

CHAPTER 3

THEORETICAL CONSIDERATIONS

3.1 Deflocculation and Protective Colloids⁽¹¹⁾

In ceramic manufacture we are always interested in the specific chemical additions we must make to a crowded particulate suspension which will provide the best rheological properties for optimum forming. These chemical additions are made to liquid phase from which they diffuse both to and away from the particle surfaces, depending upon the physical and chemical natures of both the additive and particle surface. Thus their solubility and functionality within the liquid, where they modify the liquid structure at particle/liquid interface, is very importance to optimize specific rheological properties.

For this reason we should mention to these forces; the van der Waals attraction which exists between all particles regardless of size. Then we will examine in the electrostatic, steric, and electrosteric energies between particle which may be attractive or repulsive. And also the structure of liquids, and water in particular, which determines the way in which ions and polymer are first adsorbed by the liquid, and then adsorbed from the liquid onto nearby particle surfaces, from which locations they modify all surface effects to provide the specific rheology of the crowded suspensions.

3.1.1 Van der Waals Energy of Attraction

In ceramic forming processes all crowded suspensions are controlled at some point midway between full deflocculation and

full flocculation. For good forming rheology it is imperative that we obey the following principles:

- a. Avoid full deflocculation in order to
 - minimize the rheological effect of dilatancy,
 - provide a reasonable plastic gel structure.

- b. Avoid full flocculation to van der Waals forces will draw the particles closer together over time when the interparticle separation distance (IPS) of the suspension is large and the amount of flocculant is also high, causing the auto-compression that is called syneresis.

To calculate attractive energy we use this equation for unequal radius;

$$W = - \frac{A R_1 R_2}{6r(R_1 + R_2)} \quad (3.1)$$

Where W = the total interparticle attractive energy,
 r = the interparticle separation distance (IPS),
 R = the radius of each particle.
 A = the Hamaker constant.

There have been many further modifications and advances in determining the exact value of the Hamaker constant using mathematics far beyond the scope here. For some typical ceramic powders, the Hamaker constant is $6-10 \times 10^{-20}$ J, and for water it is $3.7-4.0 \times 10^{-20}$ J. and the total attractive energy between two particles of equal radius is:

$$W = - \frac{AR}{12r} \quad (3.2)$$

These equations 3.1 and 3.2 are comprise of all the attractive interactions between molecules in two particles, and the IPS (interparticle separation distance) between the particles. These two equation predict that larger particles are attracted more strongly to

each other than small particles, and small particles are attracted more strongly to large particles than they are to each other.

These equations are only valid, however, when the particles in equation are very close to each other, that is, when the radius of each particle is much larger than the interparticle separation distance ($R > r$). When any two particles in a suspension are separated by large distances of the order of 10 nm or more, the van der Waals forces are retarded, or reduced, in that a time lag or phase difference develops between the vibrations of the two particles. According to Hiemenz⁽¹³⁾ this retardation modifies the effective Hamaker constant so it takes a value significantly different than that of either the particle or the medium.

$$A_{212} = \left(A_{11}^{\frac{1}{2}} - A_{22}^{\frac{1}{2}} \right)^2 \quad (3.3)$$

where A_{212} = Hamaker constant for two particles of type 2 separated by medium, or liquid, of type 1,
 A_{11} = Hamaker constant of two "particles" of medium of type 1,
 A_{22} = Hamaker constant of two particles of type 2.

For example the values for water (A_{11}) and quartz (A_{22}) are 3.7 and 6.5×10^{-19} J, respectively. Therefore $A_{212} = 0.39 \times 10^{-19}$ J, which is probably also appropriate for clays. For a clay/water suspension, therefore, the Hamaker constant $A_{212} = 1.53 \times 10^{-19}$ J.

To repeat, these arguments apply to colloidal size particles, not to particles larger than about 1 μm . But many of our ceramic particles are very much larger than 1 μm . If planets mutually attract, then so do the large particles in ceramic suspensions even though these equations do not perfectly describe them. So even though the theories have not yet been extended to our complete

system of particles we shall pretend they do and examine their consequences on slip gelation.

3.1.2 The Electrical double Layer

The van der Waals energy of attraction is due to interatomic electrical forces within particles. The Hamaker constant sums all these interatomic energies as a function of the volume of a particle of any material. Then the van der Waals energy calculated from the Hamaker constant, the size of the respective particles, and the IPS (interparticle separation distance, r .) So it is clear that attraction of particles is fundamentally a bulk volume (really a mass) effect which is intrinsic and cannot be changed by any outside effort. With no surface influences to modify the internally generated attractive energy all particles would ultimately flocculate together if given sufficient time. But fortunately the internal atomic structure must terminate at a surface which does indeed contain strong repulsive elements due to the broken atomic bonds at that surface.

- Two sources of repulsion

We would become a hard agglomerate instead of a soft, flexible one. The van der Waals forces are due exclusively to the mass of adjacent particles and there is no way to change or affect them. Instead we are forced to acknowledge their presence and then work on the surface of the particles with surface adsorbable chemical additions.

It is generally conceded that a repulsive energy between particles is due to an electrical phenomenon called the **electrical double layer** surrounding particles in liquids of high dielectric

constant, whereby counterions (of opposite sign to the surface) are adsorbed onto the unsaturated broken surface atomic bonds.

There are two sources of repulsive energy: Electrostatic and steric. In some specific chemical additives, such as ionic polymeric polyelectrolytes, these are combined as an electrosteric additive.

- The origin of charge on particle surface

That particles display the effect of electrical charge on their surfaces when suspended in water is so well known that almost no one questions it. Oxide minerals are perhaps the most common and simplest materials used in ceramic manufacture, and may be viewed as regular geometric arrays of oxygen anions bonded together by cations of various size and valency. These size and valency variations produce the many different crystallographic structures, particle densities, and intrinsic strength and hardness we encounter in our raw materials. When a single crystal of any material is fractured, the fracture usually occurs in the "cleavage plane" between two adjacent of the atomic structure breaking the cation-anion bonds formerly holding the planes together. These broken bonds then are exposed to the surface and produce the charge density peculiar to that particular crystallography.

Lyklema⁽¹²⁾ taught that most particles have a surface charge because most solvents contain adsorbable ionic species and most solids have dissociable groups on their surfaces. His wording seems to imply that the surface charge is due only to the adsorbed species. Hiemenz⁽¹³⁾ defines a surface as a boundary which concentration a "surface excess charge." Lyklema was mostly interested in the concentration gradient of the surface charge from

the surface into the bulk liquid, so he identified the origin of surface charges on suspended particles as being due to:

- Preferential adsorption of specific ions,
- Adsorption of polyelectrolytes, and
- Isomorphous substitution of lower valency ions within the crystal structure.

Israelachvili⁽¹⁴⁾ stated that particles suspended in water, of any high dielectric constant liquid, are usually charged by the first two points mentioned by Lyklema, above. Each of these authors major interest was in the interactions between organic colloids and liquids.

Regarding inorganic colloids Grim⁽¹⁵⁾ gave three relatively satisfactory reasons for the base-exchange capacity of clays.

- Broken bonds at the edges of the Si_2O_5 or Al_2O_3 sheets which comprise the lattice. On the clay minerals no broken bonds occur in the planes perpendicular to, or along, the c-axis.

- Substitutions within the clay lattice of lower valency ions for higher ones, such as Al^{+3} for Si^{+4} , or Mg^{+2} for Al^{+3} leave a surface charge deficiency perpendicular to the c-axis which can adsorb counterions from solution.

- This charge deficiency invites a hydrogen ion to form a hydroxyl where the hydrogen ion may then be replaced by a cation.

By adding the arguments of Israelachvili and Grim we obtain the argument of Lyklema with considerable expansion. For our purposes only the first two arguments of Grim are sources of surface charge and the third is an affect of surface charge. But now we have arguments to support our contention that the origin of surface charges on ceramic particles is primarily due to broken bonds.

Clays and many other ceramic oxide powders are mined from deposits with variable geologic history, are always imperfect in their crystallographic structure, and vary in their degree of crystallinity from place to place in the deposit. Therefore their fundamental surface charge is inconsistent. This can be easily observed by changes in deflocculant demand for different batches of powders.

Beyond these; they are further affected by variations in the soluble ion content of the suspending liquid (solvent) which are available for adsorption onto the particle surfaces. When a variable surface charge powder is suspended in a variable concentration of adsorbable chemicals the rheological response can vary from none to very large; and this is the realm of the ceramist.

So although development of charge on surfaces as a private domain applicable to colloids only, and particularly to the colloids of their field, they have given us a good start to help us understand how chemical dispersion works in powders which are not all colloids.

-Adsorption of counterions in aqueous suspensions

Since the simplest ceramic powders are composed of oxygen ions bonded together with usually smaller metal ions, it follows that the surface of an oxide powder is dominated by the negative oxygen ions thereby displaying an average electronegative surface. When placed in pure water the positive hydronium counterions H_3O^+ are attracted to the surface to neutralize the electronegative charge. In published derivations of the nature of the charges on surfaces many authors use the concept of point charges to simplify the mathematics, but in fact ions with finite diameters, in variable

states of hydration are adsorbed which limits the number of counterions a surface can accommodate.

The equations presented here are taken from the literature which is based upon wonderful simplifications but their models will immediately launch into the behavior of ceramic particles.

Fig.3.1 is modified from Lyklema and many others showing the following:

- An electronegative particle surface with electrokinetic potential Ψ_0 due to the surface charge density σ_0 .

- Several adsorbed hydrated counterions (shown as a divalent cation for a negative surface) which locates the center of the center of the countercharge at a finite distance from the surface depending upon its radius. The center of this adsorbed charge forms the **Stern layer** Ψ_δ , also called **the double layer**.

- A second, or more, hydrated cation layer which is sufficiently firmly attached to the particle to travel with it and form the boundary between the now hydrated particle and the bulk water. The residual electrical potential at this boundary is called Ψ_ζ , or ζ **the zeta potential** at the shear plane which separates the hydrated particle from the bulk liquid. Hiemenz doubts that a second hydration layer would be firmly fixed because of thermal agitation. This may be true for most materials but a second, third, or more layers may be necessary to explain the plastic behavior of clays in water.

- The van der Waals attraction for one arbitrary size particle.

- The net potential energy curve resulting from the summation of the repulsion and attraction curves. Fig.3.1 was drawn to show the potential energy barrier to flocculation into the primary energy well at the particle surface where the particles may touch each other and bond to a hard agglomerate. Measuring the true surface potential Ψ_0 of any particle is present impossible because the surface is contaminated by adsorption immediately

after fracture upon exposure to any environment. Measuring the Stern potential Ψ_s in water is also impossible because the degree of hydration is unknown. It has been estimated that the dielectric constant ϵ of water may be as low as 6 in the first hydration layer, and 32 in the second hydration layer, compared to 78 in pure bulk water. But it is relatively simple to measure zeta potential using several commercially available instruments, but great care must be taken in interpreting the results in terms of predicting rheology.

Obviously cations are attracted toward, and anions are repelled from, the surface thereby changing their concentration distribution in the water near the particle surface. There is thus an excess of cations and a deficiency of anions near the surface. This gives rise to the diffuse double layer which includes the Stern, or double layer.

- The resultant curve of the electrical potential ψ as a function of distance r from the surface.

- This produces an excess of co-ions at the far edge of the double layer before the distribution of counter-ions and co-ions becomes uniform in the bulk liquid.

The thickness of the adsorbed layer very much depends upon the ionic field strength z/a^2 of the hydrated counter-ions, where z is the valence and a is the ionic radius, and on the nature of the adsorbed liquid itself. This layer of "hydrated" ions (in the case of water) and structured liquid determines the thickness of the so-called shear plane. The adsorbed layer travels with the particle through the liquid and the boundary between the two is the shear plane. The electrical potential at the shear plane is called the zeta potential Ψ_ζ .

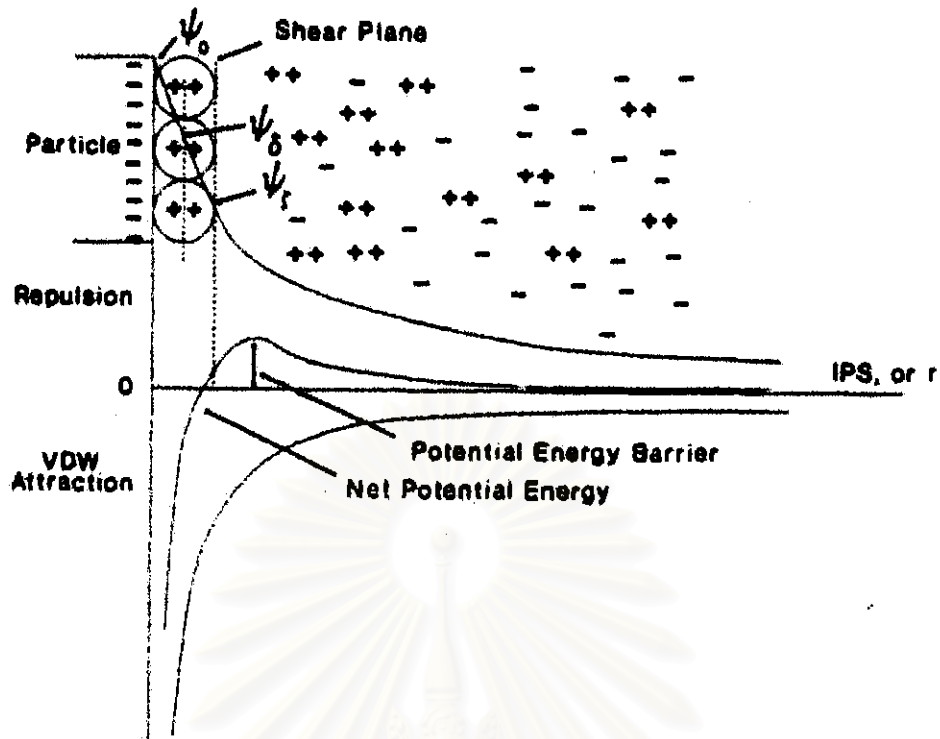


Fig. 3.1 The repulsive diffuse double layer at maximum deflocculation, with hydrated divalent cations adsorbed in the “double layer” + VDW attraction = net potential energy barrier.

Derivation of the electrical double layer

Hiemenz shows that the electrical double layer is derived from the capacitor model which leads to the Poisson-Boltzmann equation where it is assumed that the relationship between the charges and potentials are additive:

$$\frac{d^2\Psi}{dx^2} = -\frac{4\pi e}{\epsilon} \Sigma Zn \exp\left(\frac{-Ze\psi}{kT}\right) \quad (3.4)$$

Where Ψ = surface potential of the capacitor,

x, r = distance between the plates of the capacitor
IPS,

e = electronic charge,

- n = concentration of counterions in the bulk liquid,
 k = Boltzmann's constant,
 T = absolute temperature,
 z = valence of the counterion,
 ϵ = permittivity, of dielectric constant of the medium.

This equation was modified and then called the Debye-Huckel approximation where they assumed the relationship between the charges and the potentials are exponential:

$$\Psi = \Psi_0 \exp(-kr) \quad (3.5)$$

where

$$k = \sqrt{\frac{4\pi e_0 \Sigma Z^2 n}{\epsilon kT}} \quad (3.6)$$

But these equations are valid only for low potentials <25mV. As will be shown later zeta potentials for some ceramic powders may be greater than 25 mv, and Ψ_ζ or ζ s always less than Ψ_0 . The inverse $1/k$ is sometimes referred to as the thickness of the electrical double layer (i.e, the stern layer, not the diffuse double layer), but this may or may not be true depending upon the nature of both the surface and the liquid present.

Much earlier the Gouy-Chapman equation was derived from the Poisson Boltzmann equation and it does not include the limitation of low potential for its validity. The Gouy-Chapman equation is:

$$\gamma = \gamma_0 \exp(-\kappa x) \quad (3.7)$$

where

$$\gamma = \frac{\exp(Ze\psi/2kT)-1}{\exp(Ze\psi/2kT)+1} \quad (3.8)$$

and where

$$\kappa = \sqrt{\frac{4\pi e^2 \sum_i Z_i^2 n_{i0}}{\epsilon kT}} \quad (3.9)$$

n_{i0} = number of ions of type I per cm^3 far from the surface,

Z_i = valence,

ϵ = dielectric constant of medium.

Equation 3.8 shows the ratio, γ varies exponentially from the surface ψ with x (IPS) in the Gouy-Chapman theory rather than Ψ in the Debye-Huckel approximation. This equation is probably more useful for work with oxide powders.

Calculation of the repulsive interaction energy V_R , which results from overlapping the diffuse parts of the diffuse double layers, described by the Gouy-Chapman theory, surrounding two adjacent spherical particles is very complex. Hogg, Healy and Fuerstenau⁽⁵⁾ derived expressions for the repulsion energy for both constant potential and constant charge considerations, but as in the case for van der Waals attractive energy the interparticle distance must be smaller than the particle radii.

Reerink and Overbeek⁽¹⁷⁾ gave another approximate expression for repulsion energy where the interparticle separation distance is larger. For unequal spheres:

$$V_R = \frac{64\pi\epsilon R_1 R_2 k_B^2 T^2 \gamma_1 \gamma_2 \exp(-\kappa r)}{(R_1 + R_2) e^2 Z^2} \quad (3.10)$$

Where γ = Equation (3.8),

k_B = Boltzmann's constant to distinguish it from the

R_1, R_2 = the radii of the spheres.

For equal spheres:

$$V_R = \frac{32\pi\epsilon R k_B T^2 \gamma^2}{e^2 Z^2} \exp(-kr) \quad (3.11)$$

Unfortunately these equations require numbers which are almost, if not absolutely impossible, to obtain; for example, Ψ at the Stern layer, the number of liquid layers making up the hydration layer, the dielectric constant of water in the Stern layer, etc. If we use the zeta potential instead, we still have uncertainty in our measurements because we do not know how far from the particle surface it resides. But one good feature of all this explanation, of both van der Waals attraction and electrostatic repulsion, is that it provides a good visual model to explain the phenomenon of flocculation and deflocculation as follows.

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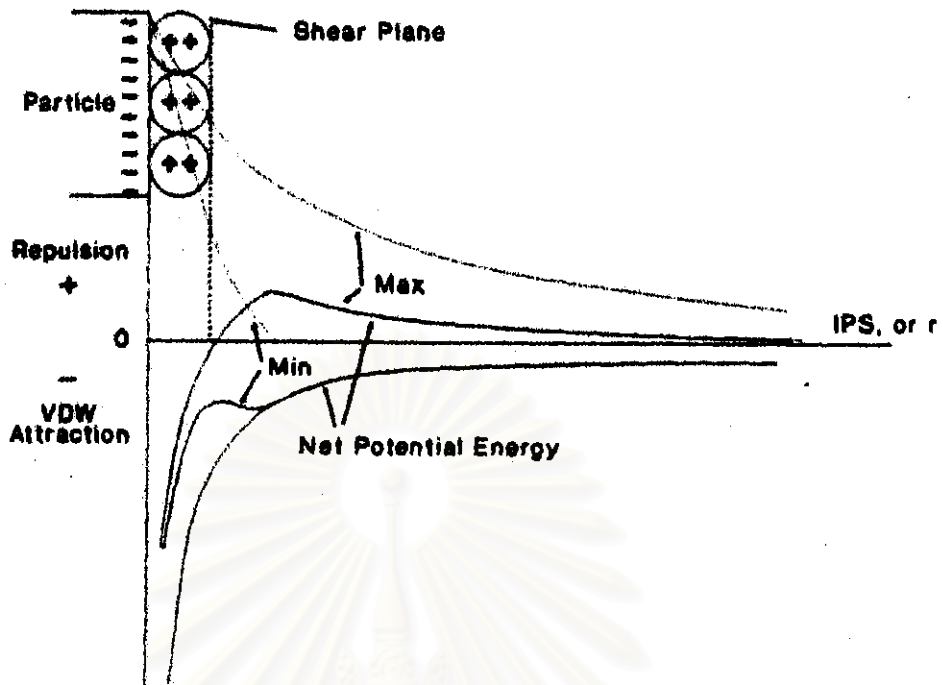


Fig. 3.2 The repulsive diffuse double layer at both maximum deflocculation and flocculation, with hydrated divalent cations adsorbed in the "double layer" + VDW attraction to provide extremes of the net potential energy barriers.

The DLVO Theory

Two teams of scientists independently of each other developed what is now called the DLVO theory of colloid stabilization; Derjaguin and Landau in Russia⁽¹¹⁾, and Verwey and Overbeek in the Netherlands⁽¹¹⁾. This theory combines the London-van der Waals energy of attraction with the electrostatic energy of repulsion, as shown in Fig. 3.1, to arrive at the net energy barrier required to prevent flocculating particles to fall into the very deep primary energy well at each particles' surface. If there were no repulsive energy between particles we should expect all suspended particles to flocculate and precipitate from suspension as a solid mass. This theory has been well tested and successfully explains the phenomenon of colloid stability.

Fig. 3.2 shows typical curves of both maximum repulsion and maximum attraction on the same plot with the net energy curve resulting from their addition. Maximum deflocculation is equivalent to maximum repulsion; maximum flocculation is equivalent to maximum attraction. For ceramic forming these two extremes will both produce poor rheological performance:

a. Maximum deflocculation.

- Large monovalent cations, required for deflocculation, diminish the thickness of the water film, allowing closer approach of particles to each other at very low viscosity.

- Reducing the thickness of the adsorbed water film exposes the particles to increased energy transfer during collisions at high shear rate, causing dilatancy.

b. Maximum flocculation.

- small multivalent cations, normally used for flocculation, increase the thickness of the adsorbed water film, preventing close approach in shear flow, thereby increasing the relative viscosity.

- The net potential energy barrier, having been eliminated, encourages close approach when quiescent or at low shear rate, allowing the particles to move close together until the flocculated mass contracts, causing syneresis.

Fig. 3.3 repeats Fig. 3.2 with addition of curves that would correspond to reasonable limits of deflocculation and flocculation. As already stated, and will be repeated several more times, maximum deflocculation or flocculation of crowded suspensions is to be avoided for optimum processing performance; Maximum deflocculation of crowded suspensions leads to dilatancy at high shear rate, and maximum flocculation of crowded suspensions leads to syneresis at low shear rate, particularly when there is a high percentage of colloidal particles in the suspensions. In Fig. 3.3 a second layer of adsorbed hydrated cations is shown and the

shear plane is consequently moved to a position farther from the particle surface.

From these figures it is clear that increasing the concentration of counterions decreases the zeta potential which is the net effective repulsive potential at the shear plane. But it should be equally clear that increasing the number of layers of hydrated counterions, provided they improve the structure of the liquid layer, will also decrease the zeta potential simply by moving down the curve farther from the particle surface.

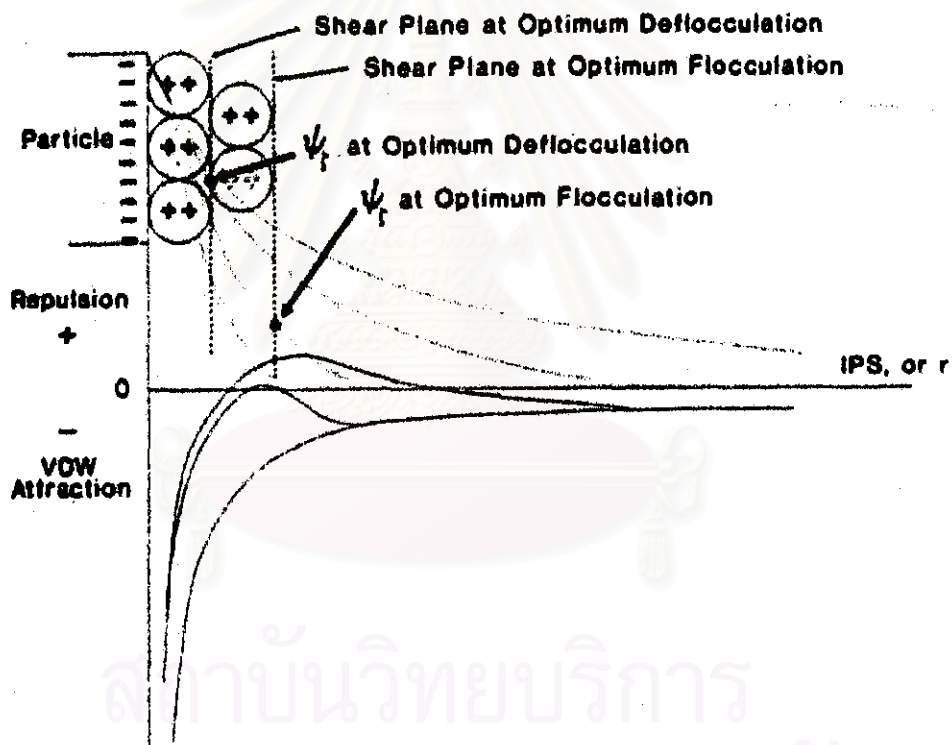


Fig. 3.3 The repulsive diffuse double layer at optimum deflocculation and flocculation, with hydrated cations adsorbed in the double layer + VDW attraction to provide stable net potential energy barriers.

The Role of the Liquid Medium

The liquid medium is the agent in which the particles are suspended and the chemical additives are dissolved. The structure and solubility of the chemical additives determine which part of the solute remains in the liquid and which part adsorbs onto the powder surfaces. It has been mentioned a couple of times that the structure of the adsorbed film of water on the surface of the particle is affected by the addition of ions so now is a good time to discuss the structure of water.

Since clay-water suspensions are the classic example of a plastic material, and since neither clay nor water are plastic by themselves, it follows that there must be some unique relationship between the two when they are combined which provides this property. Although many ceramic products are now made using neither clay nor water, it is necessary in that case to duplicate the water structure at the interface on these non-clays to provide the plasticity appropriate for all forming processes.

Water possesses two very unique properties which are responsible for its behavior: the hydrogen bond and the hydrophobic effect, both of which are important to ceramic forming.

The Hydrogen Bond

Water molecules tend to bond together in a tetrahedral configuration where the H-O-H bond angle is 104° . Israelachvili⁽¹⁴⁾ added that the tetrahedral coordination of the water molecule is more important than the H bond, which causes it. Tanford⁽¹⁸⁾ says, "Molecules of a dual nature, with one part soluble in water, and one part that is expelled from it, are forced by their duality to

adopt unique orientations with respect to the aqueous medium, and to form organized structures." This is a wonderful statement which predicts we may indeed be able to construct similar structures on any powder surface in a manner which can duplicate the clay-water interface within a clay containing suspension. This expulsion of such molecules from water, even though one part is hydrophilic, or water soluble, is called the "**hydrophobic effect.**" That is, when certain molecules are dissolved in water, although there is no electrostatic attraction of a powder for them, they will be expelled to the powder surfaces just to get them out of the water. Tanford further states, the free energy of attraction of water for itself is -144 kJ m^{-2} . So when we have ionic polymeric organic matter in an aqueous suspension, the organic matter adsorb onto the clay particle simply because the water rejects them, and not because there is any specific adsorption mechanism; the longer the hydrocarbon chain length, the higher the expulsion energy.

Adsorbed water on a clay surface.

The model described here for the structure of the water adsorbed onto a clay mineral is taken mostly from Lawrence, Hendricks and Jefferson⁽¹⁹⁾, which Lawrence quotes, described the water layer as built on the basal surface of clays from tetrahedral water molecules joined together in hexagonal groups as shown in Fig. 3.4, Fig. 3.5 is a plan view of the water structure superimposed on a basal plane of a 3 - layer clay mineral. This view shows that $\frac{1}{4}$ of the hydrogen atoms do not function within the water structure, and are therefore available to bond the water layer to the clay surface's O^{-2} of OH^{-1} . Fig. 3.6 shows the adsorption of a single water layer adsorbed onto the basal plane of the silica layer in a clay mineral.

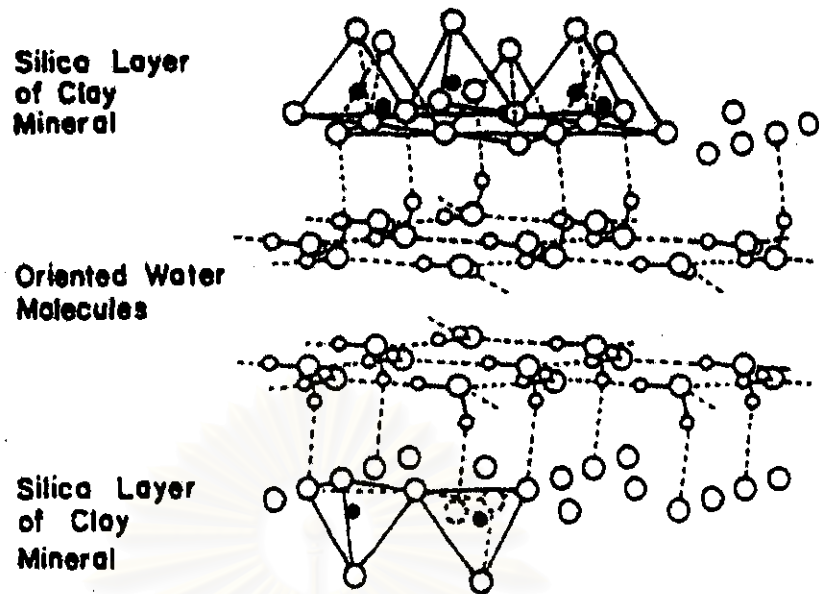


Fig. 3.4 Configuration of water adsorbed onto the basal surface of a clay mineral⁽¹⁹⁾.



Fig. 3.5 Superposition of water structure on the basal oxygen layer of vermiculite⁽¹⁹⁾.

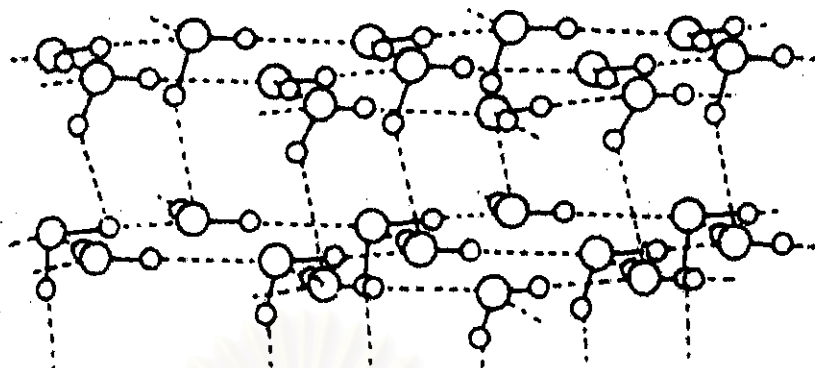


Fig. 3.6 Configuration of water structure showing the bond through hydrogens to the clay surface⁽¹⁹⁾.

Effect of Soluble Polymers on The structure of Water.

Traube's rule, cited in Tanford⁽¹⁸⁾, states: "The adsorption of organic substances from aqueous solutions increases strongly as we ascend the homologous series." That is, as the molecular weight of the hydrocarbon part of the copolymer increases, and thereby the resultant hydrophobicity and adsorption onto a foreign surface also increases.

Although it is not precisely a "hydrophobic effect," if an organic solvent has some polar molecules it will also have some structural organization, and may also expel nonpolar molecules. Although no solvent has this effect as strongly as water does, glycerol, ethylene glycol, and some alcohols are quite effective, particularly at high solute concentrations. Fortunately this is exactly the case when the particle size distribution is near maximum packing efficiency so the interparticle porosity is low and IPS (interparticle separation distance) is also small. The volume of solvent would be relatively low compared to the powder

surface area so the concentration of solute molecules would be high.

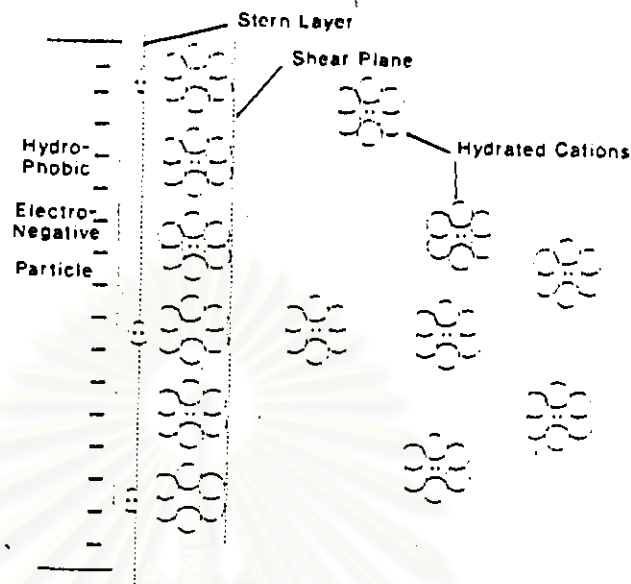


Fig. 3.7 Adsorption of hydrated cations to an electronegative hydrophobic surface.

Combining all these principles it appears that we can duplicate the plastic clay-water film using organic dispersants at least partially and to some advantage. Fig.3.7 is a schematic of hydrated cations in an aqueous suspension being drawn toward an electronegative hydrophobic surface. It is possible that the cations in the layer of hydrate nearest the surface may be stripped from within the structured water group, due to the hydrophobic repulsion of the surface, so the cation is partly bonded to the electronegative surface and partly to the water group. In such a system the water molecules are probably not bonded very tenuously to the surface so that moderate shear stress could remove them.

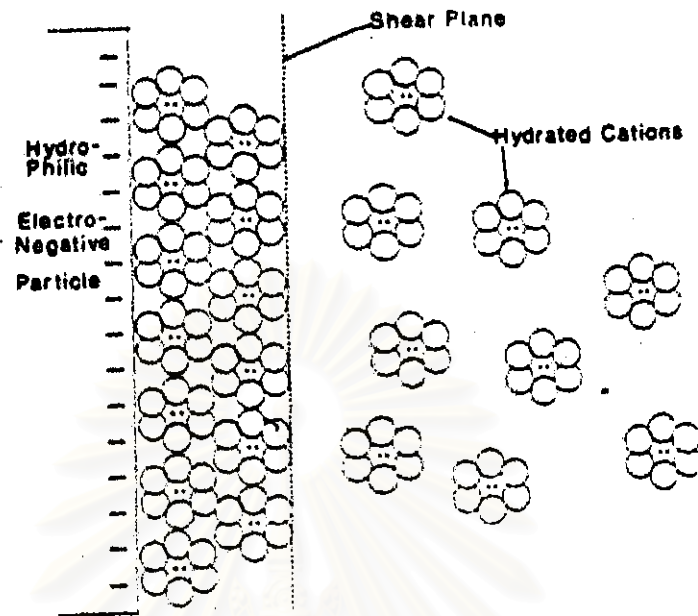


Fig. 3.8 Adsorption of hydrated cations to an electronegative hydrophilic surface.

Fig. 3.8 shows a similar arrangement as Fig. 3.7 except the electronegative surface is now hydrophilic. The water of hydration surrounding the divalent cations is bound firmly to the surface, neutralizing many of the negative surface site charges. The water film is drawn as two layers but there may be a third. The shear plane has therefore been moved farther from the surface and the ψ_c has been reduced allowing flocculation. This suspension would exhibit a high viscosity and shear thinning rheology.

In these models added ions play a somewhat different role in neutralizing the effective charge. When an ion is added to water it tends to hydrate and then be attracted to the surface or repelled from it depending upon the electric charge of the surface and the ion. The former will flocculate the suspension and the latter will

deflocculate it. But in both cases the ion will tend to react directly with the surface. When the ion is added as a part of a polymeric electrolyte, the hydrophobic tail or spine tends to adsorb onto the powder surface due to hydrophobic repulsion from the water. Then soluble counterion ion additions will tend to neutralize the ionic moieties on the side branches of the Polyelectrolyte some distance from the surface and not react with the surface at all. This effect is thought to provide a sufficiently strong yield stress for plastic forming processes. When the yield stress is exceeded the interface between adjoining particles, which is at the ends of the side branches, is easily distorted and broken, so that flow is maintained at a shear stress only slightly higher than the yield stress. This will be shown to describe a higher plasticity than what occurs with only inorganic additives.

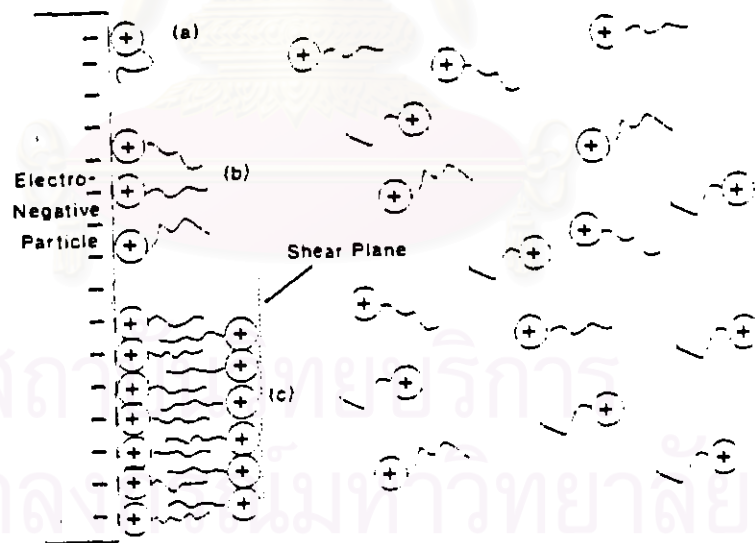


Fig. 3.9 Adsorption of a cationic copolymer to an electronegative powder surface.

Fig. 3.9 shows the effect of adding simple cationic polymers to a hydrophilic surface. The soluble cations are attracted

electrically to the surface leaving the tails in the water where they are gradually expelled toward the surface. After some time the tails will also lie on the surface and the suspension will have a vary low ψ_c and a low viscosity with dilatancy at high shear rate. As more polymer is added a second layer of polymer will begin to develop parallel to the first one as shown, analogous to a lamellar liquid crystal with the hydrophilic moieties facing outward toward the water and the hydrophobic tails facing inward toward each other. In this case the distance of the shear plane from the surface depends upon the molecular weight, and therefore the length, of the polymer, the surface is electropositive, and the ψ_c is high. This polymer will require large dosage for effective deflocculation, but the structure of the interface will essentially a fiber reinforced water structure analogous to Fig. 3.8.

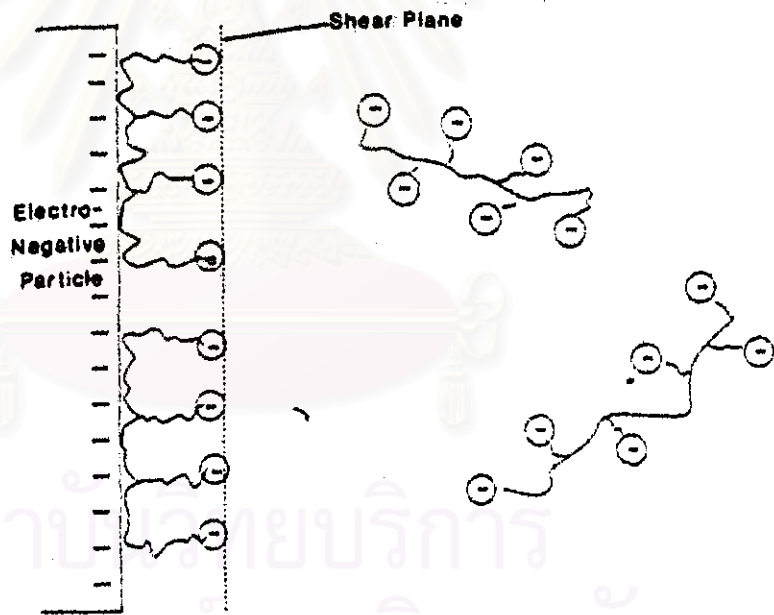


Fig. 3.10 Adsorption of a grafted anionic copolymer to an electronegative powder surface.

Fig. 3.10 shows anionic grafted copolymeric polyelectrolyte molecules adsorbing onto an electronegative surface which may be either hydrophobic or hydrophilic. In this case the hydrocarbon

spine of the polyelectrolyte is expelled from the water while the water-soluble head remains in the water. The anionic head also is repelled by the electronegative surface forcing the side branches of the polymer to stand up as far from the surface as its chain length will allow. In this case the shear plane is located at the length of the side branches from the surface and ψ_c is very large since it is the sum of the surface and the polymer. This polymer will deflocculate at relatively low concentrations of polyelectrolyte and will provide a very low viscosity since the particles can approach each other more closely without bonding.

And there is a model of adsorbed humic acid on clay particle which proposed by Richard Terry⁽²⁰⁾.

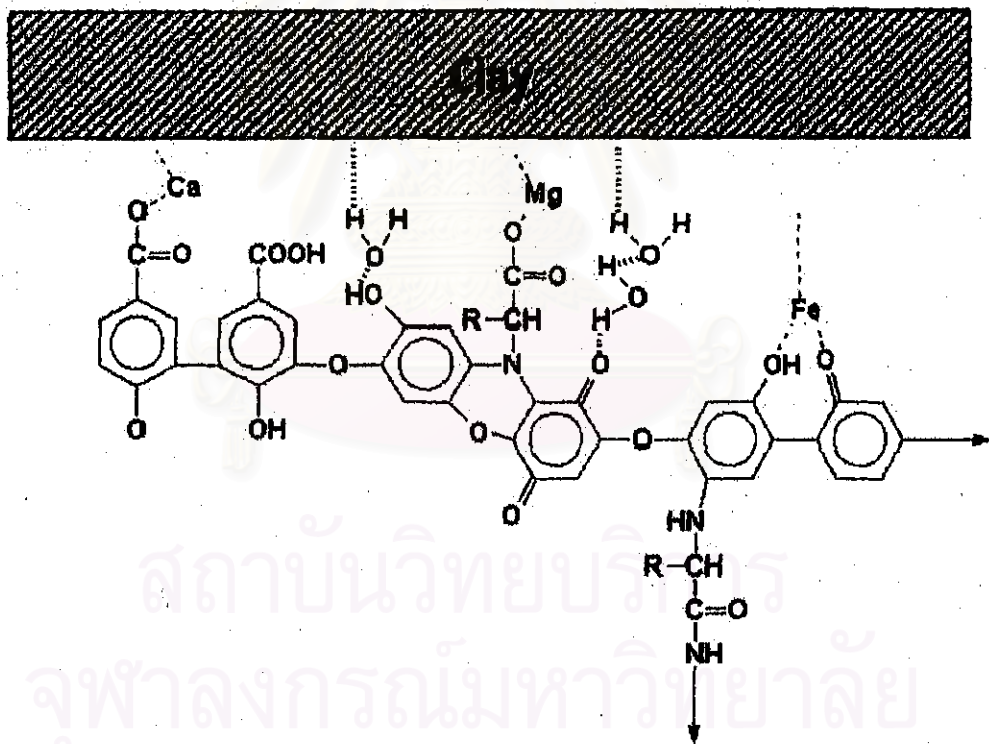


Fig. 3.11 Model of adsorbed humic acid on clay particle.

From Fig.3.11 we have seen the importance of humic acid that has both chain and ring structure and has the chelating property which can be substituted nitrogen by other cations. This

structure effect the double layer and steric repulsion on the surface of clay.

Electro-steric repulsion

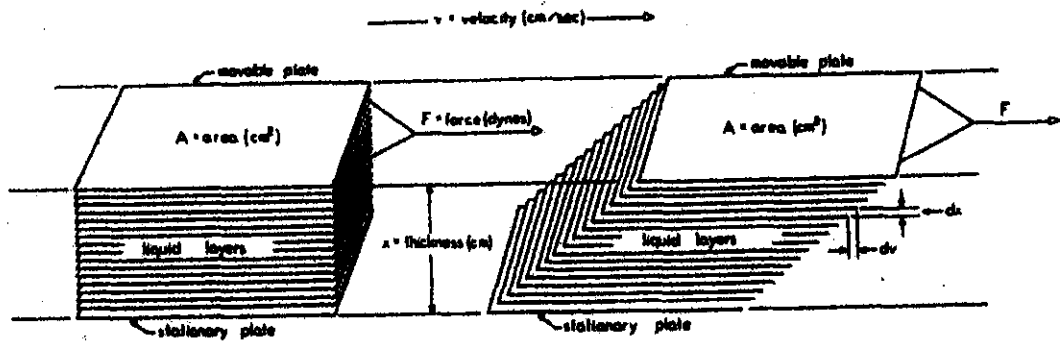
Fig. 3.9 and 3.10 show an effectively fiber reinforced water film at the interface between the particle and the bulk water. This structure provides a mechanical barrier between adjacent particles to prevent their near approach to each other. In the case of Fig.3.9, as polymer is added a sequence of events takes place between the first molecules added and a sufficient excess to form the double layer, as follows:

- I. At a), when the amount of polymer is very small, the ionic head a sequence of events takes place between the first molecules added and a sufficient excess to form the double layer, as follows:
- II. At b), as the amount of polymer is increased, polymer crowding may cause some of the tails to be forced to stand up from the surface to make room for the specifically adsorbed heads. This is analogous to Hiemenz (his Fig. 3.9 is used to describe the effect of surfactants upon surface tension). This continues until the first layer is completed, at which time a *mechanically repulsive steric* barrier has been constructed. This condition is steric repulsion only.
- III. At c), the double layer of polymer has been constructed and the surface potential has been reversed from negative to positive. This condition is a combination of electrostatic and steric, or electrosteric.

Probably the easiest way to learn which are the best dispersants to be used for any specific powder is by trial and error, using the deflocculation response of any given polymer in a crowded suspension.

3.2 Viscosity and Flow⁽²¹⁾

At the very outset it is important to develop a clear, exact concept of viscosity (the resistance of a liquid to flow). To do this, consider a model situation in which a liquid is confined between two parallel plates. One is movable and one is stationary, and they are separated by a distance x (see Fig. 3.12). Let a force F act on a top movable plate in tangential direction so that the top plate slides sidewise with velocity v relative to the bottom plate. When it so moves, layers of liquid between the two plates are also moved in sidewise direction, as depicted in the right-hand section of Fig. 3.12. The top liquid layer moves with the greatest velocity, whereas the bottom liquid layer moves with the smallest (zero) velocity. Intermediate layers move with intermediate velocities. However, the velocity gradient dv/dx (differential or incremental change of velocity dv corresponding to a differential change in thickness dx) for any portion of the liquid is constant. This velocity gradient γ is referred to as the shear rate. In the given situation, the shear rate (velocity gradient) is uniform from top to bottom. Hence dv/dx is also equal to v/x (see Eq. 3.12). Shear velocity v is conventionally expressed in centimeters per second and thickness x in centimeters. Hence shear rate γ ($= v/x$) has the dimensions of reciprocal seconds (sec^{-1}), because the centimeter unit (present in both the numerator and the denominator) is canceled out leaving only the second unit in the denominator to express the shear rate quantity.



$$\tau = \text{shear stress} = F/A \text{ (dynes/cm}^2\text{)}$$

$$\gamma = \text{shear rate} = v/x \text{ (sec}^{-1}\text{)}$$

$$\eta = \text{viscosity} = \text{shear stress} / \text{shear rate}$$

$$= \tau / \gamma \text{ (dyne sec cm}^{-2}\text{) or (poise)}$$

Fig. 3.12 Theoretical parallel plate arrangement illustrating simple (Newtonian) flow.

The total force acting tangentially on the top plate (of area A) is F . The force acting on a *unit* of top plate area is then F/A . This force per unit of area τ is called the shear stress (Eq. 3.13). Shear force F is conventionally expressed in dynes (1 gram weight = 980 dynes) and the area A over which it acts in square centimeters. Hence shear stress τ ($= F/A$) has the dimensions of dynes per square centimeter.

Now that we have developed the two ideas of shear stress and shear rate, viscosity can be defined. Viscosity η is the ratio of shear stress to shear rate (see Eq. 3.14). It is unfortunate that no consistent set of symbols for shear stress, shear rate, and viscosity has been accepted by rheologists.

In view of its importance, viscosity has been assigned as special unit, the poise. Viscosity in poises is automatically obtained when the shear stress is expressed in dyne-cm⁻² and the

shear rate in sec^{-1} . From this it is seen that the poise has the dimensions of dyne-sec-cm^{-2} . It is measure of absolute viscosity. Since a dyne in fundamental cgs units is expressed as g-cm-sec^{-2} , the poise in turn has the dimensions of $\text{g-cm}^{-1}\text{-sec}^{-1}$ (in cgs units).

Three equations (Eqs. 3.12,3.13,3.14) have been developed. They underline the science of flow and should be clearly understood for a proper understanding of all the derived formulas the develop through their use.

$$\gamma \text{ (shear rate)} = \frac{dv(\text{differential velocity})}{dx(\text{differential thickness})} \quad (3.12)$$

$$\tau \text{ (shear stress)} = \frac{F(\text{force})}{A(\text{area})} \quad (3.13)$$

$$\begin{aligned} \eta \text{ (viscosity)} &= \frac{\tau(\text{shear stress})}{\gamma(\text{shear rate})} \\ &= \frac{F/A}{dv/dx} \end{aligned} \quad (3.14)$$

The arrangement of the liquid between the two parallel plates given in Fig. 3.12 is obviously an idealistic situation.

Kinematic Viscosity

The poise, the fundamental measurement of absolute viscosity, is related to the stroke, a measurement of kinetics of viscosity. Kinematic viscosity is the ratio of absolute fluid viscosity (poise) to fluid density (grams per cubic centimeter) as given by Eq. 3.15.

$$V \text{ (stokes)} = \frac{\eta \text{ (poise)}}{\rho \text{ (g/cm}^3\text{)}} \quad (3.15)$$

The stroke is a useful unit when working with so-called kinematic viscometers (such as the orifice and bubble types) or when designing piping installations for conveying slip or slip ingredients through a plant.

As implied by the prefix "centi-," a centipoise is equal to one hundredth of a poise; a centistroke is equal to one hundredth of a stroke.

At 68 °F (20 °C) water has a viscosity of 1.0 centipoise (0.01 poise), linseed oil a viscosity of 50 centipoises (0.50 poise), and castor oil a viscosity of 1,000 centipoises (10.0 poises). These are useful reference liquids for visualising viscosity in terms of numerical values.

Newtonian (simple) flow

It is useful, however, to conceive of an ideal liquid having a constant viscosity at any given temperature for low to moderate rates of shear. Such a liquid is said to be Newtonian in flow behavior, and liquid which actually approach this idea are called Newtonian liquids (these include water, solvents, mineral oils, and some resin solutions). A linear plot of shear rate against shear stress for a Newtonian liquid results in a straight line passing through the origin. The slope of the line corresponds to the liquid viscosity (see Fig.3.13). Note that a single viscosity value serves to determine the shear stress/shear rate relationship for a Newtonian liquid over a wide range of values.

Non-Newtonian flow

Plastic Flow

Plastic flow introduces the idea of a yield value, namely, a certain minimum shear stress value that must be exceeded before flow will take place. Let this minimum shear stress value be designated τ_0 , the subscript serving to distinguish it from the total applied shear stress τ . Then $(\tau - \tau_0)$ is the portion of shear stress that is available for creating and maintaining liquid flow. The equation

for plastic flow, Eq. 3.16, is a modified form of Eq.3.14. The viscosity in this equation is marked with a prime to designate that this viscosity applies to plastic flow rather than to Newtonian flow.

$$\eta' = \frac{\tau - \tau_0}{\gamma} \quad (3.16)$$

A linear plot of shear rate against shear stress for plastic flow results in a straight line that intercepts the shear stress scale at the liquid yield point (the minimum shear stress necessary to initiate flow). The slope of the straight line corresponds to plastic viscosity(see Fig.3.13). Liquid exhibiting plastic flow are commonly called Bingham liquids.

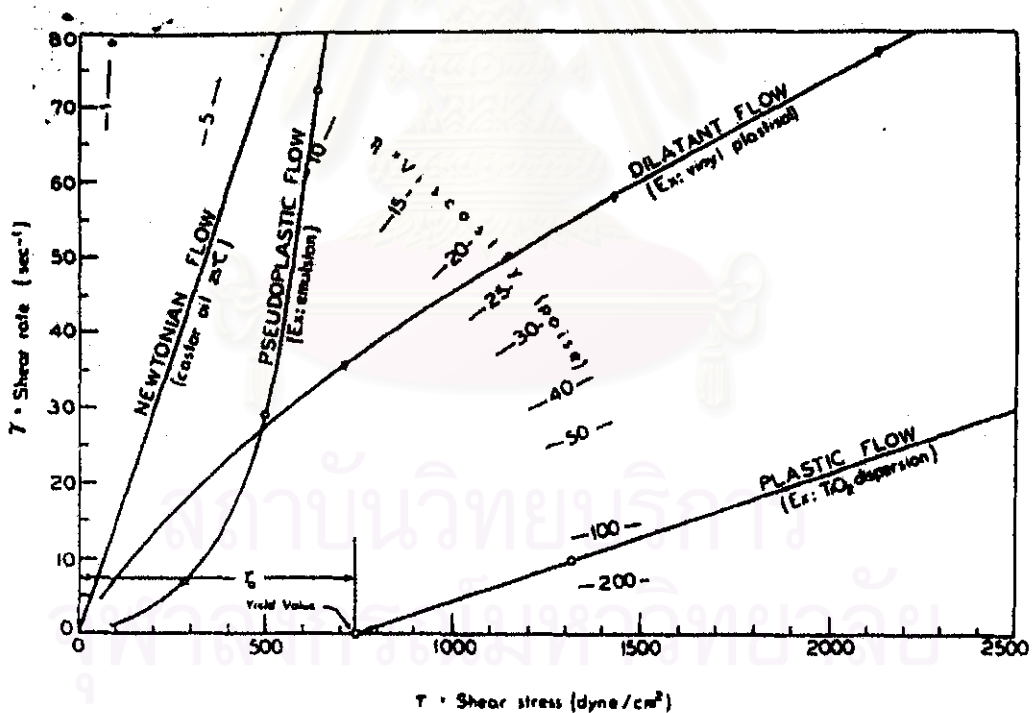


Fig. 3.13 Typical flow curves for Newtonian plastic, pseudoplastic, and dilatant flow.

Pseudoplastic Flow

Pseudoplastic flow is a sort of hybrid flow - it simulates plastic flow at moderate to high rates of shear, and Newtonian flow at low rates of shear. The change from one type of flow to the other is not sharp, but rather gradual, so that a plot of shear stress against shear rate results in a smooth curve convex to the shear stress axis (see Fig. 3.13). This curve relationship, with its constantly changing slope, means that a liquid exhibiting pseudoplastic flow has no fixed viscosity value (either of the Newtonian or the plastic type). Rather, it exhibits a series of viscosities, each one depending on the specific shear stress being imposed at the time on the pseudoplastic liquid. The viscosity value for pseudoplastic flow at any given shear stress is termed an **apparent viscosity** (although the viscosity obtained is real enough). The term apparent merely implies that the viscosity at this one point does not apply to shear-stress rate conditions at other points. A number of complex equations have been proposed to represent the relationships among the quantities τ , $\dot{\gamma}$ and η for pseudoplastic flow.

Dilatant Flow

Dilatant flow can be thought of as the opposite of pseudoplastic flow. Whereas with pseudoplastic flow the viscosity of the liquid is reduced as the shear stress is increased, with dilatant flow the viscosity of the liquid is raised as the shear stress is increased. Again, a plot of shear stress against shear rate results in a smooth curve. In this case the curve is concave to the shear stress axis.

Thixotropic Flow

The shear stress / shear rate relationships graphed in Fig. 3.14 are either straight lines or smooth curves. Hence, for every specific shear stress value (a point on the line) there is associated a corresponding fixed shear rate, since the lines were originally developed by imposing a set of shear stresses and measuring the shear rates obtained. At first glance, no difficulty is envisioned in reproducing these measurements; seemingly, it should make no difference whether the test liquid is to be stirred vigorously before the test or not; or whether the set of shear stress values is to be imposed in an ascending or descending order; or whether the measurements are to be made slowly or rapidly. However, to add another rheological complication, flow behavior may very often be dependent on just such variables. Both the history of the liquid system prior to testing and the exact pattern of testing can be of critical importance.

The word thixotropy, derived from two Greek words, means literally "change by touch." Thus flow behavior that is altered by touch (stirring, agitation) is called **thixotropic**. Thixotropic behavior is presumably due to a breakdown of some loosely knit structure resident in the liquid system. This structure may be deliberately built into the slip system by resorting to a slip additive (deflocculant) which impart the thixotropic effect. Here the thixotropy produced is the valuable property, for at high shear rates (during slip application) the lower viscosity that is produced facilitates for casting after that slip at low shear rates the restoration of structure gives the cast formation in mold. The technology of thixotropic behavior is quite complex. In general, thixotropic breakdown (loss of viscosity) is fostered by an increase in the shear stress, by prolonging the shear time, or by both. Conversely, when the shear stress is removed, recovery the

thixotropic viscosity ensure as thixotropic structure is again built up throughout the slip system. For any given pattern of testing, the amount of thixotropy present can be evaluated in terms of area enclosed by a so-called **thixotropic loop**. Such a loop is obtained by imposing and ascending series of shear stresses on the test liquid and measuring the corresponding shear rate obtained. Without interruption the process is reversed, giving a set of shear rates corresponding to a descending order of shear stresses. A plot of this data produces a loop area between ascending and descending curves. The area enclosed is the measurement of the thixotropic breakdown, which in turn serves as an index to the thixotropic viscosity resident in the liquid system (see in Fig.3.14).

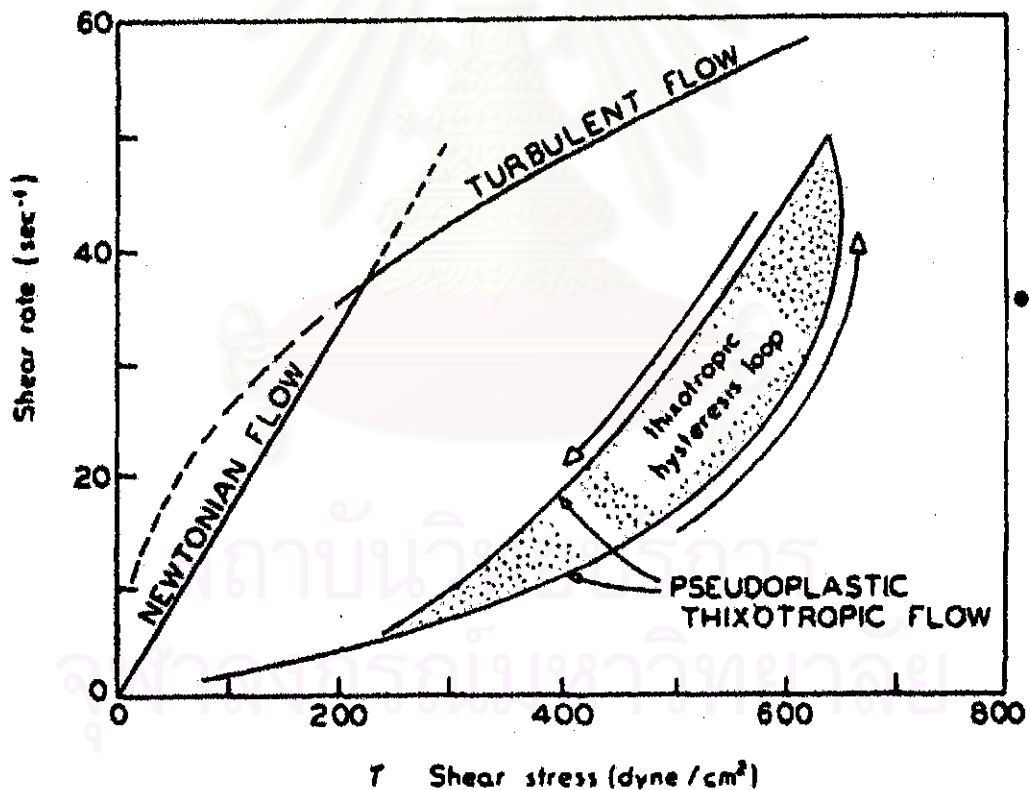


Fig. 3.14 Typical flow curves for thixotropic and turbulent flow.

3.3 Rheology⁽⁷⁾

Rheology is defined as the science of flow and deformation of matter, a branch of physics closely related to mechanics of deformable systems. Subjectively a viscous liquid might be described as thick, gluey, sticky, slow-flowing, or bodies. Such terms are picturesque and quite helpful in roughly characterizing the flow properties of a liquid, but they are qualitative at best. Ceramic rheology is concerned mainly with deformation of cohesive bodies such as slips and plastic masses. The importance of the rheology in ceramics is obvious. Slip casting involves flow in the mixing, pumping, pouring, and draining of slip and, because quiescent slips are known to thicken somewhat upon standing, the draining of excess slip from molds must be preceded by deformation and breaking of the gelled structure. Given that rheology measurement on casting slips is so widely predicted it is important that these data be properly interpreted and applied. Rheological data are easy to misinterpret, especially when obtained with the deceptively simple methods commonly employed in most plants. A proper understanding of rheological fundamentals is needed for intelligent application of test results.

The deformation of substances can be divided into two general categories: (a) spontaneously reversible deformation, termed elasticity; and (b) an irreversible deformation, called flow. A perfectly elastic body recovers the work of deformation mechanically when restored to its original shape, whereas the energy involved in sustaining flow dissipates in the form of heat. The resistance of liquid to flow is often called "internal friction," from an analogy between viscous resistance to flow and friction between solid surfaces.

3.4 CASTING RATE^(5,7,11,22)

Investigations of the mechanism of formation of solid casts from slips have shown that it is a diffusion-controlled process Hermann and Cutler⁽²³⁾ and amounts to a simple dewatering of slip Adcock and McDowall⁽²⁴⁾. The driving force for this process is the suction pressure created by the porous plaster mold. When a slip is first poured into a mold a high rate of casting is observed for a few seconds. This is due to the high rate of water diffusion in the plaster. Following this initial stage, the rate of cast formation is determined by the permeability of the solid cast. It has been shown Adcock and McDowall that the rate of cast formation can be quantitative determined by

$$\frac{L^2}{t} = \frac{2PgE^3}{5S_p^2\eta(\gamma-1)(1-E)^2} \quad (3.17)$$

where L is the thickness of the cast layer, t is time, P is the suction pressure, E is the void fraction, S is the surface area of solid particles, η is the viscosity of fluid, γ is the volume of slip containing volume $(1-E)$ of solids, and g is acceleration due to gravity.

This equation has been experimentally verified and a number of important features of the slip casting process may be predicted from it. These features are as follows.

- The thickness of the cast layer is proportional to the square root of time.

- Surface area plays an important role in casting rate because it is a squared term and also because it determines the mode of particle packing and hence the value of E and γ .

- The permeability of the cast. Measured by E , strongly influences casting rate. The term $E^3/(1-E)^2$ is very sensitive to small changes in E and therefore strongly affects casting rate.

- The viscosity of the liquid phase affects casting rate. Temperature changes may cause this term to vary.

- Casting rate is related directly to the pressure on the slip. This factor is important in techniques such as pressure casting.

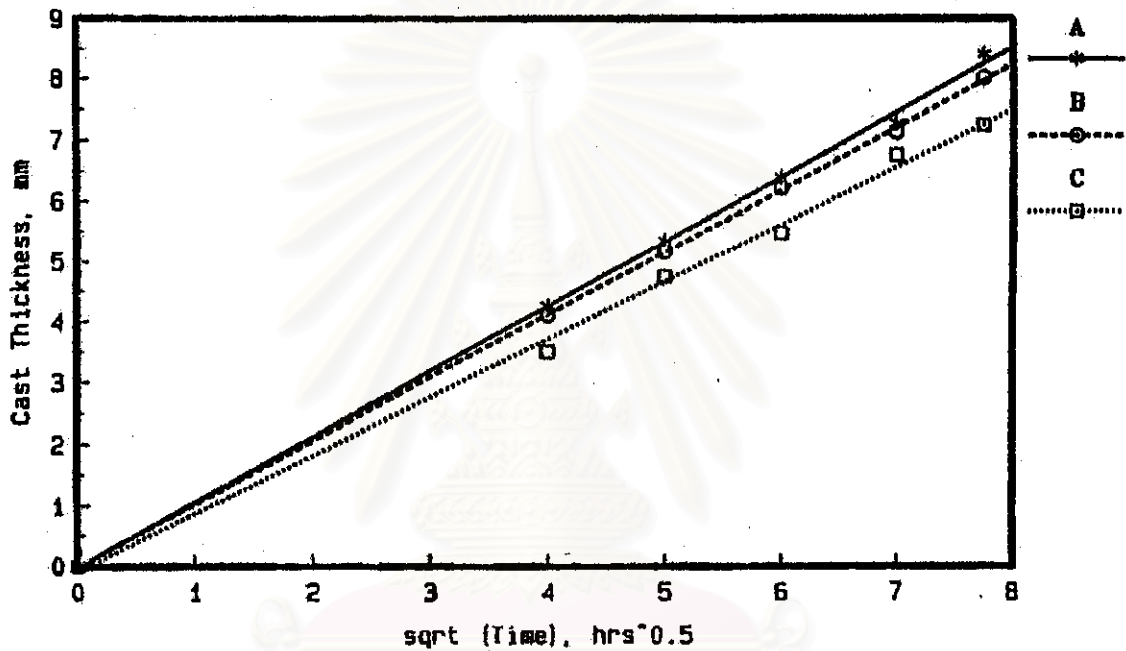


Fig.3.15 Casting rate of sanitaryware casting slip plot between cake thickness and square root of time⁽⁴⁾.

A = casting rate 8.4 mm/hr.

B = casting rate 8.01 mm/hr.

C = casting rate 7.24 mm/hr.

The Baroid Filter Press⁽¹¹⁾

Both Predispersed and HID(High Intensity Dispersion) slips were also filter pressed to determine the effects of flocculation

and solids content on the rate of dewatering. This subject can be confusing because the rate of dewatering depends upon the amount of water in the suspension as well as the ease of that water through the cake. A suspension with a high specific gravity contains less water than one with a low specific gravity, so less water egress is required for the same cake buildup. Therefore we must determine the rate of cake buildup based upon dry weight of body. A less flocculated body will produce a lower moisture content cake so it is difficult to use a single test to make these measurements. Therefore two different tests were performed and the results combined to produce an analysis of filtration rate.

Because the **Baroid filter press** (baroid Testing Equipment, Houston, TX.) uses only 50 psi air pressure on top of the sample of slip, it is impossible for it to dewater a high clay content filter cake to 20 wt% water. Measuring the rate of egress of the filtrate gives a comparison of filtration rates of the same slip specific gravity at different levels of flocculation, but different specific gravity slips contain different volumes of water, so the rate are not comparable. Therefore some simple calculations were made to normalize the results of filter pressing rate to a constant cake water content = 20 wt% even though it is impossible to reach this result using the Baroid press at 5.1 bar.

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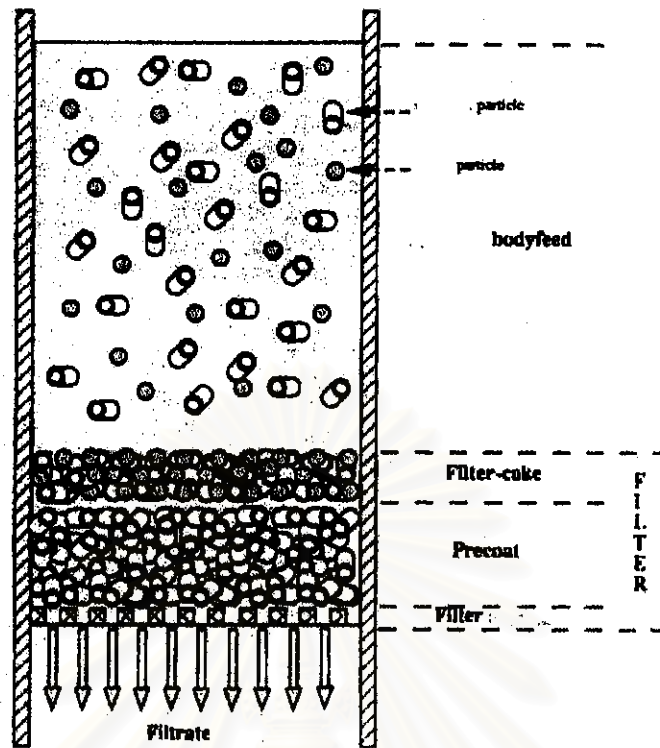


Fig.3.16 Baroid filter press schematic diagram⁽²⁵⁾.

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