All About Viscosity

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Chapter 1 - INTRODUCTION

As preparation for this course, it is assumed that the student is BS level graduate, preferably in Chemical or Mechanical Engineering, familiar with fluid flow and heat transfer calculations.

DEFINITION: **Viscosity** can be defined as the property of any fluid that determines its resistance to motion, against a containing surface or against adjacent increments of itself. It is a characteristic property that may be near-constant, always varies to some degree with temperature, and for many liquids may be highly variable with the flowing velocity. The basic, quantitative definition of viscosity is shown in the figure below.

Any flowing fluid – either in turbulent or laminar flow - exerts a resisting, frictional force on a solid surface, proportional to the rate of change of velocity, \( V \), increasing within a short distance, \( x \), from the surface. This rate is called the shear rate, \( S = \frac{dV}{dx} \) in units of \( \text{ft/sec}/\text{ft} \), or \( \text{cm/sec}/\text{cm} \), \( = 1/\text{sec} \). The force applied to the surface, is called the shear stress per unit area of the surface, \( \tau = \frac{F}{A} \), in units of \( \text{lb} \cdot \text{sec}/\text{ft}^2 \), or \( \text{dyne}/\text{cm}^2 \). The units of force are not to be confused with units of mass, such as \( \text{lb}_m = \text{lb}/\text{g} = \text{lb}/32.2 \). Absolute or dynamic viscosity is then defined as \( \mu = \frac{\tau}{S} = \frac{\text{lb} \cdot \text{sec}/\text{ft}^2}{\text{dyne} \cdot \text{sec}/\text{cm}^2} \). In the metric units, 1.0 dyne-sec/cm\(^2\) is defined as 1.0 Poise. Which is the viscosity of water at 60\(^\circ\)F. The general and most usual measurement of absolute viscosity is the centipoise, \( \text{cp} = .001 \text{ Poise} \). This is the true or **dynamic** viscosity, as opposed to the **kinematic** viscosity, defined below.

For translation to standard US engineering units, 1 Poise = 0.00209 lb-sec-ft\(^2\). This same variable is often reported in a confusing variety of different units. Table 1, below, gives conversion factors between these units\(^{(1)}\). As generally used in fluid flow and heat transfer calculations, raw viscosity data, Lbr-sec-ft\(^2\), must be converted to lbm-ft-sec, which is done by multiplication by gravity, x 32.2, as shown below. Specifically for many heat transfer formulae, \( \mu \) is required in lbm-ft-hr, requiring multiplication by 3600 sec/hr. In general, when viscosity is used in dimensionless moduli, such as Reynolds Number (Vdp/\( \mu \)) or Prandtl Number (c\(_p\)\( \mu \)/k), all variables are converted to compatible units such that dimensions will in fact cancel.
Viscosity data is also often reported in terms of **kinematic viscosity**, \( \nu \) ("nu"), which is the absolute viscosity, \( \mu \), in lb/sec-ft, divided by fluid density, lb/ft\(^3\), resulting in units of ft\(^2\)/sec or cm\(^2\)/sec, the latter in metric units being defined as a Stoke, so \( 0.001 \text{ cm}^2/\text{sec} = 1 \text{ Centistoke} \). Various industries use different units for kinematic viscosity. Measurement and direct use of kinematic viscosity is only relevant to the uncomplicated world of Newtonian fluids. Direct measurement of kinematic viscosity is generally done by observing flow rates through some calibrated orifice. Further discussion of kinematic viscosity is therefore herewith relegated to Appendix A, which offers a good discussion of the relative uses of these two properties \(^3\). Different industries generally have different systems of units for measurement of kinematic viscosity. Appendix A includes a table of translation between these units, provided here for reference. In the following discussion, unless specified otherwise, “viscosity” will refer to the absolute viscosity, \( \mu \).

There are a wide range of ways to measure viscosity. Where it is necessary to determine viscosity that may vary with variation in shear rate, the shear rate must be adjusted independently. This is traditionally done with a cup type viscometer, in which a rotating cylinder is immersed in the fluid, in a container of slightly larger diameter than the cylinder. Referring to the cross-sectional sketch below, with the cylinder rotating at \( \omega \) radians/second, the shear rate is \( S = \frac{2\pi \omega r_2}{(r_1-r_2)} \). Where the rotation is driven by a falling weight unwinding of a chord from a wheel, the shear force is computed from the weight. And the area is the cylindrical surface of the vessel. Initially, in the history such devices, \( \omega \) is determined simply by the time taken for the weight to drop a fixed distance. This \( \tau \) is/was a very simple device, yielding accurate measurements of absolute viscosity, \( \mu = S/\tau \). Different values of shear rate can be set by simply changing the weight. Currently offered apparatus, however, are motor driven and use simple electronics to directly compute viscosities. Other readily available apparatus include a variety of portable, hand-held, battery-powered devices that can be simply immersed in a stream or vessel of any material, to read its viscosity, as well as fixed in-line viscometers.

![Figure 2 - Rotary Measurement of Viscosity](image)
Non-Newtonian fluids are those for which the simple linear description described above breaks down, and viscous behavior thus requires several more dimensions to be described completely. Briefly, there are many fluids where the shear stress will decrease with the shear rate. These are shear-thinning or thixotropic, also called pseudoplastic. There are fewer fluids whose shear stress increases with shear rate, which are shear-thickening or rheotropic, also called dilatant. A Bingham plastic material is essentially solid at zero shear (motion) and requires a finite applied shear stress to “let go” and start flowing. Different writers often overlap these terms to various degrees. These, and more complications, are defined in subsequent chapters.

Table 1. Conversion of Units for Absolute Viscosity, \( \mu \)

<table>
<thead>
<tr>
<th>Absolute or Dynamic Viscosity</th>
<th>centipoise</th>
<th>poise gm/cm-sec dyne-sec/cm(^2)</th>
<th>slugs/ft-sec lbf-sec/ft(^2)</th>
<th>lbm/ft-sec poundal-sec/ft(^2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>centipoise</td>
<td>( \mu )</td>
<td>1</td>
<td>0.01</td>
<td>2.09 \times 10^{-5}</td>
</tr>
<tr>
<td>poise gm/cm-sec dyne-sec/cm(^2)</td>
<td>100(\mu)</td>
<td>100</td>
<td>1</td>
<td>0.00209</td>
</tr>
<tr>
<td>slugs/ft-sec lbf-sec/ft(^2)</td>
<td>( \mu)'</td>
<td>47900</td>
<td>479</td>
<td>1</td>
</tr>
<tr>
<td>lbm/ft-sec poundal-sec/ft(^2)</td>
<td>( \mu)(')</td>
<td>1487</td>
<td>14.87</td>
<td>1/g or 0.0311</td>
</tr>
</tbody>
</table>

\( lb = \) Pounds of force. \( lbm = \) Pounds of mass.

Figure 1, above, showed a **linear** or straight line variation of velocity from the surface, so that \( S = dV/dx = \) a constant, which is what is measured over very short distances, as in Figure 2, to compute viscosity, \( \mu \). Most low-viscosity liquids and gasses, where \( S \) in fact remains constant, are
defined as *linear* or *Newtonian* fluids, in honor of Isaac Newton, who thus provided the original definition of viscosity. Table 2 shows a brief, simple comparison of viscosities of some common household materials, collected from various open sources.

To this point, linear viscosity is consistent with Newton’s clear, simple, and completely consistent laws of motion, as applied to particles, planets or spacecraft. Unfortunately, the divine grand plan of the universe had no obligation towards the convenience of engineers dealing with areas like fluid flow and heat transfer. So many fluids are quite non-linear or non-Newtonian, where \( \mu \) is not constant with distance from a surface or between flowing layers or increments of the fluid. Mathematically, linearity is defined as a simple, “well-behaved” one-way relationship, like \( y = f(x) \). When \( x \) is also variable with \( y \), like \( y = f(x=f(y)) \), the relationship is defined as non-linear – thus complicating matters. For a linear/Newtonian fluid, a single viscometer reading generally defines the viscosity, at a constant temperature. But for a non-Newtonian fluid, multiple readings are needed to observe the non-linear lines, where \( \mu = \frac{f(\mu)}{\tau} \), as shown below (Fig.3). Mathematically, non-Newtonians might be called “misbehaving fluids,” with complications discussed later.

**Table 2. Simple Comparison of some Common Fluid’s Viscosities.**

<table>
<thead>
<tr>
<th>Approximate Viscosities of Common</th>
<th>Some Examples of Viscosity</th>
<th>Viscosity, centipoise</th>
</tr>
</thead>
<tbody>
<tr>
<td>(At Room Temperature-70°F) *</td>
<td>Benzyl ether @ 20°C</td>
<td>5.33</td>
</tr>
<tr>
<td>Material</td>
<td>Glycol @ 20°C</td>
<td>19.9</td>
</tr>
<tr>
<td>Water</td>
<td>Soybean oil @ 20°C</td>
<td>69.3</td>
</tr>
<tr>
<td>Milk</td>
<td>Olive oil @ 20°C</td>
<td>84.0</td>
</tr>
<tr>
<td>SAE 10 Motor Oil</td>
<td>Light machine oil @ 20°C</td>
<td>102</td>
</tr>
<tr>
<td>SAE 20 Motor Oil</td>
<td>Heavy machine oil @ 20°C</td>
<td>233</td>
</tr>
<tr>
<td>SAE 30 Motor Oil</td>
<td>Caster oil @ 20°C</td>
<td>986</td>
</tr>
<tr>
<td>SAE 40 Motor Oil</td>
<td>Glycerin @ 20°C</td>
<td>1,490</td>
</tr>
<tr>
<td>Castrol Oil</td>
<td>Pancake syrup @ 20°C</td>
<td>2,500</td>
</tr>
<tr>
<td>Karo Syrup</td>
<td>Chocolate syrup @ 20°C</td>
<td>25,000</td>
</tr>
<tr>
<td>Honey</td>
<td>Ketchup @ 20°C</td>
<td>50,000</td>
</tr>
<tr>
<td>Chocolate</td>
<td>Peanut butter @ 20°C</td>
<td>250,000</td>
</tr>
<tr>
<td>Ketchup</td>
<td>Tar or pitch @ 20°C</td>
<td>30,000,000,000</td>
</tr>
<tr>
<td>Mustard</td>
<td>Soda Glass @ 575°C</td>
<td>1</td>
</tr>
<tr>
<td>Sour Cream</td>
<td>Blood or Kerosene</td>
<td>10</td>
</tr>
<tr>
<td>Peanut Butter</td>
<td>Ethylene Glycol or Anti-Freeze</td>
<td>15</td>
</tr>
<tr>
<td>SAE Motor Oil (SAE 10)</td>
<td>Motor Oil (SAE 10)</td>
<td>50</td>
</tr>
<tr>
<td>Corn Oil</td>
<td>Unfilled Rigid Urethane Resin</td>
<td>60 - 120</td>
</tr>
<tr>
<td>Maple Syrup or Motor Oil (SAE 30)</td>
<td>150 - 200</td>
<td></td>
</tr>
<tr>
<td>Castrol Oil or Motor Oil (SAE 40)</td>
<td>250 - 500</td>
<td></td>
</tr>
<tr>
<td>Glycerin or Motor Oil (SAE 60)</td>
<td>1,000 - 2,000</td>
<td></td>
</tr>
<tr>
<td>Pourable Urethane Rubbers</td>
<td>1,000 - 3,000</td>
<td></td>
</tr>
<tr>
<td>Honey or Corn Syrup</td>
<td>2,000 - 3,000</td>
<td></td>
</tr>
<tr>
<td>Molasses</td>
<td>5,000 - 10,000</td>
<td></td>
</tr>
<tr>
<td>Chocolate Syrup</td>
<td>10,000 - 25,000</td>
<td></td>
</tr>
<tr>
<td>Pourable Silicone Rubber</td>
<td>14,000 - 40,000</td>
<td></td>
</tr>
<tr>
<td>Ketchup or Mustard</td>
<td>50,000 - 70,000</td>
<td></td>
</tr>
<tr>
<td>Brushable Silicone Rubber</td>
<td>100,000 - 150,000</td>
<td></td>
</tr>
<tr>
<td>Peanut Butter or Tomato Paste</td>
<td>150,000 - 250,000</td>
<td></td>
</tr>
<tr>
<td>Brushable Urethane Rubber</td>
<td>200,000 - 300,000</td>
<td></td>
</tr>
<tr>
<td>Lard or Crisco Shortening</td>
<td>1,000,000 - 2,000,000</td>
<td></td>
</tr>
<tr>
<td>Caulking Compound</td>
<td>5,000,000 - 10,000,000</td>
<td></td>
</tr>
<tr>
<td>Window Putty</td>
<td>100,000,000</td>
<td></td>
</tr>
</tbody>
</table>
Table 3 shows a further comparison of viscosities of various liquids, and includes a column that identified which fluids are Newtonian and which are Thixotropic. This distinction can be quite critical in fluid flow or heat transfer calculations. Those designated as Thixotropic are beyond the scope of discussion in the following Chapter 2, and will be covered in detail in Chapter 3.

Table 3. Viscosities of Various Fluids, Identified as Newtonian or Thixotropic.

<table>
<thead>
<tr>
<th>Liquid</th>
<th>Specific Gravity at 16°c</th>
<th>Absolute Viscosity Cp</th>
<th>Temperature °C</th>
<th>Viscosity Type</th>
</tr>
</thead>
<tbody>
<tr>
<td>China wood Oil</td>
<td>0.94</td>
<td>300</td>
<td>21</td>
<td>N</td>
</tr>
<tr>
<td>Coconut Oil</td>
<td>0.93</td>
<td>55</td>
<td>24</td>
<td>N</td>
</tr>
<tr>
<td>Coconut Oil</td>
<td>0.93</td>
<td>30</td>
<td>38</td>
<td>N</td>
</tr>
<tr>
<td>Corn Oil</td>
<td>0.92</td>
<td>28</td>
<td>57</td>
<td>N</td>
</tr>
<tr>
<td>Cotton Seed Oil</td>
<td>0.88</td>
<td>62</td>
<td>24</td>
<td>N</td>
</tr>
<tr>
<td>Cotton Seed Oil</td>
<td>0.83</td>
<td>24</td>
<td>52</td>
<td>N</td>
</tr>
<tr>
<td>Linseed Oil Raw</td>
<td>0.93-0.94</td>
<td>29</td>
<td>38</td>
<td>N</td>
</tr>
<tr>
<td>Olive Oil</td>
<td>0.91</td>
<td>40</td>
<td>38</td>
<td>N</td>
</tr>
<tr>
<td>Palm Oil</td>
<td>0.92</td>
<td>43</td>
<td>38</td>
<td>N</td>
</tr>
<tr>
<td>Peanut Oil</td>
<td>0.92</td>
<td>38</td>
<td>38</td>
<td>N</td>
</tr>
<tr>
<td>Soya Bean Oil</td>
<td>0.93</td>
<td>60</td>
<td>24</td>
<td>N</td>
</tr>
<tr>
<td>Soya Bean Oil</td>
<td>0.93</td>
<td>12</td>
<td>80</td>
<td>N</td>
</tr>
<tr>
<td>Turpentine</td>
<td>0.86</td>
<td>2.0</td>
<td>16</td>
<td>N</td>
</tr>
<tr>
<td>Acetate Glue</td>
<td>1.22</td>
<td>1200-1400</td>
<td>20</td>
<td>T</td>
</tr>
<tr>
<td>NaOH 20%</td>
<td>1.33</td>
<td>1.0</td>
<td>18</td>
<td>N</td>
</tr>
<tr>
<td>NaOH 30%</td>
<td>1.43</td>
<td>1.0</td>
<td>18</td>
<td>N</td>
</tr>
<tr>
<td>NaOH 40%</td>
<td>1.43</td>
<td>1.0</td>
<td>18</td>
<td>N</td>
</tr>
<tr>
<td>Cresol Crystals</td>
<td>1.26 at 20°C</td>
<td>1200</td>
<td>20</td>
<td>N</td>
</tr>
<tr>
<td>Glycerine 100%</td>
<td>1.76</td>
<td>176</td>
<td>38</td>
<td>N</td>
</tr>
<tr>
<td>Glycerine 100%</td>
<td>1.11</td>
<td>1.9</td>
<td>38</td>
<td>N</td>
</tr>
<tr>
<td>Isopropyl Alcohol</td>
<td>1.11</td>
<td>1.9</td>
<td>85</td>
<td>N</td>
</tr>
<tr>
<td>Lacquer 25% Solids</td>
<td>1.11</td>
<td>1.9</td>
<td>85</td>
<td>N</td>
</tr>
<tr>
<td>Polyester</td>
<td>1.1 at 30%</td>
<td>3000</td>
<td>30</td>
<td>T</td>
</tr>
<tr>
<td>Polypropylene</td>
<td>1.09 at 85°</td>
<td>240,000</td>
<td>50</td>
<td>T</td>
</tr>
<tr>
<td>Polyisobutylene</td>
<td>1.09 at 85°</td>
<td>24000</td>
<td>85</td>
<td>T</td>
</tr>
<tr>
<td>Plastisol</td>
<td>2.5</td>
<td>28,000</td>
<td>18</td>
<td>T</td>
</tr>
<tr>
<td>Printers Ink</td>
<td>1.09 at 85°</td>
<td>560-2200</td>
<td>38</td>
<td>T</td>
</tr>
<tr>
<td>Printers Ink</td>
<td>1.09 at 85°</td>
<td>560-2200</td>
<td>38</td>
<td>T</td>
</tr>
<tr>
<td>Resin Solution</td>
<td>1.09 at 85°</td>
<td>560-2200</td>
<td>38</td>
<td>T</td>
</tr>
<tr>
<td>Resin Solution</td>
<td>1.09 at 85°</td>
<td>560-2200</td>
<td>38</td>
<td>T</td>
</tr>
<tr>
<td>Resin Solution</td>
<td>1.09 at 85°</td>
<td>560-2200</td>
<td>38</td>
<td>T</td>
</tr>
<tr>
<td>Sulphonic Acid</td>
<td>1.04</td>
<td>125</td>
<td>30</td>
<td>T</td>
</tr>
<tr>
<td>Triacetate Dope</td>
<td>1.04</td>
<td>125</td>
<td>30</td>
<td>T</td>
</tr>
<tr>
<td>GLYCOL PRODUCTS</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Propylene</td>
<td>1.04</td>
<td>52</td>
<td>21</td>
<td>N</td>
</tr>
<tr>
<td>Triethylene</td>
<td>1.12</td>
<td>40</td>
<td>21</td>
<td>N</td>
</tr>
<tr>
<td>Diethylene</td>
<td>1.12</td>
<td>32</td>
<td>21</td>
<td>N</td>
</tr>
<tr>
<td>Ethylene</td>
<td>1.12</td>
<td>18</td>
<td>21</td>
<td>N</td>
</tr>
</tbody>
</table>
All of the above tables and charts give simple values for fluids in the temperature ranges for which they are most commonly used. For those designated thixotropic, the values given assume completely developed turbulence at relatively high shear rates, to be discussed further in Chapter 3.

A Unifying Principle

Returning to Newton’s basic law of viscosity, \( F = \mu \frac{dV}{dx} \) or \( Fdx = \mu dV \), and converting \( F \), lb to units of mass, lb \( \times \) g = ft-lb/s-sec\(^2\), both sides of the equation are now in units of ft-lb/sec, which are units of energy transfer, convertible to m-gm/sec, kcal/hr, or watts. The equation is thus a measure of momentum transfer between layers of flowing fluid, \( \frac{dV}{dx} \), or between fluid and containing wall. This is the rate of energy loss along the path of flowing fluid, causing a pressure drop. So the basic equations for all forms of energy transfer, analogous with proportionality constants, bring properties of the energy conducting substance \( \mu \), \( k \), and \( R \) all in appropriate units of energy transfer per area.

Viscosity, fluid flow: \( F = \mu \frac{dV}{dx} \)

Heat transfer: \( Q = k \frac{dT}{dx} \)

Electrical resistance: \( I = \frac{1}{R} \frac{dE}{dx} \)

This analogy also extends to diffusion:

Concentration gradient, \( C(x) = D \frac{dc}{dx} \) or \( = D \frac{dp}{dx} \), where \( c = \) concentration, mol fraction or \( p = \) partial pressure of a diffusing component.

Scope: For the purposes of this work, “fluid” refers to any flowing or flowable liquid or gas, of uniform properties, of which viscosity is one. This includes any functionally single-phase material, such as stable suspensions, emulsions, pastes, gels, colloids or some slurries, in which fine suspended solids do not settle or separate when the fluid is not flowing. It does not completely cover conditional slurries, in which solid particles, however fine, are in suspension only when the carrier fluid is in motion, depending on turbulence to remain in suspension. Such materials have totally different rheological properties, which will be discussed only briefly in a later chapter.
Author’s Note: My first job after graduation, way back in 1958, was in the quality control lab of a sodium silicate plant. Every morning, my first task was to collect liquid silicate samples from the past 24 hours production and run viscosity tests, using an old, dropping-weight type, Brookfield viscometer.

~~ End of Chapter 1
Chapter 2 - VISCOSITY VARIATION WITH TEMPERATURE

While still dealing with simple, linear, Newtonian fluids, the only significant process variable is temperature. All fluid viscosities decrease with temperature, to some degree. For most fluids, temperature variation can be looked up, or simply measured. There is not much to be said about this except to simply present some reference data\(^{(2)}\) below (Figs. 4 & 5) for some common fluids that are generally presumed to be essentially linear or Newtonian. As these are all liquid at ambient to moderately hot temperatures, viscosities are given in centipoises.

Figure 4.
1. Ethane (C₂H₆)
2. Propane (C₃F₈)
3. Butane (C₄H₁₀)
4. Natural Gasoline
5. Gasoline
6. Water
7. Kerosene
8. Distillate
9. 48 Deg. API Crude
10. 40 Deg. API Crude
11. 35.6 Deg. API Crude
12. 32.6 Deg. API Crude
13. Salt Creek Crude
14. Fuel 3 (Max.)
15. Fuel 5 (Min.)
16. SAE 10 Lube (100 V.I.)
17. SAE 30 Lube (100 V.I.)
18. Fuel 5 (Max.) or Fuel 6 (Min.)
19. SAE 70 Lube (100 V.I.)
20. Bunker C Fuel (Max.) and M.C. Residuum
21. Asphalt

Data extracted in part by permission from the Oil and Gas Journal.
To define the viscosity-temp relationship mathematically, it would be desirable to have an equation describing the fundamental relationship between these variables. An approach to this need is found in the following (Source: Wikipedia): “A molecular view of liquids can be used for a qualitative picture of the decrease in the shear (or bulk) viscosity of a simple fluid with temperature. As the temperature increases, the thermal velocity increases. However, much more important is the rapid decrease of the mean free path with temperature. The reason for this is that temperature increase releases more and more molecules to move around and interact with any given molecule. The actual process can be quite complex and is typically represented by simplified mathematical or empirical models.” Perhaps a simpler way of saying this is that viscosity decreases with the rate of momentum transfer from the fluid towards the containing wall, which in turn is proportional to turbulence. Temperature is a measure of the molecular activity or micro-turbulence in a fluid. So the micro-turbulence of increasing temperature simply augments the turbulence caused by gross fluid motion, thereby assisting momentum transfer.

Many attempts have been made to describe this behavior mathematically. The simplest is a function of the form:

$$\mu(T) = \mu_0 e^{-bT}$$

where $$\mu_0$$ and $$b$$ are empirical constants for each/any specific fluid,

which exist only theoretically and are thus not available for reference. But given viscosities at 2 or 3 temperatures, these values can be fairly easily determined. Method: From $$\mu$$ and T columns on your Excel spreadsheet, insert an x-y “scatter” chart and add a trendline. Select an exponential trendline and show equation plus R^2 on chart. So for water, using 4 $$\mu$$ values from a table, this equation for water is:

$$\mu(T), cP = 2.1742 e^{-0.01T}$$

with T in °F, with a very good correlation factor, R^2, of 0.9718.

While water viscosity varies but little with temperature, such an equation can be extremely valuable for other fluids, where viscosity may vary widely over your range of interest. Thus the empirical constants above are defined. As an alternative procedure, selecting a power function trendline, $$y = ax^{-b}$$, gives an equation for water of:

$$\mu(T), cP = 5648 T^{-0.875}$$

with an even better correlation factor of 0.9914.

For those wishing to dig deeper into the fundamental chemistry of fluid thermodynamics, another theoretical correlation is:

$$\mu(T) = \mu_0 e^{(E/RT)}$$

-- where E is activation energy and R is the universal gas constant, T

This dimension of study, however, is beyond the scope of this work.

Figure 6, below, shows viscosity data for molten iron and tar from Athabasca tar sands, selected at random from open sources (internet), in various units of viscosity and temperature. They are included here simply to show how all “well behaved” fluids can be described by empirical curves at least similar to the above form.
So far, it has been assumed that all the Newtonian/linear fluids considered are also of uniform, single-phase composition. Some of them are stable emulsions or suspensions, with quite high viscosities, but behave like uniform fluids. Some show a great increase approaching the lower end of their temperature, where the above power function $\mu = aT^b$, approaches infinity – and thus does not apply. This is generally due to a phase change, as the material approaches its melting/freezing point and crystallization begins, with solid particles impeding free turbulence.

A separate category is glass, defined as any mineral or mixture of amorphous, rather than crystalline structure, having no temperature of “melting” or crystallization. In simplest terms, glass may be described as liquid of extremely high viscosity - approaching infinity – at ambient temperatures. Figure 7, below, shows $\mu(T)$ curves for several glass varieties. Note the extremely high viscosities at relatively low temperatures, beyond which most metals and minerals would melt – that is, change from a solid, crystalline phase to a visually recognizable liquid of relatively low viscosity. Borosilicate glass (“Pyrex”) is commonly used for laboratory glassware because it can be softened to a malleable, easily worked “solid,” in the 600~800ºC range, that can be manually formed, stretched, twisted and joined to create a wide variety of shapes with minimal skill. (Author’s note: ‘Once had a most enjoyable job for a couple of months as apprentice glass blower in a university chemistry department, making and repairing laboratory glassware. Joining and bending Pyrex was easy, but I never mastered soda-lime glass that would simply melt as it reached a working point.)

This gradual transition from viscous liquid to malleable solid also describes most metals, such as iron in Figure 6 above, although metals in this range are more crystalline solids than “Glassy” liquids. In practical applications, knowing the numerical value of their viscosity is seldom of interest. Thus the value of any predictive formulae is limited to relatively low temperature ranges where it is necessary to compute pressure drops or neat transfer rates. Concern with high viscosities at relatively low temperatures arises in some food product applications, such as mayonnaise, mustard, catchup, and various thick syrups, where increasing the temperature to lower viscosity would greatly accelerate mixing operations, but would chemically damage heat sensitive components.
As an exercise in establishing empirical description of undocumented fluids, Figure 8 shows a range of viscosity curves, in units of poises, for slag formed from molten ash of various coals consisting of a very broad and widely variable sedimentary rock compositions\(^4\) which are similar to natural flowing lava. Special viscometers are readily available for measurement of such high temperature materials. These highly complex, glassy materials, probably becoming 2-phase with decreasing temperature, are probably non-Newtonian. The basis for interest is in coal gasification processes, where residual ash is drained from reactors, where temperature is critical. If viscosity becomes too high, this “synthetic lava” solidifies and plugs up the drain hole. If the temperature is allowed to become too high, to minimize viscosity, then the molten slag functions as a solvent etching away refractory linings, and may also start to melt steel.
From this collection of data, Figure 9 has selected coals from 2 North Dakota mines, and attempted to use the power function, $\mu = aT^b$, with trendlines as indicated. Note that the correlation, $M^2$, is rather poor, due mainly to the steep increase at the lower end. This is attributed to be beginning of crystallization/solidification, where the material is no longer a uniform liquid.

Figure 9. Viscosity-Temperature Data for Molten Slag from Ash/Mineral Content of Two North Dakota Lignites. Units: Poises vs. °C
Summary

For uniform, homogenous, single phase liquids, viscosity decreases with temperature in a generally predictable manner.

Approaching the lower limit of measurable viscosity-temperature measurements, viscosity may increase at a high and unpredictable rate as crystallization begins.

For amorphous materials designated as “glassy”, there is no crystallization, but fluid viscosity simply approaches infinity.

For homogenous, “well-behaved” fluids, viscosity-temperature curves can generally be approximated by empirical exponential ($\mu = \mu_0 e^{-bt}$) or power functions ($\mu = aT^b$).

~~ End of Chapter 2 ~~
Chapter 3 - NON-NEWTONIAN FLUIDS

The term non-Newtonian, or non-linear, is used to describe the rheological behavior of any fluid whose shear stress and viscosity varies with shear rate in any way other than a straight line. Definitions of categories of non-Newtonianism are rather vague and variable, and often overlapping, depending on reference source. So this section may lead to some confusion. Reconsider Figure 3, repeated here for reference.

The most common and important category of non-Newtonian fluids is those which are shear-thinning – or less-commonly pseudoplastic - meaning that the shear stress increases at a decreasing rate with increasing shear rate. Since viscosity is defined as \( \frac{\tau}{S} \), it decreases with increasing shear rate. So, the faster it is flowing, the thinner or less viscous it becomes. But these fluids generally do not respond instantaneously to changes in shear rate, but take some finite amount of time. This time dependence is strictly defined as thixotropic. But since most shear-thinning fluids are also thixotropic, the term thixotropic is commonly applied to all of these fluids. So for this discussion, thixotropic will be used for all shear-thinning fluids, regardless of their specific time-dependency, which is generally not known.

Shear-thickening, or dilatant behavior is relatively rare and little-studied, and is discussed later in this chapter. Fluids which exhibit this property are usually called rheopectic. Examples of rheopectic fluids include some gypsum pastes, printer inks, and lubricants. There is intensive ongoing research into rheopectic materials especially with regard to potential uses in shock absorption. In addition to obvious potential military applications, rheopectic padding and armor could offer significant advantages over alternative materials currently in use in a wide range of fields from sporting goods and athletic footwear to skydiving and automobile safety.

As another categorical definition, many thixotropic / shear-thinning fluids, have an initial, threshold shear stress, below which they will not start flowing. These, in Figure 3, are called Bingham plastics. Examples are mayonnaise and toothpaste. At this point, definitions become more complicated. Many viscous fluids also exhibit more-or-less Binghamatic behavior, in which the fluid will not move until some threshold shear force is applied. As a very practical example, Figure 10 shows \( \tau(S) \) for fresh cement/concrete. Some of the curves are slightly shear-thinning, but all show Bingham Plastic behavior, requiring a shear stress, \( \tau \), between zero and 30 Pa to start flowing.
Explanation of the different lines in Fig.10 are not included here, but are differences in solids loading (wt. % solids) and particle size range, which represent a dimension in fluid properties only marginal to the scope of this work.

This threshold force for Bingham plastics may be erratic and inconsistent, as the decreasing slope, \(-\frac{d\mu}{dS}\), becomes very steep and difficult to measure accurately, as \(S\) approaches zero. This will be demonstrated in a later example.

A good, illustrative example of the most common thixotropic fluid, close to you, the Reader, is your blood. Examples of blood viscosity vs. shear rate are shown in Figure 10, below.

**Figure 11. Examples of Viscosity Data for Human Blood.** *(References lost)*

These plots show how the viscosity of your blood, if flowing velocity comes close to stopping, can increase by 3 or 4 times viscosity at normal flow rates. When this happens, it may start to form clots, and this may lead to death.

For further clarification — or possibly confusion - of shear-thinning and thixotropic behavior, the following is lifted directly from Wikipedia.

"Thixotropy is a time-dependent shear thinning property. Certain gels or fluids that are thick or viscous under static conditions will flow (become thin, less viscous) over time when shaken, agitated, sheared or otherwise stressed (time dependent viscosity). They then take a fixed time to return to a more viscous state. Some non-Newtonian pseudoplastic fluids show a time-dependent change in viscosity; the longer the fluid undergoes shear stress, the lower its viscosity. A thixotropic fluid is a fluid which takes a finite time to attain equilibrium viscosity when introduced to a steep change in shear rate. Some thixotropic fluids return to a gel state almost instantly, such as ketchup, and are called pseudoplastic fluids. Others such as yogurt take much longer and can become nearly solid. Many gels and colloids are thixotropic materials, exhibiting a stable form at rest but becoming fluid when agitated. Thixotropy arises because particles or structured solutes require time to organize."
Some fluids are anti-thixotropic: constant shear stress for a time causes an increase in viscosity or even solidification. Fluids which exhibit this property are generally called rheopectic. Anti-thixotropic fluids are less well documented than thixotropic fluids.

Some clays are thixotropic, with their behavior of great importance in structural and geotechnical engineering. Some clay deposits found in the process of exploring caves exhibit thixotropism: an initially solid-seeming mudbank will turn soupy and yield up moisture when dug into or otherwise disturbed. These clays were deposited in the past by low-velocity streams which tend to deposit fine-grained sediment. Drilling muds used in geotechnical applications can be thixotropic. Honey from honey bees may also exhibit this property under certain conditions. Both cytoplasm and the ground substance in the human body are thixotropic, as is semen.

A thixotropic fluid is best visualized by an oar blade embedded in mud. Pressure on the oar often results in a highly viscous (more solid) thixotropic mud on the high pressure side of the blade, and low viscosity (very fluid) thixotropic mud on the low pressure side of the oar blade. Flow from the high pressure side to the low pressure side of the oar blade is non-Newtonian. (i.e.: fluid velocity is not linearly proportional to the square root of the pressure differential over the oar blade).

Many kinds of paints and inks—e.g. plastisols used in silkscreen textile printing—exhibit thixotropic qualities. In many cases it is desirable for the fluid to flow sufficiently to form a uniform layer, then to resist further flow, thereby preventing sagging on a vertical surface. Some other inks are designed to regain viscosity even faster, once they are applied, in order to protect the structure of the dots for accurate color reproduction.”

As a visual summary of non-Newtonian rheology, for a wide variety of fluids, see Table 4, below. It should be kept in mind that many or most shear-thinning fluids are also thixotropic, but with variable and often very short time delays in response to changes in shear rates. Therefore, the terms thixotropic and shear-thinning often used interchangeably.

Adding a further dimension of complexity in characterizing non-Newtonian fluids, many shear-thinning fluids exhibit hysteresis in their plots of shear stress vs. shear rate, as shown in Figure 11 below. This is where their descending \( \tau(S) \) curve is lower than their ascending curve, though between the same end points. This is because the suspended solids, when at rest, tend to partially agglomerate into globs or clots, which do not break up immediately when motion begins, but take time for full viscosity to develop to disperse them. This is illustrated in Figure 11, showing particles in a fluid in laminar flow, with many of them in the form of solid clots that have not yet been sheared apart by flowing layers of fluid. This sort of \( \tau(S) \) plot is therefore not a true property of the material, but rather an “experimental artifact,” determined by time of measurement of each point along the ascending curve.
Table 4. Classification of Fluids by Rheological Category.\textsuperscript{5}

<table>
<thead>
<tr>
<th>Classification</th>
<th>Example Properties</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Viscoelastic</strong></td>
<td><strong>Kelvin material, Maxwell material</strong> &quot;Parallel&quot; linear of elastic and viscous effects\textsuperscript{[2]} Some lubricants, whipped cream, Silly Putty</td>
</tr>
<tr>
<td><strong>Rheopecty</strong></td>
<td><strong>Apparent viscosity</strong> with duration of stress Synovial fluid, printer ink, gypsum paste</td>
</tr>
<tr>
<td><strong>Thixotropic</strong></td>
<td><strong>Apparent viscosity</strong> with duration of stress\textsuperscript{[2]} Yogurt, peanut butter, xanthan gum solutions, aqueous iron oxide gels, gelatin gels, pectin gels, hydrogenated castor oil, some clays (including bentonite, and montmorillonite), carbon black suspension in molten tire rubber, some drilling muds, many paints, many floc suspensions, many colloidal suspensions</td>
</tr>
<tr>
<td><strong>Non Newtonian Viscosity</strong></td>
<td><strong>Shear thinning</strong> \textsuperscript{(pseudoplastic)} Apparent viscosity decreases with increased stress\textsuperscript{[4][5]} Nail polish, whipped cream, ketchup, molasses, syrups, paper pulp in water, latex paint, ice, blood, some silicone oils, some silicone coatings, sand in water</td>
</tr>
<tr>
<td><strong>Generalized Newtonian fluids</strong></td>
<td><strong>Viscosity is constant. Stress depends on normal and shear strain rates and also the pressure applied on it</strong> Blood plasma, custard, water</td>
</tr>
</tbody>
</table>
When viscosities are measured by a traditional, dropping weight viscometer, the time for each data point is determined by the distance the weight is dropped. In most modern electronic viscometers, the applied shear rate, as rotation speed, is programmed for a fixed time in seconds for each data point, or is a continuous ascending and then descending rate, typically rather short, as shown in Figure 12 (used for some measurement of fresh cement). Such standardized measurements are valid only for true shear-thinning fluids, such as blood, where a time response for fluidization of the clots or blobs is near instantaneous.

Figure 13. Example Shear Rate vs. Time for Typical Programed Viscometer Test.

For further/alternative discussion of non-Newtonian rheology, see Appendix B, which goes deeper into the time dependency of thixotropic behavior. It also shows an excellent example of thixotropy in the application of paint to a vertical surface. When the paint brush is moving, applying the paint, viscosity is low, so that paint spreads evenly without brush marks. But when motion stops, as the brush is removed from the wall, viscosity almost instantaneously increases to a level high enough that the paint cannot respond to gravity and flow down the wall, which would leave streak. So the paint can be called truly shear-thinning, but also thixotropic with an extremely short time response.

All of the fluids covered by this discussion so far are assumed to be stable suspensions, emulsions, or pastes that do not separate when not in motion. A true slurry here is defined as suspension of solids in a liquid, where the suspension is maintained by turbulence, so that the solids settle when the fluid is not in motion. The following example, in Chapter 4, deals with a stable non-settling suspension that is therefore not truly a slurry.

Mixing

Viscosity may also be defined as the cohesive force between adjacent molecules of the same fluid. In mixing fluids of different viscosities, the energy applied must overcome this force to insert different molecules between them.

Summary

- Non-Newtonian rheological behavior of shear-thinning fluids is described as thixotropic, pseudoplastic, Bingham plastic (“binghamatic”), and with hysteresis (“hysterical”?). These categories often overlap and terms are applied interchangeably by different sources, causing some ambiguity in the use of these classifications.
• Many or most simple, purely shear-thinning fluids, may be at least marginally Binghamatic, as they are simply non-fluid as Shear rate approaches zero, but have no specific, measurable plastic yield strength.

• Plots of viscosity, \( \mu \) vs. S (Shear rate), are generally ambiguous as S approaches zero, where viscosity may appear to approach infinity. This is because \( \mu \) is defined as a fluid property, but such materials essentially cease to function as fluids when not in motion.

• For “hysterical” fluids, the upper (increasing shear) line is useful to determine the initial viscosity when the fluid begins to flow, either by gravity or pumped. It determines the pumping power or pressure drop to start the fluid moving in a filled pipe. After some time, as full turbulence is developed, the lower line (lower viscosity) will apply.

• For such fluids, viscosity curves produced by “standard tests” with programmable viscometers, may be essential for comparison with published data for other fluids, but are experimental artifacts, variable with the time span of the measurements.

• Some fluids of high viscosity are generally Newtonian, but may be marginally thixotropic or Binghamatic. The distinction is not well-defined.

~~~ End of Chapter 3 ~~~
Chapter 4 - AN EXAMPLE: CASE HISTORY

Hydrothermally Dried “Coal-Water Fuel.”

Here we shall see an example of a previously non-existent fluid, studied intensively and found to display all of the characteristics defined above. Lignite is a “low rank” (young) coal, generally deposited in early Cenozoic times. Lignites generally are high in moisture and ash, thus reducing their calorific value, compared with higher rank (older) coals, such as bituminous and anthracite. Because of this, the cost per ton-mile of shipment is generally too high to justify shipping lignites across long distances. Some lignites are as high as 50% moisture, and appear dry to eye and touch, but can actually squirt moisture when fed into a jaw crusher. The fixed carbon component of lignites, however, is far more reactive than for older coals and burns faster. Uncovered piles of lignite, after drying for some weeks, tend to ignite spontaneously, sometimes with catastrophic results.

Extensive research demonstrated that when lignites are subjected to high temperatures in a pressurized, saturated steam or hot water environment, at temperatures of 250ºC to 400ºC, bound moisture in the coal is expelled irreversibly, so that a high moisture lignite can be converted to a stable slurry of solids content sometimes comparable to the raw coal. Lignite also has a high thermal friability, so that the finely ground coal, during such HWD (Hot Water Drying) process, breaks down to even finer particles. The resulting suspension proves quite stable and does not settle/separate when stored. Such fluids, with top particle sizes less than 300 microns, and 40% to 50% solids, are shear-thinning/thixotropic. At high shear rates (flowing velocities) they have viscosities comparable to heavy fuel oils. Therefore, with modified atomizer design, such HWD lignite slurry can be used simply as a direct, cheap substitute for fuel oil in an existing oil-fired boiler! They burn with a clear, bright flame, like oil, without the sparks seen when burning powdered coal, or slurries of higher rank coals. Because of the higher reactivity of the carbon content of lignites, they are a superior feedstock for gasification processes, enabling over twice the throughput capacity of higher rank coals, for the same reactor system design.

Following, as Fig. 14, are viscosity curves for HWD lignite slurries from two North Dakota mines. While the process of pilot-scale production of these slurries was varied and recorded in minute detail, the viscosity curves were done by a “standard method” in a rheology lab, for comparison with comparable curves for different coal slurries and fuel oils.

These two examples below, along with many other coal slurries and dry, pulverized coals, were tested in a pilot scale, ash fouling test furnace, of 34 kg/hr (75 lb/hr) capacity, designed to simulate the effects of ash deposits on boiler tubes. The HWD lignite slurries were delivered to the test furnace in drums, having been stored for several days or weeks after production. Upon inspection, this material looked like black mayonnaise. A sturdy, 5-foot pole inserted into it almost stood up like a spoon in a mayonnaise jar. Initial manual stirring took substantial muscle, but after a minute or so of effort, resistance fell sharply and it felt almost like stirring water. The drums were picked up by a crane and dumped into a tapered feed tank, where it drained by gravity into a Moyno screw pump, feeding the material via several yards of pipe to a specially designed atomizer, and spraying it upward into the test furnace. The maximum flow constriction was in the slots of the swirling atomizer tip, with widths of roughly one to three millimeters from which the fluid sprayed as a fine mist, igniting immediately in a clear bright flame.
Besides the 2 HWD lignite slurries described above, standard viscosity measurements were done on a wide variety of other coal slurries, shown here as Fig. 15. For these HWD lignites, at solids loadings of 45.7% and 53.8% solids loading, showing the effect of solids loading as expected. Note the much higher curves of a raw ND lignite slurry, of only 40% solids. This is because of the larger particles of the raw slurry, which both shrink and fragment upon drying. All these curves so far are shear thinning with conspicuous hysteresis. Finally, note the rheogram for a “commercial” meaning offered for potential fuel or pipeline transportation – bituminous coal slurry. Surprisingly this slurry is rheotropic or shear thickening! No explanation for this difference is obvious.
From the rheograms of Fig. 15, plotting shear force against shear rate, consider some of the same data plotted as viscosity vs. shear rate, in Fig. 16. Again, this shows the major reduction in viscosity of lignite slurries, by hot water drying. It also shows once again the rheotropic or shear-thickening of the bituminous coal slurry.

The raw, dry, pre-processed ND lignite contained roughly 30% moisture, or 70% solids. It was pulverized with added water to make slurries of down to 40% solids loading, which was not stable and tended to settle/separate when not in motion. In Fig. 14, note that this slurry was almost Newtonian, showing only a slight, linear viscosity decrease with shear rate, but highly hysterical, showing a wide divergence between ascending and descending curves, attributed to settling of solids.

This raw, unstable lignite slurry settled into a solid layer on the bottom of the feed tank, so that resistance at start-up resulted in a broken shaft of the Moyno feed pump. Therefore, combustion testing of this slurry was not possible.

After HWD processing at slightly different temperatures, with the addition of more water as necessary to maintain fluidity, the lignite was tested as two samples. These samples were of 45.7% and 53.8% solids loading, which resulted in typical thixotropic curves but at substantially different viscosity ranges by roughly an order of magnitude for the 8.1% difference in solids loading (after HWD processing with the addition of water to maintain fluidity). This demonstrates the extreme sensitivity of slurry viscosity to solids loading as well as shear rate.

A surprising result of these tests was the striking shear-thickening, rheotropic behavior of the "commercial" bituminous coal slurry. This may be attributed to the "secret/proprietary" additives and the "unknown" method of preparation. The origin of this bituminous coal slurry is both unknown and was of little interest at the time (1985) of that project. Thus, no further hypothesizing about this behavior is now (2018) possible. Although this slurry had a high heating value of 34 MJ/kg, compared with only around 23 MJ/kg for the HWD lignite slurries, its rheology would only recommend it for pipeline transportation or use as a fuel at carefully controlled low shear rates. Its maximum energy transportation rate, MJ/hr-km or Btu/hr-mile, would be achieved by low flow velocities through large diameter pipes.
This project was perpetrated by funding from the US Department of Energy, in the early 1980s, when anticipation of massive emerging technologies in coal processing was at its peak, with millions spent on coal slurry pipeline transportation conferences alone. While there is now no apparent market for this product, the above experience provides guidance for fluids with similar complex rheological characteristics.

Potential Design Problems

Starting with a tank or vat full of this viscous, shear-thinning, thixotropic, “hysterical” product, it needs to flow by gravity into some kind of pump to start it through a possibly substantial length of pipe, to the next processing step, packaging or final application.

Gravity flow involves minimal pressure drop at very low shear rates. The shear-ascending viscosity curve will apply, with viscosity quite high but not specifically defined.

Initial turbulence inside the pump – whether a Moyno or centrifugal pump – will apply a very high shear rate for a second or less, initiating a rapid decrease in viscosity. This initial high viscosity will determine the power requirement for the pump. Once past the pump, the shear rate will be constant for the length of the pipe run. The viscosity may be reduced to the fully developed turbulence level – or it may not. This would depend on the time delay for any clots/blobs/agglomerations to break up by the level of turbulence after the pump. The time delay for shear-thinning fluids, or recovery time, as discussed in detail in Appendix B, is not generally known, but can be measured. The “standard” viscosity tests used in this project used a programed viscometer, wherein the programmed shear rate was ramped up and down, as shown in Figure 13, although the actual time span was not reported. It is generally presumed that the high shear, passing through the pump will eliminate this delay time. However, any extended study of the fluid’s rheology should include viscosity measurements using longer times at each shear rate point.

The lignite slurries covered by this project was produced by steam heating the raw slurries in a single tube heat exchanger, wherein the rheology changed massively, as indicted in the lower part of Figure 16. Suggested process scale-up designs for estimating plant costs, assumed shell-and-tube heat exchangers, which suggests a potential problem. Consider the fairly steep ascending and descending viscosity curves below say 200 sec\(^{-1}\). If there is any variation in the flow rate of material between parallel tubes, due to small random changes in concentration or rate of drying, the spot viscosity may change significantly. If decreasing, this could have a positive feedback effect, resulting reduced flow and further increased viscosity and pressure drop, shifting flow to adjacent tubes. This could progress to actual plugging of some tubes, and overheating. This problem was apparently never addressed.

(If any engineer taking this course has had experience with heating or cooling thixotropic fluids in heat exchangers with multiple parallel flow paths, Hauserman Associates, Inc. would love to share your observations, at hauserman1@msn.com)

Mixing

Viscosity may also be defined as the cohesive force between adjacent molecules of the same fluid. In mixing fluids of different viscosities, the energy applied must overcome this force to insert different molecules between them. As a simple example, when mixing...
whiskey and soda, the turbulence of pouring one into the other is quite adequate to insure complete mixing. But when mixing a Christmas Cheer of eggnog and brandy, at least 30 seconds of vigorous stirring is generally needed to mix the separate layers in the glass. To use very viscous “Tom-and-Jerry” mix, a much longer stirring time is needed to separate the long strands of the egg white albumen polymer, to let water and alcohol molecules get between them.

Uncertainty

So far, it has been assumed that the slurries discussed have been clearly of one kind or another. In practice, this distinction is not always well definable. The data plots shown here for the lignite slurries were neat, typical examples. Many others, during the project, showed a much more erratic scatter of data points and were essentially useless. Possible explanations may be:

- how well stirred the samples were immediately before doing the standard tests
- how long the material had been in storage before taking samples
- slight variations in temperature or residence time during processing
- whether samples were from the surface or bottom of storage vessels

Chapter 3 discussed the matter of agglomeration into blobs or clots that may take unpredictable times to break up when again in motion. This is probably true of many kinds of slurries, especially food and other organic products that have limited “shelf life” when once opened. When viscosity data cannot be repeated until consistent or reliable, it is recommended that engineers assume worst-case scenarios when designing equipment

Summary

- When preparing preliminary process designs, without specific lab data for materials vs. engineers should be very critical of limited, published viscosity data for non-Newtonian fluids.

- Viscosity curves (µ vs. S) for shear thinning or thixotropic fluids normally show an empirical function of the form $\mu = kS^n$, where K and n are empirical constants. At very low shear rates however, where the fluid is starting to flow, this kind of function approaches infinity and is thus invalid and useless. For maximum viscosity, to start a fluid flowing, it is **recommended to simply use the highest point on the ascending data curve, and multiply by 2 or 3**. Use this in $Re = \frac{Vd}{\mu}$ to guesstimate pressure drops and pump discharge pressure requirements.

- For established flow rates, it is recommended to use the lowest $\mu$ value, at maximum reported shear rate, to estimate pressure drops.
- As a fluid passes through any kind of pump, shear rates between the impeller, rotor or screw will **probably** be high enough to reduce the viscosity to or near the predicted value in the downstream piping.

- When classifying a previously undocumented slurry, based on matching best-fit curves to erratic rheogram data, the result may appear primarily one type and marginally another, or it may be too ambiguous or inconsistent to make a decision.

- In processes with long runs of piping, or in a cross-country slurry pipeline (if such a thing is ever built), any sudden shut-down may result in major increase in viscosity, which may require prohibitively high pressures to start it flowing again. (Think of how hard one sometimes has to shake a bottle of catchup to start it flowing.)

- If a laboratory viscometer is available, a standard, programmed viscosity curve (See Fig.13), done with uniform time intervals between points, is acceptable for comparison with different fluids, But to fully understand any shear-thing fluid, viscosity tests should be done with longer times.

- In general, when dealing with highly thixotropic or shear-thinning materials: Good luck!

~~ End of Chapter 4 ~~
Chapter 5 - “CONDITIONAL” SLURRIES

The scope of this work has been limited to stable slurries, suspensions and emulsions that do not separate or settle when at rest. However, in sheer tonnage of material processed, such as moving sand or ground mineral products with water, system design requires knowledge of conditional slurries. These are herewith defined as process flows in which solid particles are kept in uniform suspension, behaving as slurries, due to the turbulence of the flowing liquid. When the flow stops, the solids separate and settle. More details of process design for such conditional slurries are thus “beyond the scope of this work.” To pursue this area in much greater depth, a strongly recommended reference is the McGraw-Hill, “Slurry Systems Handbook” – any edition.

An assumption defining strictly Newtonian or conditional slurries is that there is no adhesion, cohesion, surface bonding, agglomeration or chemical reaction between suspended particles. The viscosity, only while the particles are in complete suspension by turbulence of the carrier liquid, is determined by the size and shape of particles, and the solids loading. The latter can be defined as either weight or volume % of solids in suspension. Viscosity is dependent on the ease with which particles can move past each other in turbulent suspension, which is influenced by the particles’ shape. Perfectly smooth, spherical particles offer less resistance to motion and thus result in lower slurry viscosity.

An attempt at mathematical modeling of an “ideal” conditional slurry has been done, with the result shown in Figure 15. Here the relative viscosity is defined as 1.0 for the carrier liquid, at any given shear rate or flow condition, and increasing with solids loading. In this experiment, the solid consisted of silica beads of 0.54 mm diameter, suspended in ethylene glycol, (viscosity = 15.5 cp at 27°C). Near perfectly spherical beads were used for minimum friction between particles. Thus, at about 50% solids loading/concentration, the relative viscosity is about 12, so the actual viscosity, at 27°C will be 12x15.5 = 186 cp.

As an example of the bead size on viscosity, catalysts for fluid bed reforming is delivered as coating on similarly spherical titanium beads. When attempting to hold a handful of such dry material, it leaks between fingers, almost like water. It has an angle of repose approaching zero, and feels like a liquid.

A major commercial product based on this property is “frac sand.” To allow release of petroleum fractured rock deposits, a slurry of frac sand is pumped down a new oil well at very high pressures, forcing it into cracks in the oil-bearing strata, to keep the cracks from collapsing shut. The high sphericity of frac sand particles makes a slurry of minimal viscosity, to be more easily forced into the cracks, at achievable pressure. This allows the oil to flow more freely toward the well, to be pumped to the surface. This sphericity also provides lower friction against surfaces of the cracks, further reducing pressure required. Frac sand is mined from deep sedimentary strata, where the grains were once tumbled and polished to roundness by some swift-flowing ancient river.
The shape of the solid particles and their specific gravity will make a significant difference in the apparent viscosity. Particles with sharp edges slide past each other less easily than smooth round particles, and thus result in higher slurry viscosities. Figure 16 shows examples for three relatively low density carbonaceous materials as slurries in water.

It was assumed above that these kind of slurries are made of inert particles that have no form of chemical interaction. However, pure physical contact can result in viscosity vs shear curves that are remarkably similar to thixotropic, shear-thinning behavior described in Chapter 3. The physical reaction here is frictional resistance to motion, which increases with non-spherical particles with sharp edges.
Figure 17 shows some examples of sand slurries, at different solids loadings\textsuperscript{10}. This because, at very low shear/flow rates, the sand ceases to be suspended by turbulence, and simply settles to the bottom of the pipe/channel. In Figure 17, at shear rates below about 300, the sand is settling to the bottom, or moving in waves or slugs, but is no longer dispersed as a slurry. And as the shear/flow rate approaches zero, all of the sand settles, reducing the pipe/channel flow cross section to one minus the percent solids loading.

As the flow rate decrease, the sand becomes less suspended, as shown in Figure 18, below. For vertical flows, changes are more complicated. As flow stops completely, all the sand settles. To resume flow, a higher velocity and some time is required to stir up the sand to the point of homogeneity, below which the material is simply not quite a “slurry,” as defined in previous chapters, and the basic definition of viscosity, can only be applied to part of the flow for only conditions of high shear at maximum turbulence.

Figure 20 – State of Particle Suspension at decreasing shear rates.

- High velocity.
- Fully developed turbulence.
- Minimal velocity.
- Most of sand settled.

This concludes our brief consideration of conditional slurries. For further study on this type of slurry behavior, Appendix C\textsuperscript{10} is recommended. As a quick rule-of-
thumb, to predict velocities needed to move sand or other dense mineral products, the following table is suggested:

<table>
<thead>
<tr>
<th>Type of Material</th>
<th>Particle Size (Mesh)</th>
<th>Minimum Flow Velocity</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>M/sec</td>
</tr>
<tr>
<td>Fine</td>
<td>Over 200</td>
<td>1~1.5</td>
</tr>
<tr>
<td>Sand</td>
<td>200 ~ 20</td>
<td>1.5~2</td>
</tr>
<tr>
<td>Coarse</td>
<td>20~4</td>
<td>2~3,25</td>
</tr>
<tr>
<td>Sludge</td>
<td></td>
<td>0.6~3</td>
</tr>
</tbody>
</table>

Finally, we consider a combination of stable shear thinning fluid with solids to form a conditional slurry. This is “drilling mud,” which is pumped down oil wells during drilling, to maintain pressure, provide cooling, lubricate the cutting bit, and to flush rock chips up the hole in a separate annular channel. The new fluid is a stable, very dense slurry of barite (BaSO$_2$, sg = 4.48) and/or bentonite clays (BaTiSi$_3$O$_9$, sg = 3.65), along with a complex variety of emulsifiers and other organics to maintain stability. The solids content of this fluid is adjusted as needed and may have a specific gravity of around 2.0, which is high enough to float sizable chips of common minerals such as quartz (sg = 2.65) or calcite (sg = 2.71) with minimal turbulence. The recirculating stream is therefore a conditional slurry, bearing rock cuttings, most of which may be separated by gravity or centrifuges, while cuttings as fine as a few microns can become part of the carrier fluid, gradually reducing its density. Therefore, maintaining the fluid composition is a complex and critical component of a drilling project. It is included here as a good large-scale example, where the types of slurry behavior covered here overlap (there are others as well).

~~ End of Chapter 5 ~~

*After completing this course, if you have any questions, or comments to share, you may feel free to contact Hauserman Associates, Inc., at hauserman1@msn.com.*
Appendix A. More about Kinematic Viscosity

Conversion of Units for Kinematic Viscosity, n.

The following table will give a comparison of various viscosity ratings so that if the viscosity is given in terms other than Saybolt Universal, it can be translated quickly by following horizontally to the Saybolt Universal column.

<table>
<thead>
<tr>
<th>Seconds</th>
<th>Kinematic Viscosity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Saybolt Universal ssu</td>
<td>Saybolt Furol (Standard)</td>
</tr>
<tr>
<td>---------</td>
<td>---------------------</td>
</tr>
<tr>
<td>31</td>
<td>1.00</td>
</tr>
<tr>
<td>35</td>
<td>2.50</td>
</tr>
<tr>
<td>40</td>
<td>4.30</td>
</tr>
<tr>
<td>50</td>
<td>7.40</td>
</tr>
<tr>
<td>60</td>
<td>10.3</td>
</tr>
<tr>
<td>70</td>
<td>13.1</td>
</tr>
<tr>
<td>80</td>
<td>15.7</td>
</tr>
<tr>
<td>90</td>
<td>18.2</td>
</tr>
<tr>
<td>100</td>
<td>20.6</td>
</tr>
<tr>
<td>120</td>
<td>22.1</td>
</tr>
<tr>
<td>150</td>
<td>34.2</td>
</tr>
<tr>
<td>200</td>
<td>54.0</td>
</tr>
<tr>
<td>300</td>
<td>65.0</td>
</tr>
<tr>
<td>400</td>
<td>87.60</td>
</tr>
<tr>
<td>500</td>
<td>110.0</td>
</tr>
<tr>
<td>600</td>
<td>132.0</td>
</tr>
<tr>
<td>700</td>
<td>154.0</td>
</tr>
<tr>
<td>800</td>
<td>176.0</td>
</tr>
<tr>
<td>900</td>
<td>199.0</td>
</tr>
<tr>
<td>1000</td>
<td>220.0</td>
</tr>
<tr>
<td>1500</td>
<td>330.0</td>
</tr>
<tr>
<td>2000</td>
<td>440.0</td>
</tr>
<tr>
<td>2500</td>
<td>550.0</td>
</tr>
<tr>
<td>3000</td>
<td>660.0</td>
</tr>
<tr>
<td>4000</td>
<td>880.0</td>
</tr>
<tr>
<td>5000</td>
<td>1100.0</td>
</tr>
<tr>
<td>6000</td>
<td>1320.0</td>
</tr>
<tr>
<td>7000</td>
<td>1540.0</td>
</tr>
<tr>
<td>8000</td>
<td>1760.0</td>
</tr>
<tr>
<td>9000</td>
<td>1990.0</td>
</tr>
<tr>
<td>10000</td>
<td>2200.0</td>
</tr>
<tr>
<td>15000</td>
<td>3300.0</td>
</tr>
<tr>
<td>20000</td>
<td>4400.0</td>
</tr>
</tbody>
</table>

* Kinematic Viscosity (in centistokes) = Absolute viscosity (in centipoises) / Specific Gravity

Above 250 ssu, use the following approximate conversion

\[ ssu = \text{centistokes} \times 4.62 \]

Above the range of this table and within the range of the viscometer, multiply their rating by the factors to convert to SSU.

<table>
<thead>
<tr>
<th>Viscometer</th>
<th>Factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>Saybolt Furol</td>
<td>10</td>
</tr>
<tr>
<td>Redwood Standard</td>
<td>1.095</td>
</tr>
<tr>
<td>Redwood Admiralty</td>
<td>10.87</td>
</tr>
<tr>
<td>Engler - Degrees</td>
<td>34.5</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Viscometer</th>
<th>Factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>Parlin cup #15</td>
<td>98.2</td>
</tr>
<tr>
<td>Parlin cup #20</td>
<td>187.0</td>
</tr>
<tr>
<td>Ford cup #4</td>
<td>17.4</td>
</tr>
</tbody>
</table>
“What is the Difference Between Dynamic and Kinematic Viscosity?”
Source: CSC Scientific Blog (3)

At first glance, viscosity seems like a fairly simple concept. It helps describe how thick a product is, or how well it flows. That's all, right?

In reality, there are several different terms that come under the heading of viscosity. These terms are derived from how the viscosity is measured. When people talk about viscosity, they are talking about one of two things: kinematic viscosity or dynamic viscosity.

It's not easy to find a lot of information on the differences between dynamic and kinematic viscosity. This is my attempt to bring clarity to these two principal concepts.

One way is to measure a fluid's resistance to flow when an external force is applied. This is dynamic viscosity.

The other way is to measure the resistive flow of a fluid under the weight of gravity. The result is kinematic viscosity. Put another way, kinematic viscosity is the measure of a fluid's inherent resistance to flow when no external force, except gravity, is acting on it.

To further complicate my attempt to simplify these concepts, two fluids that have the same dynamic viscosity can have different kinematic viscosities. This is because kinematic results are dependent on the density of the fluid. Density is not a factor with dynamic viscosity.
Measuring Dynamic Viscosity

Rotational viscometers are one of the more popular types of instruments used to measure dynamic viscosity. These instruments rotate a probe in the liquid sample. Viscosity is determined by measuring the force - or torque - needed to turn the probe.

The rotational viscometer is particularly useful in measuring non-Newtonian liquids. Non-Newtonian liquids change viscosity when exposed to different conditions. For example, some of these liquids show an increase in viscosity with an increase in applied force while other non-Newtonian liquids decrease in viscosity with an increase in applied force.

The rotational viscometer can adjust the turning speed of the probe as it moves in the liquid. The viscometer detects the variation in the viscosity of the sample as the speed, sometimes call shear rate, is changed.

*The unit of measure for dynamic viscosity is Centipoise (cP).*

Measuring Kinematic Viscosity

There are several ways to find the kinematic viscosity of a fluid, but the most common method is determining the time it takes a fluid to flow through a capillary tube. The time is converted directly to kinematic viscosity using a calibration constant provided for the specific tube.

*The unit of measure of kinematic viscosity is Centistokes (cSt).*

A basic difference between the dynamic and kinematic viscosity measurements is density. Density actually provides a way to convert between a kinematic and a dynamic viscosity measurement. The formula for the conversion is:

- Kinematic (cSt) x Density = Dynamic (cP)
- Dynamic (cP) / Density = Kinematic (cSt)

For a given sample, with a density greater than one, dynamic viscosity will always be the higher number.

When Should You Use Dynamic Viscosity Measurements?

You test dynamic viscosity when you want to know the internal resistance of a fluid, or the force required to move one plane of the liquid over another.
The measurement of dynamic viscosity is most useful for liquids which change their apparent characteristics as force or pressure is applied. These liquids are known as non-Newtonian fluids. Non-Newtonian fluids are sensitive to changes in the amount of force exerted on them, and can sometimes even permanently change their viscosity if a constant force has been exerted on them over a period of time.

An example of the importance of dynamic viscosity measurement is to indicate the proper flow characteristics of ketchup. This product needs to have lower viscosity as it flows, to get it out of the bottle, but needs to be thick (or not as inclined to flow) when sitting on the burger. Testing the viscosity of the ketchup at different speeds (equating to different levels of force) will help ensure that the ketchup is behaving as it should.

Another application is in the design of pumping systems. Because the viscosity of non-Newtonian liquids changes with the speed of movement, pressure and pump velocity have serious impact on the specification of proper pumps, pressure and piping size. Testing the product at different speeds will help provide guidelines for the design of the pumping system.

**When Should You Use Kinematic Viscosity Measurements?**

This measurement is used mostly for Newtonian liquids - liquids that do not change viscosity with changes in applied force (shear rate).

Testing lubricating oils is a significant application. Using this testing method, changes in viscosity at different temperatures and under differing environmental conditions can be determined. With this information, changes in lubricating effectiveness can be evaluated.

Some other products for which the kinematic method is suitable are blood and plasma, paints, polymers, and asphalt.

Viscosity measurement for Newtonian fluids can be accomplished using rotational viscometers (via the conversion formula listed above). However, it is simpler to use capillary-based instruments. In some cases, capillary-based instruments are more accurate for determining kinematic viscosity.

When you need to determine the viscosity characteristics of a liquid which is not exposed to outside physical forces (in other words, when gravity is the only force acting on the liquid), kinematic should be the method of choice.

**Summary**

Newtonian fluids have an inherent viscosity that does not change as you change the force applied to the liquid. This inherent viscosity can be easily and accurately measured with a capillary-type apparatus, using gravity to move the fluid.

On the other hand, non-Newtonian fluids exhibit wide variations in viscosity based on the force applied. These tests require instruments such as rotational viscometers that can measure changes over time and over a range of applied forces.

To delineate between these two type of liquids:

- **Dynamic Viscosity**: viscosity related to the external force applied to non-Newtonian fluids.
- **Kinematic Viscosity**: inherent viscosity of Newtonian fluids, that does not change with a change in applied force.
While this comparison is not exhaustive, I hope it serves to further your understanding of the differences between dynamic viscosity and kinematic viscosity. Please share it with anyone who might be interested.
Many products used in daily life can be characterized by their thixotropic behavior. Thixotropy is the property that explains why personal care products like hair gels and toothpaste are liquid when squeezed out of the tube but recover to their initial solid state afterwards in order to remain in place. The perfectly adjusted rheological properties of structural decomposition and regeneration as a function of time are responsible for the quality of a product. This article describes how thixotropy testing can be performed with a rotational viscometer/rheometer to control/influence the application behavior of materials.

Thixotropy is the property of certain fluids and gels of becoming thinner when a constant force is applied and after reduction of the force the viscosity recovers fully to the initial state in an appropriate period of time. The higher the force that is applied, the lower the viscosity becomes. Thixotropy is a time-dependent phenomenon, as the viscosity of the substance must recover after a certain period of time when the applied force is removed. The term thixotropy consists of the Greek words “thixis” (to touch) and “trepein” (to turn). It means the change or transition of a substance due to mechanical load. Examples of thixotropic materials are lotions, gels, ketchup, paints, and gypsum. For example, ketchup flows out of the tube when it is pressed. Its viscosity becomes lower as force is applied. After the force lessens, the viscosity of the ketchup recovers to its initial state for perfect leveling on French fries. This means that thixotropic behavior is always combined with shear-thinning flow behavior. Shear thinning, also called ‘pseudoplastic’ flow behavior, is characterized by a decrease in viscosity due to an increasing applied force (shear load).

All in all, there are three different types of time-dependent flow behaviors:

**Thixotropic behavior**

In thixotropic materials the structural strength decreases with a higher load (in rheological terms: while shearing) and recovers completely after a certain rest period. The rest period needed for recovery strongly depends on the application and has to be defined prior to the test. Thixotropic behavior is an important quality characteristic of, for example, paints and coatings. It influences the way paint levels out and prevents sagging but also ensures a sufficient and consistent wet layer thickness.

**Non-thixotropic behavior**

In non-thixotropic materials the structural strength decreases while shearing but the viscosity does not fully recover after an appropriate rest period. It remains thinner than the initial state which means that the structure does not fully recover (<100 %). A typical
sample which shows this behavior is yogurt. After stirring, the viscosity of yogurt remains thinner than initially.

**Rheoplectic behavior**

In rheoplectic materials the structural strength increases while shearing and recovers after a certain rest period. This phenomenon is rare but can be found in suspensions with a high solid content like latex dispersions or ceramic casting slips.

**Test methods for thixotropy testing**

Thixotropy testing can be carried out with a viscometer or rheometer in rotation or oscillation. Rotational tests are described in the next chapter. There are diverse test methods available for analyzing thixotropic behavior. The focus of this article lies on the most common test methods. It has to be noted that each of the following test methods is performed with a different test procedure and, therefore, the outputs will differ from each other. Only thixotropic behavior tests conducted with the same method under the same conditions can be compared to each other.

**Step test (3 intervals thixotropy test, 3ITT)**

A step test is usually performed with a rotational rheometer by fast speed changes. The step test consists of three intervals and is therefore called “3 intervals thixotropy test (3ITT)”. It can be either performed in a controlled shear rate (CSR) mode or in a controlled shear stress (CSS) mode: In CSR mode the shear rate or rotational speed is preset, whereas in CSS mode the shear stress or torque is preset on the viscometer.

The test is performed at two different speeds/shear rates. The first and last intervals are performed at a low shear rate and the second interval is performed at a high shear rate (Figure 1). In CSS mode the first and last intervals are performed at a low shear stress and the second interval is performed at a high shear stress.
Figure 1: Step procedure of a rotational test consisting of a low-shear, high-shear, and low-shear phase. $\dot{y} =$ shear rate; $t =$ time

Time-dependent changes in viscosity during the 3ITT test represent the sample’s real behavior before, during, and after the application (see Figure 2):

- **Low-shear phase:** The aim of the first interval is to obtain a constant viscosity at a constant low shear rate. This interval provides the reference viscosity of the sample at rest.
- **High-shear phase:** In this interval the sample is strongly sheared at a constant high shear rate to simulate the sample’s behavior during application, e.g. during stirring, rolling, painting, spraying, and pumping. The structural decomposition can be determined due to the sample’s shear-thinning behavior, also known as pseudoplastic behavior.
- **Low-shear phase:** Here, the same constant low shear rate is preset as in the first interval. This interval allows the sample to recover its structure/viscosity. The structural regeneration of the sample can be determined with one of the following analysis methods.

![Graph showing time-dependent viscosity](image)

Figure 2: Time-dependent viscosity of a sample with thixotropic behavior. $\eta =$ viscosity, $t =$ time

**Analysis methods for the step test**

The third interval of the 3ITT test is used for analyzing the thixotropic behavior of the sample. There are different methods for analyzing the structural regeneration:

- **Recovery ratio after a given time:** Prior to starting the test, the user has to define the point of time at which the structural recovery should be analyzed. The points of time have to be set according to the requirements of the application. The viscosities at these points are then compared to the viscosity of the rest phase in the first interval. For
example, the structure of the paint recovered up to 80 % after 60 seconds of the third interval (Figure 3).

Figure 3: Analyzing the recovery ratio after a given time. \( \eta = \) viscosity, \( t = \) time

- Time for a given recovery ratio: The time needed for structural recovery (100 %) is often very long. For example, after shaking paraffin oil, it needs about eight hours to fully recover to its initial solid state. For this reason, the time for a lower recovery ratio is usually analyzed. The recovery ratio of interest is set prior to the test. Then the time needed to recover to the set recovery ratio is calculated. The time is measured from the beginning of the third interval, the recovery interval. In Figure 4 the time needed for 25 % and 50 % structural recovery is analyzed.

Figure 4: Analyzing the time for a given recovery ratio. \( \eta = \) viscosity, \( t = \) time
Hysteresis area method

Another simple method for analyzing the time-dependent flow behavior is the hysteresis area. In older literature that is not up to date anymore, this behavior is called thixotropic or rheopectic, respectively. However, according to modern standards such as DIN spec 91143-2 and ISO/WD 3219-1 they are no longer valid in principle. The reason is: This measuring method evaluates the amount of structural breakdown (or build-up) under high shear conditions, but there is no interval available to evaluate structural recovery under really low shear conditions. In this test the sample is sheared at different speeds. The viscometer/rheometer is first set to a low speed. The speed is increased stepwise to higher speeds, generating an upwards ramp (e.g. 1 rpm to 100 rpm). After reading the shear stress at the top speed, the speed is either kept for a certain holding time (e.g. 60 seconds) and finally decreased stepwise to the lowest speed, generating a downwards ramp (e.g. 100 rpm to 1 rpm) or the downwards ramp is generated immediately without a holding period. The result is plotted as a flow curve diagram showing the shear rate on the x-axis and the shear stress on the y-axis. Usually the shear rate is preset on the rheometer and the torque/force needed to rotate the bob in the cup filled with sample is measured. The area between the upwards- and downwards ramp is called the hysteresis area (Figure 5).

![Flow curve showing the hysteresis area.](image)

Figure 5: Flow curve showing the hysteresis area. 1 = indication for structural breakdown; 2 = indication for structural build-up, $\tau$ = shear stress, $\dot{\gamma}$ = shear rate

The flow curve diagram shows how the shear stress changes with increasing shear rate/speed. A decrease in shear stress during the holding interval at a constantly high speed indicates that the viscosity of the sample decreases. If the upwards and downwards ramp do not differ from each other the sample’s behavior is independent of time when shearing. If the upwards ramp shows a higher shear stress reading than the
downwards ramp the sample’s behavior is time-dependent under shear load, showing shear-thinning behavior then. If the upwards ramp shows a lower shear stress reading than the downwards ramp, then the sample shows time-dependent behavior when shearing, showing shear-thickening behavior.

The amount of the hysteresis area is calculated as follows:

Difference between

- Area between the upwards ramp and \( y \)-axis
- Area between the downwards ramp and \( y \)-axis

If the value is positive the sample shows structural breakdown and if the value is negative the sample shows structural build-up on shearing.

For very simple quality control tests some users perform the following method in order to evaluate thixotropic behavior. To analyze the time needed for recovery of the viscosity after shearing, the viscometer has to be stopped after the downwards ramp. After a certain waiting period, the viscometer is started again at the lowest speed available in order to see the build-up of the viscosity (structural regeneration). Comparing the viscosity of the sample before and after turning the viscometer off and on illustrates how quickly the sample’s viscosity returns to its initial state after shearing. If the viscometer shows the same viscosity value as before, the viscosity has fully recovered in the waiting period.

"Thixotropic Index"

Sometimes the term “Thixotropic Index (TI)” is used in different ways concerning measurement methods and analysis.

1. Some call TI the ratio between the viscosity of a sample at a low (\( \eta_A \)) and at a high (\( \eta_B \)) rotational speeds. For example, a material’s viscosity was measured at 5 rpm (\( \eta_A \)) and at 50 rpm (\( \eta_B \)). Afterwards \( \eta_A \) is divided by \( \eta_B \). If the value of TI = 1 the sample shows Newtonian flow behavior, i.e. it remains unchanged. If TI > 1 the sample shows speed-dependent shear-thinning flow behavior and if TI < 1 the sample shows speed-dependent shear-thickening flow behavior. However, here the term “thixotropic index” is misleading since this ratio quantifies time-independent non-Newtonian (shear-thinning or shear-thickening) behavior and not thixotropy. To quantify thixotropy, time-dependent structural decomposition and regeneration have to be measured. TI is sometimes also called the “Shear Thinning Index”\(^{vi}\), which is the better term in fact.

2. Others may call TI the ratio between the viscosity values at two different points of time obtained at a constant rotational speed. For example a material’s viscosity is measured after 30 s (\( \eta_A \)) and after 600 s (\( \eta_B \)) at 20 rpm. Afterwards \( \eta_A \) is divided by \( \eta_B \). If TI = 1 the material shows time-independent flow behavior. If TI > 1 the material shows time-dependent shear-thinning behavior and if TI < 1 the material shows time-
dependent shear-thickening behavior. Also here, the term "thixotropic index" is misleading since this ratio quantifies time-dependent structural decomposition of a material but not its structural regeneration.

"Thixotropic breakdown coefficient"

The “thixotropic breakdown (Tb) coefficient” is a simple test for analyzing the time-dependent behavior of samples. It is especially used for quick quality control checks with entry-level rotational viscometers. In this test the sample is sheared at a constant speed (or shear rate) for a certain period of time. The change in viscosity over time indicates the sample’s time-dependent behavior. If the viscosity decreases, the sample shows time-dependent shear-thinning behavior and if the viscosity increases over time the sample features a time-dependent shear-thickening behavior.

For example, paint is measured while in rotation for 10 minutes by constantly maintaining 50 revolutions per minute (rpm). The viscosity of the sample has to be recorded at regular intervals (e.g. every 30 seconds). The viscometer reading (viscosity) is then plotted against time. Afterwards the Tb is quantified by a single number using equation 1.

\[ Tb = (S_{t_1} - S_{t_2}) \cdot \ln\left(\frac{t_2}{t_1}\right) \cdot F \]

\[ S_{t_1} = \text{Viscometer reading at } t_1 \text{ minutes} \]
\[ S_{t_2} = \text{Viscometer reading at } t_2 \text{ minutes} \]
\[ F = \text{Factor for spindle/speed combination} \]

Equation 1: Formula for calculating the "thixotropic breakdown coefficient"

Tb has the unit of viscosity (Pa•s or mPa•s, or in old literature P or cP).

Also here, “Thixotropic breakdown coefficient” is not a very suitable name: According to modern standards this ratio does not describe thixotropic behavior since there is no structure recovery interval available afterwards.

Conclusion

Thixotropy tests give an insight into the sample’s time-dependent flow behavior and can thereby be employed for quality control of various products. According to modern standards such as DIN spec 91143-2 and ISO/WD 3219-1 thixotropy is characterized by decreasing viscosity over time when a shear rate is applied and full structural regeneration after the shear rate is set to a very low value. Only materials which fully recover their structure after shearing, like most ketchup samples, are called thixotropic materials and can be analyzed using the step test. Simple methods, such as analyzing the hysteresis area, “thixotropic index”, and the “thixotropic breakdown coefficient” are
often used as a simple and quick quality control method. However, according to state-of-the-art standards they do not entirely evaluate thixotropic behavior.

References


ii ISO 3219/WD 3219-1: General terms and definitions for rotational and oscillatory rheometry (2019)


vi ASTM D2196-10: Standard Test Methods for Rheological Properties of Non-Newtonian Materials by Rotational (Brookfield type) Viscometer


The effect of particle sizes and solids concentration on the rheology of silica sand based suspensions

by N. Mangesana*, R.S. Chikuku*, A.N. Mainza*, I. Govender*, A.P. van der Westhuizen*, and M. Narashima†

Paper written on project work carried out in partial fulfillment of Bsc (Chem. Eng.)—N. Mangesana degree and Bsc (Honours in Chem. Eng.)—R.S. Chikuku degree

Synopsis

The effect of high solids concentration and coarse particle sizes (d50 ranges 90–300 μm) on the viscosity of a suspension of water and silica sand was investigated. The experiments were designed to include conditions that have been tested by other authors and those encountered in the operation of tumbling mills.

The rheological data was measured using a tube rheometer with operating pseudo shear rates of up to 1500 s⁻¹. The rheograms obtained depicted dilatant behaviour. The Otswald–de Waele, Bingham, Herschel-Buckley and Casson models were fitted to the experimental data. The Herschel-Buckley model, which approximates the yield point and gives an indication of the shear thinning or shear thickening behaviour of the suspension, was found to provide the best description of the flow curves for all slurries. The Herschel-Buckley model was then used to determine the apparent viscosity of all the tests.

The apparent viscosity and yield stress increased with solids concentration and particle size at the different pseudo shear rates. The increase in slurry viscosity with solids concentration was attributed to increased frequency of particle–particle interactions. The increase in slurry viscosity with particle size was attributed to increased inertial effects. At low shear rates the sand slurry exhibited shear thinning behaviour for all solids concentrations. At higher shear rates above 1000 s⁻¹ the high solids concentration suspensions exhibited a transition from shear thinning to a shear thickening behaviour.

Introduction

Comminution using tumbling mills involves two sub processes, namely: transport and breakage. In order to develop a mechanistic model for the transport sub process, viscosity measurements at high solids concentration and relatively coarse particles are required. The models used to describe slurry transport for grinding applications are either empirical or semi-empirical. The model developed by Morrell and Stephenson from a combination of laboratory, pilot and plant-scale studies on high aspect ratio tumbling mills is widely used for design and optimization studies (Morrell and Stephenson, 2005). However, for low aspect mills, South African style mills slurry pooling and other problems related to transport and discharge are encountered and the model developed by Morrell and Stephenson cannot accurately predict the performance of these mills because most of the design variables are outside its window of application.

A mechanistic model is required for use in design and optimization studies that can be applied to different aspect ratio mills. Slurry viscosity is one of the most important inputs in the slurry transport and discharge mechanistic model for tumbling mills (Shi, 1994). The mechanistic model being developed has a similar structure to the Ergun Equation which is used to describe flow in static beds. This study was initiated to investigate the effect of particle size and solids concentration on viscosity, which is a significant input in the viscous energy loss term of the transport model.

There is generally a lack of knowledge concerning the flow properties of processes involving suspensions with fast settling solids. It has been noted that there are significant discrepancies in existing literature concerning the effects of key parameters such as high solids concentration and coarse particle sizes on slurry viscosity. This is because viscous properties are difficult to measure in an unstable system of settling particles (Clarke, 1967). Tumbling mills are usually operated at solids concentrations ranging between 40 and 60% by volume. However, most of the measurements to characterize the rheology for slurries were performed for slurries with a maximum solids concentration of 30% by volume. This is most probably influenced by the limitations imposed by the equipment used in obtaining the rheological measurements and the properties of the slurry being tested. The work in this study extended the experiments to include slurries with solids concentrations in the tumbling mills operations range.

Typical measurements for rheology characterization of slurries are performed using very fine particles mixed with water. In this study
The effect of particle size and solids concentration

The effect of particle size was evaluated on three different particle size fractions of silica sand with d50 values of 90, 180 and 300 microns. These slurries with relatively coarse particles are a representation of what is typically found in the primary mill discharge.

Literature review

The effect of solids concentration on slurry viscosity

Physical particle interactions and the operating shear rate ranges are the two main factors that affect the solids concentration when one determines slurry viscosities. The viscosity of a suspension will increase with solids concentration. This phenomenon is attributed to the physical particle interactions that occur when a solid is dispersed in a liquid. According to Cheng (1980) there are three main categories of these physical interactions:

- Interparticle attraction promotes the formation of flocs and aggregates. This phenomenon occurs mostly in fine particle suspensions
- Hydrodynamic interactions give rise to viscous dissipation in the liquid
- Particle-particle contact brings into play frictional interactions.

At low to medium solids concentration the effect of hydrodynamic interactions dominate, whereas at low solids concentration viscosity appears to increase linearly with increasing solids concentration. However, Rutgers observed that after a certain solids concentration, the viscosity of the slurry increases significantly with small increments of the concentration (1962). According to Cheng, from medium to high solids concentration, particle frictional contact dominates and at very high solids concentration the particle effect predominates over the hydrodynamic effects (1980).

The effect of operating shear rate ranges on slurry viscosity

According to Cheng (1980), as the concentration increases from medium to high, non-Newtonian behaviour is exhibited. The transition from Newtonian to non-Newtonian is not only dependent on concentration but also on shear rate. The shear rate at which the non-Newtonian behaviour starts decreases as concentration increases. As the shear rate increases, the suspension first becomes shear thinning and then shear thickening. Ferreira and Olhero (2003) noted similar observations in studies with silica sand-water suspensions. The experiments were conducted using particle sizes ranging from 2.2 to 19 microns with a solids concentration up to 46% by volume. The rheological measurements were conducted using a rotational controlled stress rheometer. They observed that the shear thinning behaviour occurred at low shear rates. This was followed by a shear thickening behaviour at intermediate shear rates and a trend to Newtonian behaviour at the highest shear rate region (Figure 1). The transition from shear thinning to shear thickening at higher shear rates for narrow particle size distribution was attributed to particle rearrangements and the increasing average distances between layers of particles. Under these conditions the capillary forces oppose to the flow and the suspension thickens.

The effect of particle size on slurry viscosity

Kawatra and Eisele observed that at a constant solids concentra-

tion, a reduction in particle size will result in an increase in slurry viscosity (1998). This was attributed to increased surface area, which binds up water molecules and thus increases the effective solids concentration. This is in contradiction with the work of Clarke, (1967) and De Bruijn, (1951) as reported by Thomas, (1968), which revealed that slurry viscosity increases with particle diameter. They attributed this to inertial effects, which resulted in additional energy dissipation. Clarke conducted his investigations on silica sand suspensions in water having particle sizes of up to 211 microns and concentrations of up to 50% by volume. A rotational viscometer was used to determine the rheological measurements of the suspensions.

Experimental work

Test materials and particle characterization

Silica sand with different particle size distributions, known by their commercial names as Sand 2 and Sand 55, were used. A portion of Sand 2 was milled to produce a third sample with a finer distribution. The particle size distribution curves of these sands are shown in Figure 2. Three distinct particle size distributions were used and they all appear to be narrow.

The experimental set-up

The experimental set-up used to conduct the viscosity measurements on the different sand-water suspensions consisted of a 45 sump, Weir Enviro Tech variable speed pump of up to 50 Hz and maximum power of 50 kW. An

Figure 1—Equilibrium viscosity curves for the suspensions of the sand mean particle size of 2 μm with different amounts of fine silica particle size (FS) with mean size of 0.07 μm (total solid loading 46 vol.%) and different milling times

Figure 2—Particle size distribution curves for the different sands
agitator was used to ensure that the material in the sump was well mixed. A Paterson and Cooke Consultants computerized tube rheometer was used. The tube rheometer works on a principle of measuring the pressure drop across a measured length of tube. The pressure drop determines the shear stress. The slurry flow rate in the tube determines the pseudo shear rates. These results are used to plot a pseudo rheogram (Kahn, 2005). Table I shows the dimensions of the tube rheometer.

At solids concentrations above 40% by volume shear rates above 1000 s\(^{-1}\) could not be obtained. Settling rates increased more rapidly for the coarser particle size of d\(_{50}\) - 300 microns. Due to the above-mentioned limitations solids concentrations above 50% by volume could not be tested. Details of the experimental programme are given in Table II. Temperature and surface chemistry effects were minimized by maintaining similar experimental conditions, and temperature readings were logged continuously. The surface chemistry of the sand-water suspension was kept constant by adding 2 g/l of sodium chloride for all tests. The effect of particle shape was not considered due to the difficulties associated with quantifying particle shape. To ensure that the shapes for the two sand types used in the experimental work were not very different, a qualitative comparison was performed using an electron microscope. The shapes for particles from the three samples were found to be predominantly spherical. The solids concentration was varied to cover the range 10 to 50 per cent by volume.

### Results and discussion

For each test condition the tube rheometer provided the variation of shear stress with shear rate. Figure 3 to Figure 5 show the rheograms obtained for the three sand size distributions at solids concentrations ranging from 8 to 50% by volume. The flow curves appear to be non-Newtonian in all cases and can be described as yield dilatants. It was also observed that the yield stress increased with increase in the solids concentrations for all cases. Klimpel also observed dilatant behaviour at low solids concentrations but his results appeared to be pseudoplastic behaviour at solids concentrations greater than 45% solids by volume (Klimpel, 1984).

The rheological data was then fitted to the Ostwald-de Waele, Bingham, Herschel-Buckley and Casson models to identify the rheological model that best describes the data.

### Table I

<table>
<thead>
<tr>
<th>Tube rheometer dimensions</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Active volume (l)</td>
<td>5.72</td>
</tr>
<tr>
<td>Internal tube diameter (m)</td>
<td>9.90 x 10(^{-3})</td>
</tr>
<tr>
<td>Measuring tube length (m)</td>
<td>9.64</td>
</tr>
<tr>
<td>Pipe roughness</td>
<td>30</td>
</tr>
</tbody>
</table>

### Table II

<table>
<thead>
<tr>
<th>Experimental programme for the viscosity tests</th>
</tr>
</thead>
<tbody>
<tr>
<td>Particle size</td>
</tr>
<tr>
<td>---------------</td>
</tr>
<tr>
<td>d(_{50}) - 90 microns</td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td>d(_{50}) - 180 microns</td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td>d(_{50}) - 300 microns</td>
</tr>
</tbody>
</table>

Figure 3—Rheograms for the d\(_{50}\) - 90 \(\mu\)m sand at different solids concentrations

Figure 4—Rheograms for the d\(_{50}\) - 180 \(\mu\)m sand at different solids concentrations

Figure 5—Rheograms for the d\(_{50}\) - 300 \(\mu\)m sand at different solids concentrations
The effect of particle size and solids concentration

Model fitting

In an attempt to find the model that best describes the data, four models from the literature, namely the Ostwald-de Waele, Bingham, Herschel-Buckley, and Casson models were fitted to the data. It should be noted that all the models, used in this work have the yield stress and power parameters, and inspection of the experimental data appears to suggest that these would be the most suitable models. Figure 6 to Figure 9 show the fitting results from the four models on the same data-set. It can be seen that all the models fitted the general trend well but the Herschel-Buckley model matched the experimental yield stress closely. All the models had high R² values ranging from 0.95 to 0.99 and the highest value was from the Herschel-Buckley fit. The same procedure was applied to the data from all the tests and similar results were obtained; the Herschel-Buckley model appears to fit the data better than the other models tested.

Figure 10 and Figure 11 show a comparison of the Herschel-Buckley fit for all three size fractions at solids concentrations of 20% and 40%, respectively. Reasonably high R² values were obtained in all cases. The corresponding Herschel-Buckley model parameters obtained for each of the fits are given in Table III and Table IV, respectively. The power index (P) is greater than 1 in all cases, suggesting that the flow curves exhibit dilatant behaviour. It was observed from Table III and Table IV that the yield stress parameter \( \tau_{HB} \) increased with particle size.

The shear stress values obtained from the Herschel-Buckley model were then used to calculate apparent viscosity using Equation [1]. The effect of solids concentration and particle size on apparent viscosity were then analysed.

\[ \eta = \frac{\tau}{\gamma} \]

where \( \eta \) is apparent viscosity, \( \tau \) is the shear stress and \( \gamma \), the shear rate.

Effect of solids concentration on viscosity

Figure 12 to Figure 14 show the variation of apparent viscosity with shear rate at different solids concentration for the three size fractions. It can be seen that the apparent viscosity increased with increase in solids concentration. The exception to this trend was the test for the 40% solids concentration for the size fractions with \( d_{50} \) of 300 \( \mu \)m where...
The effect of particle size and solids concentration

Table III

<table>
<thead>
<tr>
<th>d50</th>
<th>τ_{HB} ± Δτ_{HB} (Pa)</th>
<th>C ± ΔC (Pa.s)</th>
<th>P ± ΔP</th>
</tr>
</thead>
<tbody>
<tr>
<td>90 μm</td>
<td>0.918 ± 0.1</td>
<td>(18.4 ± 5)*10^-5</td>
<td>1.545 ± 0.04</td>
</tr>
<tr>
<td>180 μm</td>
<td>2.810 ± 0.2</td>
<td>(40.1 ± 1)*10^-5</td>
<td>1.458 ± 0.05</td>
</tr>
<tr>
<td>300 μm</td>
<td>5.441 ± 0.2</td>
<td>(4.27 ± 4)*10^-5</td>
<td>1.780 ± 0.1</td>
</tr>
</tbody>
</table>

The curve approaches the 30% solids concentration curve at shear rates above 600 s^-1. This result could be erroneous because difficulties were encountered in using the rheometer at high solids concentration. Due to these problems the maximum shear rate that could be measured for the d50 of 180 μm sand was 500 s^-1 for Cv = 40% and Cv = 50%.

Similar to the results obtained by Cheng, the increase in apparent viscosity with increase in solids concentration can be attributed to increased particle-particle interactions in the fluid (Cheng, 1980). The study by Cheng suggests that the relatively coarse particles have negligible interparticle attraction, which promotes the formation of flocs, aggregates, agglomerates and structure.

Thus at low to medium solids concentrations, the effect of hydrodynamic interactions prevails and they give rise to the viscous dissipation of the liquid. As a result, the viscosity increases with increase in concentration. This is also observed at high solids concentrations but the particle-particle contact effect predominates over the hydrodynamic effect. This particle-particle contact brings into play frictional interactions. The frictional interactions per unit volume increase with solids concentration, thereby increasing the viscosity of slurry. Cheng did not quantify what low, medium or high solids concentration was, thus the observed phenomenon could be due to either hydrodynamic interactions or particle-particle contact.

Shear thinning behaviour was observed in the low shear rate region of the curve and the curves appear to depict slight shear thickening behaviour at higher shear rates. Similar results were obtained by Olhero and Ferreira from experiments performed on fine silica powder of average size 19 μm (Olhero and Ferreira, 2003).

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Figure 10—Comparison of Herschel-Buckley fit for the three different size fractions at Cv = 20%

Figure 11—Comparison of Herschel-Buckley fit for the three different size fractions at Cv = 40%

Table IV

<table>
<thead>
<tr>
<th>d50</th>
<th>τ_{HB} ± Δτ_{HB} (Pa)</th>
<th>C ± ΔC (Pa.s)</th>
<th>P ± ΔP</th>
</tr>
</thead>
<tbody>
<tr>
<td>90 μm</td>
<td>2.574 ± 0.3</td>
<td>(26.6 ± 20)*10^-5</td>
<td>1.550 ± 0.08</td>
</tr>
<tr>
<td>180 μm</td>
<td>7.638 ± 0.4</td>
<td>(122 ± 17)*10^-5</td>
<td>1.274 ± 0.2</td>
</tr>
<tr>
<td>300 μm</td>
<td>9.699± 0.3</td>
<td>(104 ± 7)*10^-5</td>
<td>1.382 ± 0.1</td>
</tr>
</tbody>
</table>

Figure 12—Apparent viscosity of d50 - 90 microns sand as function of shear rate

Figure 13—Apparent viscosity of d50 - 180 microns sand as a function of shear rate
The effect of particle size and solids concentration

Effect of particle size on apparent viscosity

Figure 15 to Figure 17 show that viscosity increases with particle size at a fixed concentration for any given shear rate. This is similar to what was observed by Clarke (1967). The reason suggested for this increase was that particles of greater size possess greater inertia such that on interaction, the particles are momentarily retarded and then accelerated. In both these stages their inertia affects the amount of energy required. This dissipation of energy is what may appear as extra ‘viscosity’.

Relationship between yield stress and particle size and concentration

Yield stress is used to characterize slurry rheology and it represents the threshold amount of stress to initiate flow. Figure 18 shows the effect of particle size and concentration on the yield stress. For a given particle size, as solids concentration increases, the yield stress increases. The trends in Figure 18 indicate that the yield stress for the larger particle size is higher than that of smaller particle sizes at a fixed solids concentration. slurries with higher yield stresses require a higher initial input energy before the fluid starts to flow. For the smallest sized fraction at 10% solids concentration the yield stress is close to zero but increases to as high as 4 Pa at 50% solids concentration. For coarser particle sizes tested the yield stress is almost 10 Pa at 40% solids concentration.

Conclusions

Tests were performed to characterize the rheology of the silica-sand water suspension at conditions that are encountered in tumbling mills. The flow curves appear to be non-Newtonian and exhibit shear thickening behaviour in all cases and can be described as yield dilatants. Of the models tested, the Herschel-Buckley model was found to give the best description of the flow curves.

Shear thinning behaviour was observed in the low shear rate region of the curve, and the curves appear to depict slight shear thickening behaviour at higher shear rates.
The effect of particle size and solids concentration

The apparent viscosity increased with increase in particle size and solids concentration. It was also observed that the yield stress increased with increase in particle size and solids concentrations for all cases.

Acknowledgements

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4. Table “Comparison of non-Newtonian, Newtonian, and viscoelastic properties” Source: wikipedia.org/wiki/Non-Newtonian_fluid


