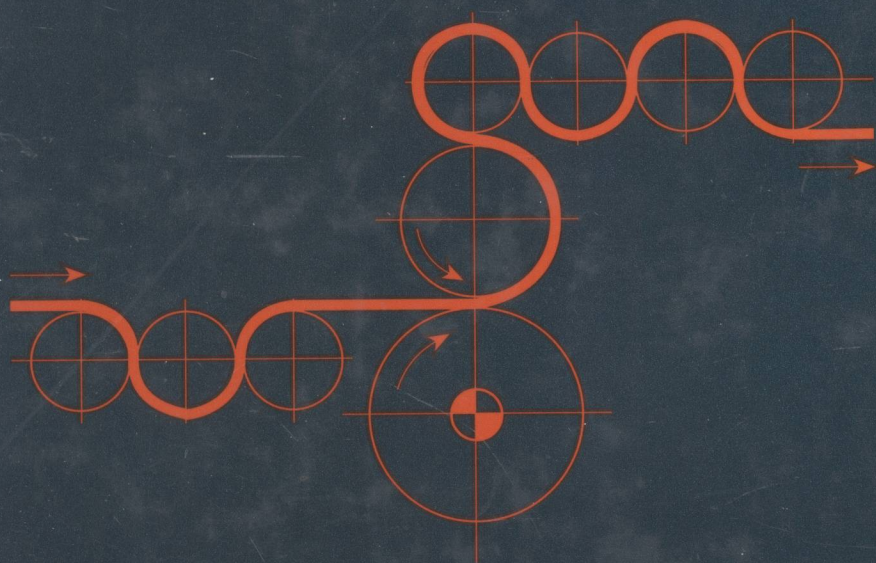

An Introduction to Polymer Rheology and Processing



Nicholas P. Cheremisinoff

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PREFACE

This volume is intended as a practical introduction to the subject of rheology with emphasis given to polymer applications. It was written with the practitioner in mind, specifically those individuals requiring a working knowledge of major rheometric techniques available and the practical constitutive equations that can be applied to data analysis.

The subject of rheometry is extremely important to numerous engineering applications. To the author, this subject has played a dominant role over the years in the development of a variety of new elastomeric products. Rheometric techniques on a practical plane help to define the flow properties of materials. For elastomers and plastics, the rheology of a material establishes whether or not the product can be processed, shaped, and formed into a desired article in an efficient and economical manner, while maintaining dimensional stability and high quality. Laboratory-scale studies on the rheological properties of a polymer melt provide information that can be used to predict processing performance of prototype polymers, to provide guidance in developing optimum processing conditions for polymer compounds and blends, to guide in the molecular and compositional design of the polymer, and to help develop compound formulations that enhance end-use performance characteristics. The rheology of a polymer melt is affected not only by the polymer structure (including composition, levels of crystallinity and branching, and molecular weight and molecular weight distribution), but by the compound formulation (type of ingredients, level of ingredient incorporation, and use of plasticizers, oils, etc.) and the specific processing operation and conditions of processing. Hence, the rheology of polymers is of keen interest not only to the product design specialist, but to the compounder, the fabricator, and the engineer. It is a complex subject about which scores of textbooks have been written over the years, many of which address the fascinating and perplexing aspects of the theoretical foundations of the subject.

This volume is not intended as a textbook, nor are theoretical considerations addressed in detail. It is intended as a practical desk reference, providing an overview of operating principles, data interpretation, and qualitative explanation of the importance and relation of rheology to polymer processing operations.

Nicholas P. Cheremisinoff

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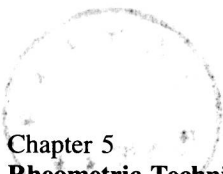
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INTRODUCTION TO RHEOLOGY

I. GENERAL REMARKS

The subject of rheology is concerned with the study of flow and deformation. From a broad perspective, rheology includes almost every aspect of the study of the deformation of matter under the influence of imposed stress. In other words, it is the study of the internal response of materials to forces. Between the extremes of the conceptual views of the Newtonian fluid and the Hookean solid lie materials of great interest. Commercial interest in synthetic polymeric materials has given the greatest impetus to the science of rheology.

When a small stress is suddenly exerted on a solid, a deformation begins. The material will continue to deform until molecular (internal) stresses are established, which balance the external stresses. The term "deformation" refers to the equilibrium deformation that is established when the internal and external stresses are in balance. Most solids exhibit some degree of elastic response, in which there is complete recovery of deformation upon removal of the deforming stresses. The simplest such body is the Hookean elastic solid, for which the deformation is directly proportional to the applied stress. Elastic response may also be exhibited by non-Hookean materials, for which the deformation is not linearly related to the applied stress.

Not all materials reach an equilibrium deformation. In a fluid, if an external stress is exerted, deformation occurs, and continues to occur indefinitely until the stress is removed. A fluid response is one in which no resistance to deformation occurs. Internal frictional forces retard the rate of deformation, however, and an equilibrium can be established in which the rate of deformation is constant and related to the properties of the fluid. The simplest such fluid is the Newtonian, in which the rate of deformation is directly proportional to the applied stress. Many fluids exist which exhibit a nonlinear response to stress and are referred to as non-Newtonian fluids. Most synthetic polymer solutions and melts exhibit some degree of non-Newtonian behavior.

Between the extremes of elastic and fluid response lies a spectrum of combinations of these basic types of material behavior. For example, there is plastic response, wherein a material deforms like an elastic solid as long as the applied stress is below some limit, called the yield stress. If the applied stress exceeds the yield stress the material behaves as a fluid. A common example is paint. Brushing imposes stresses sufficiently large that paint behaves like a fluid. When paint lies on a vertical surface in a thin film, however, the stresses that arise from the weight of the fluid are below the yield stress, and the paint remains on the surface to dry as a uniform film.

Another important class of materials is the viscoelastic fluid. Such a material resists deformation, but at the same time resists a time rate of change of deformation. These materials exhibit a combination of both elastic and fluid response.

A materials response to a stress not only depends on the material, but also on the time scale of the experiment. For example, water behaves like a Newtonian fluid in ordinary experiments, but, if subjected to ultrahigh frequency vibrations, it will propagate waves as if it were a solid. The reason for this apparent change in the type of behavior lies in the fact that response is ultimately molecular in nature, and involves the stretching of intermolecular bonds and the motion of molecules past one another. In general, bonds can be stretched very quickly by an imposed stress, since little motion is involved. On the other hand, considerably more time is involved in causing molecules to "flow". Thus, in a stress field with a very short time scale (high frequency vibration is an example) the stress may reverse itself before molecules have time to move appreciably, and only mechanisms giving rise to elasticity may have time to be excited. Because behavior can depend upon the type of stress field imposed, it is important that both the rheological properties of a material as well as the range of conditions over which these properties were measured be recorded. Only in this way can rheological properties be used with any assurance that they have pertinence to the application at hand.

II. CONSTITUTIVE EQUATIONS

The response of any element of a body to the forces acting upon that element must satisfy the principle of conservation of momentum. In a continuum this principle is embodied in the "dynamic equations", written in Cartesian coordinates as

$$\rho \left(\frac{\partial v_i}{\partial t} + v_j \frac{\partial v_i}{\partial x_j} \right) = \rho f_i + \frac{\partial \tau_{ji}}{\partial x_j} \quad (1)$$

for an incompressible fluid of density ρ subject to an external force field f . The stress tensor τ is usually interpreted as being comprised of the mean normal stress $p = -1/3\tau_{ii}$, and the excess over the mean due to dynamic stresses $\bar{\tau}$. For a fluid at rest, $\bar{\tau} = 0$, and the mean normal stress is just the hydrodynamic pressure. Thus, with $\tau = -p\delta + \bar{\tau}$, the dynamic equations become

$$\rho \left(\frac{\partial v_i}{\partial t} + v_j \frac{\partial v_i}{\partial x_j} \right) = \rho f_i - \frac{\partial p}{\partial x_i} + \frac{\partial \tau_{ji}}{\partial x_j} \quad (2)$$

Of course, Equation 2 represents three equations, one for each direction of the coordinate system. Note that repeated subscripts imply summation over

that subscript. δ is the Kronecker delta, or unit tensor. The negative sign in front of p corresponds to the convention that a pressure is a negative stress and a tension is a positive stress. By these definitions of p and $\bar{\tau}$, $\tau_{ii} = 0$.

In addition to the dynamic equations and equation that expresses the principle of conservation of mass (known as the continuity equation), we may write for an incompressible material (in Cartesian coordinates)

$$\frac{\partial v_i}{\partial x_i} = 0 \quad (3)$$

Often one wishes to use cylindrical or spherical coordinates in the solution of a problem. In that case, Equations 2 and 3 must be transformed. Standard textbooks on fluid mechanics provide Equations 2 and 3 in Cartesian, cylindrical, and spherical coordinate systems. The number of unknowns in these equations is much greater than the number of equations at hand. Normally f is given in a dynamic problem and p is known. Hence, the unknowns are the three components of v , the pressure p , and the nine components of $\bar{\tau}$. For most real fluids, $\bar{\tau}$ is a symmetric tensor and has only six independent components. Hence, ten unknowns are to be found from only four equations. The additional six equations required are the so-called constitutive equations for the material, which relate the components of τ to the velocity and its derivatives.

For example, a simple constitutive equation is that of the Newtonian fluid:

$$\tau_{ij} = \eta_0 \left(\frac{\partial v_i}{\partial x_j} + \frac{\partial v_j}{\partial x_i} \right) \quad (4)$$

where η_0 is a constant and is known as the coefficient of viscosity.

Once the constitutive equation is established, the dynamic problem is determinate. Unfortunately, it may not be amenable to solution for complex materials (defined by the constitutive equation) or for complex boundary conditions.

Fluids respond to stress by deforming or flowing. Flow is basically a process in which the material deforms at a finite rate. The basic kinematic measure of the response of a fluid is the rate of deformation tensor $\bar{\Delta}$,

$$\Delta_{ij} = \frac{\partial v_i}{\partial x_j} + \frac{\partial v_j}{\partial x_i} = \Delta_{ji} \quad (5)$$

Motion may exist in a fluid even if $\bar{\Delta}$ is identically zero. Each element of fluid may be translating at the same linear velocity, and each element may, in addition, have the same angular velocity about some axis, due to a rigid rotation of the fluid. However, uniform translation and rotation do not contribute to the deformation of the fluid, and so are not associated with that part of the response of the material that is of interest.

In addition to a dynamic response, real fluids exhibit a thermodynamic response. Deformation gives rise to frictional forces within the fluid, and this friction dissipates a part of the kinetic energy of the fluid and causes it to appear as heat. It is possible that sufficient heat is generated to raise the temperature of the fluid appreciably.

This leads one to observe that no flow is isothermal, despite any precautions of thermostating the boundaries of the system. However, for relatively low rates of deformation, the temperature rise is insufficient to change the properties of the fluid. On the other hand, for many important flows, the viscosity of the fluid is so high that even small deformation rates generate significant amounts of heat. In this case one must be able to correct any calculations based on an isothermal analysis. This requires a knowledge of the temperature field in the fluid, as well as a knowledge of the effect of temperature on fluid properties such as viscosity.

The temperature field in an incompressible fluid satisfies an energy equation which, in Cartesian coordinates, has the form

$$\rho \hat{C}_p \left(\frac{\partial T}{\partial t} + v_j \frac{\partial T}{\partial x_j} \right) = \frac{\partial}{\partial x_j} \left(k \frac{\partial T}{\partial x_j} \right) + \tau_{ij} \frac{\partial v_i}{\partial x_j} \quad (6)$$

The heat capacity per unit mass is \hat{C}_p and the thermal conductivity is k . The term gives the volumetric rate of conversion of kinetic energy into heat through friction. It is a dissipation term.

III. SHEAR FLOW

A well-known flow situation is "simple shear flow", in which a nonzero component of velocity occurs only in a single direction. If the subscripts 1, 2, and 3 denote, respectively, the flow direction, the direction of velocity variation, and the neutral direction, then a simple shear flow is defined by

$$\mathbf{v} = (v_1, 0, 0) \quad (7)$$

$$\bar{\Delta} = \dot{\gamma}(x_2) \begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix} \quad (8)$$

These flows are sometimes called "viscometric flows", because they are achieved in capillary, Couette, and cone and plate viscometers. Note that in Equation 8, $\dot{\gamma}(X_2)$ is a scalar function of the X_2 coordinate. $\dot{\gamma}$ is a "shear" component of the rate of deformation tensor, and is commonly referred to as "shear rate".

The correspondence of the simple shear flow notation to the more common coordinate notation is given in Figure 1 for some simple flows of interest. The flows shown correspond to the most common flows found in viscometric instruments, but are by no means the only simple shear flows.

IV. CLASSIFICATION OF NON-NEWTONIAN BEHAVIOR THROUGH FLOW CURVES

A plot of τ_{xy} vs. $\dot{\gamma}$ results in a straight line passing through the origin and having slope μ . The resultant plot is known as a flow curve. Fluid materials that display nonlinear behavior through the origin at a given temperature and pressure are non-Newtonian (refer to Figure 2). Non-Newtonian fluids are broadly classified time-independent fluids, time-dependent fluids, and viscoelastic fluids. The first category is comprised of fluids for which the shear rate at any point is solely a function of the instantaneous shear stress. In contrast, time-dependent fluids are those for which shear rate depends on both the magnitude and duration of shear. Some fluids in this second class also show a relationship between shear rate and the time lapse between consecutive applications of shear stress. Less common viscoelastic fluids display the behavior of partial elastic recovery upon the removal of a deforming shear stress.

Time-dependent non-Newtonian fluids can exhibit the property of a yield stress. Yield stress τ_y can be thought of as a minimum stress value that must be exceeded for deformation to occur. In other words, when $\tau_{xy} > \tau_y$ the internal structure of the fluid remains intact, and when $\tau_{xy} > \tau_y$, shearing movement takes place. Flow curves for this type of materials are illustrated in Figure 3B. An idealistic fluid is the Bingham plastic, in which an attempt is made to describe non-Newtonian behavior with a linear constitutive equation. The rheological flow curve in Figure 3B for this fluid can be stated as:

$$\mu_{\alpha} = \eta + \frac{\tau_y}{\dot{\gamma}} \quad (9)$$

where μ_{α} is the apparent viscosity of the fluid and is analogous with the Newtonian apparent viscosity

$$\mu_{\alpha} = \frac{\tau_{xy}}{\dot{\gamma}} \quad (10)$$

The Bingham plastic constitutive equation contains a yield stress, τ_y , and a term η referred to as the plastic viscosity. Equation 9 states that the apparent viscosity decreases with increasing shear rate. In practical terms this means that a value of the apparent viscosity can only be related as a flow property

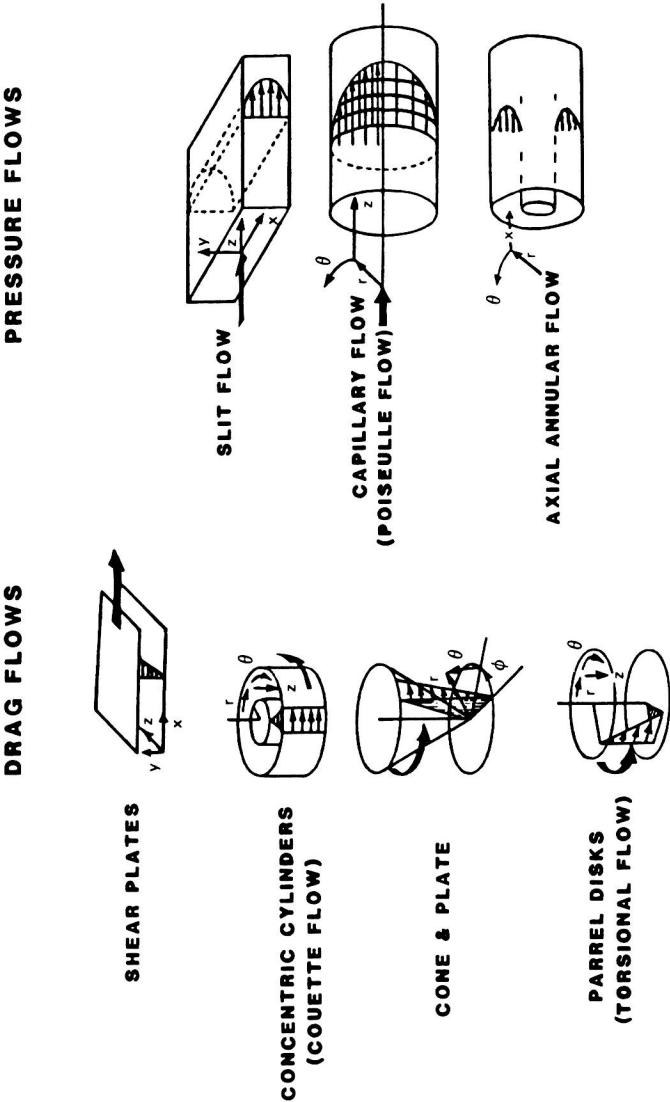


FIGURE 1. Common shear flow geometries.

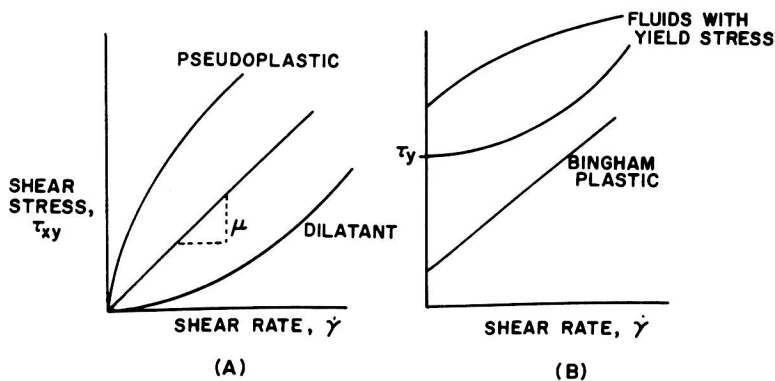


FIGURE 2. Flow curves for non-Newtonian, time-independent materials.

with a corresponding shear rate. Although the Bingham plastic fluid itself is idealistic, it can be applied to modeling a portion of a real non-Newtonian's flow curve. Also, as shown in subsequent chapters, many materials show only a small departure from exact Bingham plasticity and therefore can be approximately described by Equation 9.

A large variety of industrial fluid-like materials may be described as being pseudoplastic. The flow curve is illustrated in Figure 2. In examining this curve, note that it is characterized by linearity at very low and very high shear rates. The slope of the linear region of the curve at the high shear rate range is referred to as the viscosity at infinite shear (μ_∞), whereas the slope in the linear portion near the origin is the viscosity at zero shear rate (μ_0). A logarithmic plot of τ_{xy} vs. $\dot{\gamma}$ is found to be linear over a relatively wide shear rate range and hence may be described by a power law expression (known as the Ostwald-de Waele model):

$$\tau_{xy} = K\dot{\gamma}^n \quad (11)$$

The slope n and intercept K are given the names "flow behavior index" (or "pseudoplasticity index") and "consistency index", respectively. The power law exponent ranges from unity to zero with increasing plasticity (i.e., at $n = 1$, the equation reduces to the constitutive equation of a Newtonian fluid). The value of the consistency index is obtained from the intercept on the τ_{xy} axis and hence represents the viscosity at unit shear rate. As shown later for a variety of polymers, K is very sensitive to temperature, whereas n is much less sensitive. By analogy to Newton's law, the apparent viscosity of a power law fluid is

$$\mu_a = K\dot{\gamma}^{n-1} \quad (12)$$

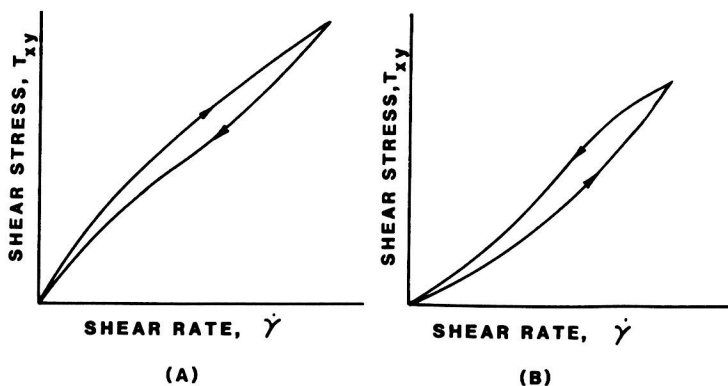


FIGURE 3. Hysteresis loops for time-dependent fluids. (A) Thixotropic hysteresis; (B) rheopectric hysteresis.

Since $n < 1$, the apparent viscosity of a pseudoplastic fluid decreases with increasing shear rate, and hence these materials are often referred to as shear thinning.

The next class of time-independent fluids are dilatant materials. Volumetric dilatancy refers to the phenomenon whereby an increase in the total fluid volume under application of shear occurs. Rheological dilatancy refers to an increase in apparent viscosity with increasing shear rate. The flow curve is illustrated in Figure 2. As in the case of a pseudoplastic fluid, a dilatant material is usually characterized by zero yield stress. Hence, the power law model may also be used to describe this fluid behavior, but with n -values greater than unity.

Time-dependent non-Newtonian fluids are classified as thixotropic and rheopectic. Thixotropic fluids display a reversible decrease in shear stress with time at a constant shear rate and temperature. The shear stress of such a material usually approaches some limiting value. Both thixotropic and rheopectic fluids show a characteristic hysteresis as illustrated by the flow curves in Figure 3. The flow curves are constructed from data generated by a single experiment in which the shear rate is steadily increased from zero to some maximum value and then immediately decreased toward zero. The arrows on the curves denote the chronological progress of the experiment. An interesting complexity of these materials is that the hysteresis is time history-dependent. In other words, changing the rate at which $\dot{\gamma}$ is increased or decreased in the experiment alters the hysteresis loop. For this reason, generalized approaches to defining an index of thixotropy have not met with much success.

Rheopectic fluids are sometimes referred to as antithixotropic fluids because they exhibit a reversible increase in shear stress over time at a constant rate of shear under isothermal conditions. The location of the hysteresis loop shown in Figure 3B is also dependent on the time history of the material, including the rate at which $\dot{\gamma}$ is changed.

TABLE 1
Examples of Non-Newtonian Materials

Time-independent fluids	
Fluids with a yield stress	Various plastic melts, oil well drilling fluids, oils, sand suspensions in water, coal suspensions, cement and rock slurries, peat slurries, margarine, shortenings, greases, aqueous thorium oxide slurries, grain water suspensions, toothpaste, soap, detergent slurries, paper pulp
Pseudoplastic fluids (without yield stress)	Rubber solution, adhesives, polymer solutions and melts, greases, starch suspensions, cellulose acetate, mayonnaise, soap, detergent slurries, paper pulp, paints, certain pharmaceutical suspensions, various biological fluids
Dilatant fluids (without yield stress)	Aqueous suspensions of titanium dioxide, corn flour/sugar solutions, gum arabic in water, quicksand, wet beach sand, deflocculated pigment dispersions with suspended solids such as mica and powdered quartz, iron powder dispersed in low-viscosity liquids.
Time-dependent fluids	
Thixotropic fluids	Melts of high molecular weight polymers, some oil well drilling fluids, various greases, margarine and shortening, printing inks, various food substances, paints
Rheopectic fluids	Bentonite clay suspensions, vanadium pentoxide suspensions, gypsum suspensions, various soils, dilute suspensions of ammonium oleate
Viscoelastic fluids	Bitumens, flour dough, napalm, various jellies, polymers and polymer melts (e.g., nylon), various polymer solutions

The final category of non-Newtonians is viscoelastic fluids, which are materials exhibiting both viscous and elastic properties. Viscoelasticity is described in some detail later. It should be kept in mind that for purely Hookean elastic solids the stress corresponding to a given strain is time-independent, but with viscoelastic materials the stress dissipates over time. Viscoelastic fluids undergo deformation when subjected to stress; however, part of their deformation is gradually recovered when the stress is removed. Therefore, viscoelastic substances may be fancifully referred to as fluids that have memory. Viscoelasticity is frequently observed in the processing of various polymers and plastics. For example, in the production of synthetic fibers such as nylon for ultrafine cable, material is extruded through a die consisting of fine perforations. In these examples the cross-section of the fiber or cable may be considerably larger than that of the perforation through which it was extruded. This behavior is a result of the partial elastic recovery of the material. Table 1 provides examples of the various types of non-Newtonian fluids.

This book attempts to relate rheological characteristics observed in laboratory studies to commercial processing problems. The materials discussed