for two solutions of different polymer molecular weight and concentration is given in Figure 4. Over the range of viscosity investigated, the τ^* values for 100 ppm. WSR-205 and 5 ppm. Coagulant are in close agreement. This is significant because the drag reduction behavior of aqueous solutions of these two concentration-molecular weight combinations (observed in unpublished capillary tube experiments conducted at NRL) are also very similar.

Early turbulence is not an entrance effect since the phenomenon was clearly observable at both 230 and 745 diameters from the upstream end of the 0.660 cm. diameter tube. The latter distance is substantially larger than that ordinarily associated with the entrance region. Also, τ^* was measured at both locations for the 100 ppm. WSR-205 solution of viscosity .0438 poise. The average upstream value of τ^* was 60 dynes/sq.cm., compared to 63 dynes/sq.cm. at the downstream location. The difference in these values is well within the probable error (± 5%).

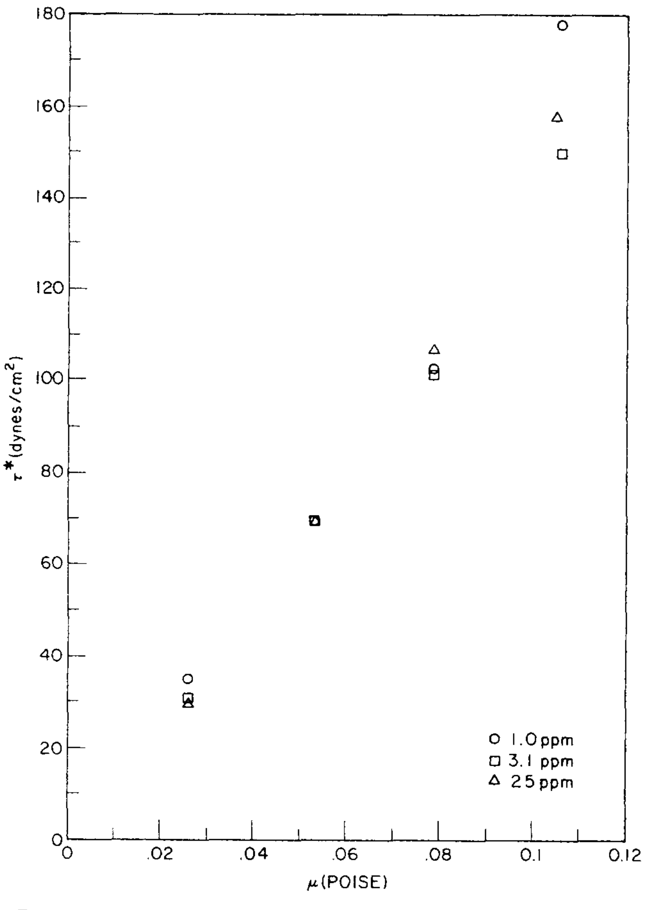

Fig. 3. The effect of viscosity on the onset wall shear stress for early turbulence (WSR-Coagulant solutions in the 0.553 cm. tube).

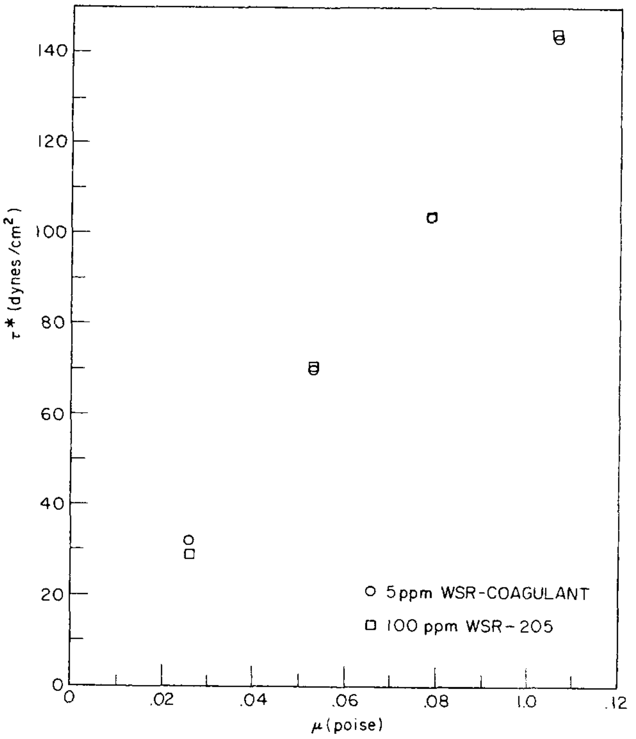

Fig. 4. Comparison of the onset behavior of 5 ppm. WSR-Coagulant and 100 ppm. WSR-205 solutions in the 0.553-cm. tube.

DISCUSSION

The suggestion has been made (2, 6) that early turbulence at low polymer concentrations (below that at which τ^* is a minimum) and turbulent flow drag reduction may be closely related phenomena. The onset data presented above seem to be consistent with this view. The 5 ppm. coagulant and 100 ppm. WSR-205 solutions exhibit very similar onset behavior for early turbulence, as well as for drag reduction. Also, the best fit straight line through the 100 ppm. WSR-205 data (Figure 4) has a value of $\tau^* =$ 7.4 dynes/sq.cm. when extrapolated to $\mu = .009142$ poise, the viscosity of water at 24°C. This differs by less than a factor of two from 11 dynes/sq.cm., the wall shear stress at the onset of drag reduction for a 57.2 ppm. aqueous solution of the same polymer in a 0.660 cm. pipe. It is of interest to note, moreover, that a plot of Hansen and Little's drag reduction onset data for WSR-205 (in terms of τ^* versus log conc.) follows a linear relation over the 3 to 57.2 ppm. experimental range. Extrapolation of the plot to a concentration of 100 ppm. yielded an estimate of $\tau^* = 8.5$ dynes/sq.cm., a value not greatly in disagreement with the early turbulence data when the concentration dependence of drag reduction onset is accounted for. (The difference in magnitude of the onset values for early turbulence and drag reduction reported previously (2) may have been due to the difference in tube diameter in which the two phenomena were compared.)

At low concentrations, a decrease in τ^* with increasing concentration is observed (Figure 5). A similar trend in the onset wall shear stress for drag reduction has been reported by the present authors (*5*) and by other investigators (*7*). Since an increase of the onset point for drag reduction with concentration paralleling the early turbulence results presented here has never been reported it is possible that the mechanisms responsible for drag reduction and for early turbulence at sufficiently high concentrations are basically different. Alternatively, careful onset-of-drag reduction studies in sufficiently viscous solvents and/or high polymer concentrations to determine possible increases in the onset wall shear stress with concentration may not yet have been performed.

A possible explanation for early turbulence at polymer concentrations below which τ^* is a minimum is suggested by the very weak dependence of S^* on μ for each concentration of a given additive. In the steady laminar shear flow of a dilute solution of rigid spheres the probability of collision of two spheres (of their coming within one diameter of each other) is directly proportional to shear rate (*8*). Shear rate and collision probability should be similarly related in a dilute polymer solution, to a good approximation. That is to say, the polymer molecules in a steady laminar shear flow are not greatly distorted from their rest configuration (*9*). Consequently, the small variation in S^* with μ implies that early turbulence is initiated when the collision frequency reaches a critical value near the wall. Above this frequency interpenetration of polymer coils may occur, with two or more molecules sticking together for some period of time after collision. The formation and destruction of molecular aggregates thus formed will approach an equilibrium distribution which is dependent upon the conditions of shear and solution composition. A similar explanation was offered by Peterlin and co-workers (*10*) for their observations (*10, 11*) of increased resistance to flow of more concentrated polymer solutions at sufficiently high shear rates. Associating the onset of early turbulence with interparticle effects is consistent with the decrease in τ^* with increasing concentration at the lower concentrations, since collision frequency is expected (*12*) to increase with concentration at a given shear rate. Because τ^* increases with concentration at higher concentrations, a different explanation on the molecular level for early turbulence and the observed linearity between τ^* and μ is expected to be appropriate in these circumstances. Ram and Tamir (*3*) have suggested that the breakup of polymer networks may contribute to the early turbulence observed in such concentrated solutions.

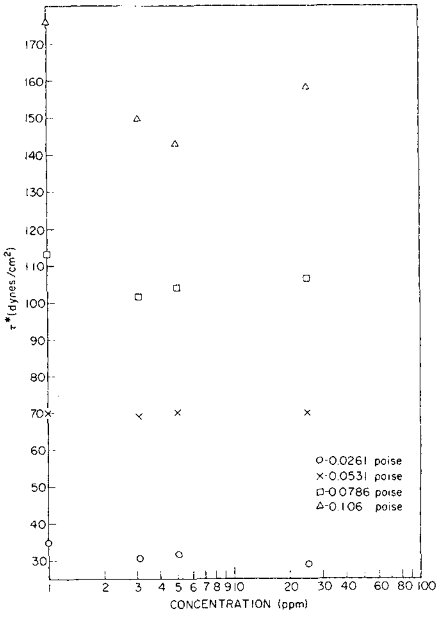

Fig. 5. The polymer concentration dependence of onset behavior in the 0.553-cm. tube (WSR-Coagulant).

If the relationship between events occurring on the molecular level (molecular aggregation, polymer network formation and/or breakup) and macroscopic solution properties such as relaxation time could be developed, it might be possible to ultimately determine whether or not a hydrodynamic instability could be ascribed directly to these molecular events. The merits of such an explanation can be only partially assessed at present, because comprehensive theoretical studies of laminar pipe flow stability have not been conducted for polymer solutions (that is, for liquids characterized by the convected Maxwell (*13*) or Oldroyd three-constant (*14*) constitutive equations, which are known to approximate the continuum behavior of dilute polymer solutions). The Poiseuille flow stability problem, however, has been treated by Derman (*15*) for a fluid with the following constitutive equation:

$$\left(1 + \lambda \frac{\partial}{\partial t}\right)(\tau_{ij} + p\,\delta_{ij}) = \mu\left(\frac{\partial v_i}{\partial x_j} + \frac{\partial v_j}{\partial x_i}\right) \tag{4}$$

Here λ denotes relaxation time, p the hydrostatic pressure, δ_{ij} the Kronecker delta, τ_{ij} the ij^{th} component of the stress tensor, x_i the i^{th} distance coordinate, and v_i the associated velocity component. This relationship is in some respects similar to the convected Maxwell model, suggesting that the results of Derman's analysis may be relevant to the polymer solution behavior observed in this report. It shows that axially symmetric perturbations in a fluid described by (*4*) are amplified above a critical Reynolds number N_c and that, for sufficiently large values of the parameter $\tau_c\lambda/2\mu$, N_c is less than the transition Reynolds number for a Newtonian fluid. Here τ_c denotes the wall shear stress at N_c. The following expression for τ_c, valid in the range of Reynolds numbers studied in the present experimental work, may be derived from Derman's analysis:

$$\tau_c = \frac{\mu}{\lambda}\,(2.40 \times 10^{-8}) \Big/ \left[1 + (.833 \times 10^{-12})\,\frac{D^2\rho}{\lambda\mu}\right] \tag{5}$$

This equation predicts an increase in τ_c with increasing μ, which is in qualitative agreement with the dependence of τ^* on μ in Figures 3 and 4. The relationship of τ_c to polymer concentration implied by Equation (5) cannot be determined with certainty at present, because λ does not correspond precisely to the convected Maxwell relaxation time obtained from normal stress measurements (*16, 17*) or from theoretical predictions of the steady state compliance of dilute polymer solutions (*5, 18*).

CONCLUSIONS

Early turbulence may be observed in substantially larger tubes than those of capillary type employed in previous investigations if solvents of sufficiently high viscosity are used. The onset wall shear stress for early turbulence increases linearly with solvent viscosity, to a good approximation. It decreases to a minimum and then increases with increasing polymer concentration. These results suggest that molecular aggregation may be in part responsible for early turbulence. A hydrodynamic instability explanation of the phenomenon appears possible, based on presently available theoretical work and experimental results.

NOTATION

D = pipe diameter
N_c = critical Reynolds number predicted by Derman analysis
N^* = Reynolds number at the onset of early turbulence
p = hydrostatic pressure
Q^* = flow rate at the onset of early turbulence
S^* = wall shear rate at the onset of early turbulence
t = time
v_i = i^{th} component of the fluid velocity
x_i = i^{th} distance coordinate

Greek Letters

δ = solubility parameter
ρ = polymer solution density
μ = polymer solution viscosity
λ = polymer solution relaxation time associated with the Derman analysis
τ_{ij} = ij^{th} component of the shear stress tensor
τ_c = critical wall shear stress predicted by the Derman analysis
τ^* = wall shear stress at the onset of early turbulence

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Halogen Affinities—A New Ordering of Metals to Accomplish Difficult Separations

DONALD F. OTHMER

Department of Chemical Engineering
Polytechnic Institute of Brooklyn, Brooklyn, New York 11201

and RUDOLF NOWAK

Tellus, A.G. Frankfurt/Main, Germany

Metallurgical separations utilize the relative ability of one metal to replace another in a compound. The desired metal is obtained in a pure form or more easily worked compound. In general, a "strong" metal replaces a "weak" metal in a solution of its salt, for example, iron added to a solution of copper sulfate replaces the weaker copper to yield metallic copper and iron sulfate.

Metals listed in order of their ability to replace one another in solutions form the electromotive series. The order of the metals in this series is not a function of temperature for aqueous solutions, and the displacement of a weaker metal in a salt by a free stronger metal may be complete and quantitative.

However, dry oxidation and reduction are equally important in extractive, physical, and mechanical metallurgy, and in the use of metals for coatings. Of growing importance is the reduction of oxides by hydrogen or by the displacement of the metal by a more active metal. For example, pure zinc may be produced by reducing zinc oxide by metallic iron.

A NEW ORDER OF METALS—CHLORIDE-FORMING AFFINITIES

A new ordering of metals according to their activity or strength depends on the affinity of a metal in an oxide to