CHAPTER 1

INTRODUCTION

1.1 GENERAL BACKGROUND

Fine coal cleaning is a necessary operation to produce consistent quality product to the consumer. The most difficult and costly part of the cleaning operations is usually the process of cleaning fine particles. In general, the costs of cleaning fine particles are approximately 3 times higher than those for coarse particle, while the fine product contains higher levels of impurities including ash, sulfur and particularly moisture. For this reason, it is often more economical to discard the fines if the fine particle constitutes only a small fraction (5 to 10%) of the product stream. This has been the case with many coal producers in the U.S. As a result, approximately 2 billion tons of fine coal has been discarded in abandoned ponds, and 500 to 800 million tons are still in active ponds. On a yearly basis, the U.S. coal producers discard approximately 30 to 40 million tons of fresh fine coal to ponds. This represents a loss of valuable natural resources, loss of profit for coal producers, and creation of significant environmental concerns [1-10].

The reason for the difficulty of dewatering fine particle is that the fine particles have larger surface area than coarse particles, which creates smaller capillaries in filter cake resulting in grater retention of water. Significant improvements for cleaning processes have been made during the last 20 years for efficiency of the separating fine particles. In contrast, relatively little improvement has been made for removing the water from the fine products obtained using the separation processes. In some companies, thermal drying may be an option to dewater the fine product, but for many it is too costly and pollution creating operation [1,2,5]. Therefore, the lack of efficient dewatering processes (e.g. vacuum, pressure and centrifuge) on the fine particle dewatering is forcing many companies to discard the fines to tailing ponds.

A large part of the cost for cleaning fine coal consists of the cost of dewatering fines. Figure 1.1 shows the costs of dewatering as a function of particle size [1]. As can be seen, the cost of the dewatering fines sharply increases when the particle size is below 0.5 mm. The cost data corresponds to mechanical and thermal drying methods, both of which are the only practical methods for drying fine particles to below 10% moisture by weight. In the plants, large thermal dryers are built to take advantage of the economy of the scale. On the other hand, it is difficult to justify large capital expenditures to process the relatively small fraction of the product stream in a coal preparation plant. This is particularly true in the case with pond fines recovery projects, whose life spans are typically in the range of two to five years. It is also difficult to obtain permissions to install thermal dryers in many states of the US. An alternative would be to improve the mechanical dewatering techniques for the fine particles to be dewatered [1-3,5-14].

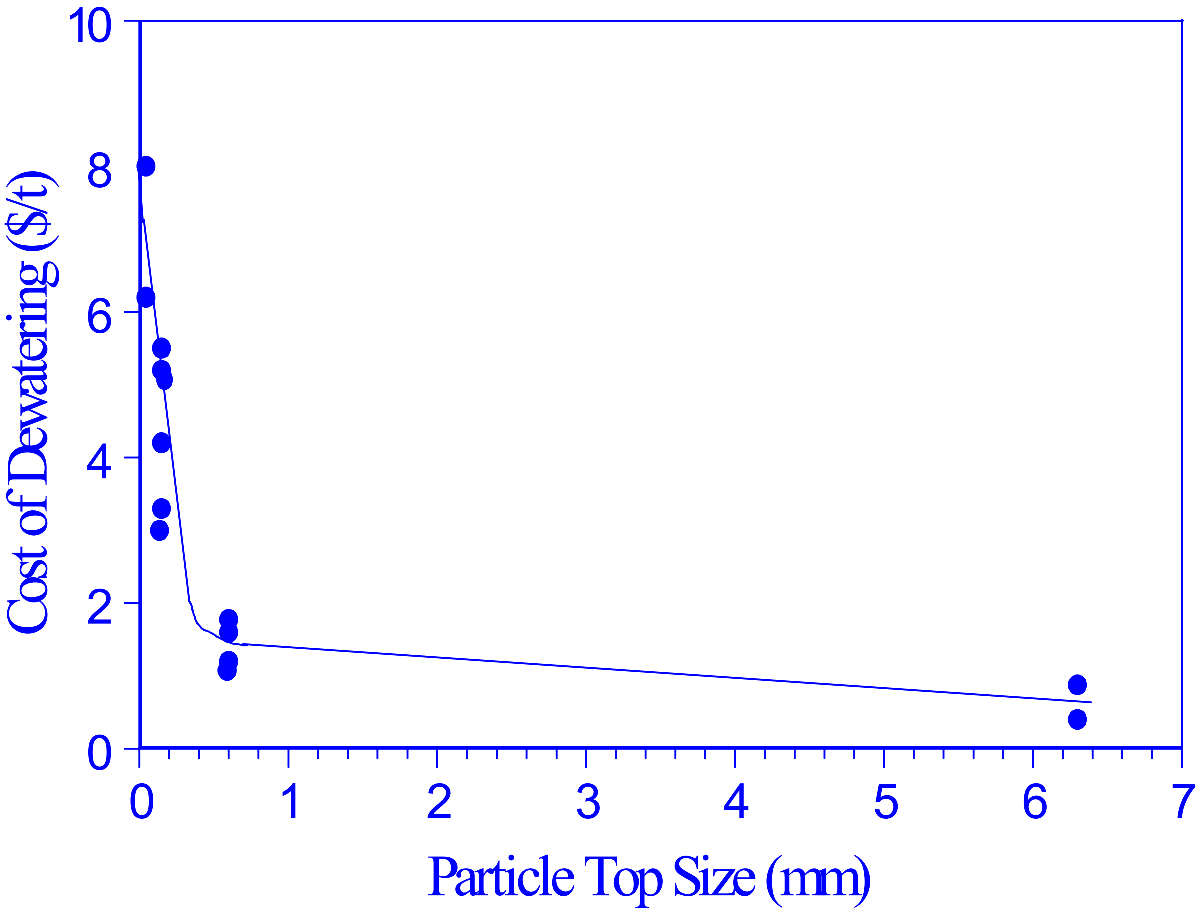


Figure 1.1 Effects of particle size on the cost of dewatering coal [1]

Availability of efficient processes that can remove moisture from fine particles will greatly benefit the companies. If they can be used to reduce the moisture content of fine coal, an operator can produce higher-ash products in his coarse particle circuit without compromising product quality, so that the overall plant yield can be increased substantially. As a rule of thumb, 4 tons of steam coal can be added to clean coal product stream for every ton of moisture removed, which is a powerful incentive for developing advanced fine particles dewatering technologies [1,3,7-14].

There is a great deal of interest in recovering the fine coal that has been discarded in ponds over the years. Because of the limited reserves in ponds, many pond recovery projects use relatively simple process flowsheet which require low capital investments. It consists of only one or two major unit operations. Typically, coarse coal (e.g., 1 x 0.15 mm) is cleaned by spirals and finer coal (e.g., 0.15 mm x 0) is cleaned by flotation. However, the flotation is more costly of the two processes. Hence, many pond recovery plants use only spirals and return the finer fractions back to ponds, which makes it difficult to make the operation profitable. The companies that have recently entered the pond recovery businesses are usually taking advantage of the so-called Section 29 Tax Credit to make their operations profitable. This indicates that pond recovery is a costly business, the major cost item being dewatering fine coal [1-7].

In order to solve the problem associated with the fine particles dewatering, two new dewatering methods have been developed at Virginia Tech and successfully tested on the dewatering of the fine coal and mineral particles. The first one is novel dewatering aids, and the second one is novel centrifuge. The present study will deal with the problem in reducing the dewatering cost of fine particles and at the same time increase the throughput of current dewatering techniques.

1.2 LITERATURE REVIEW

1.2.1 General Information

When fine coal or mineral fines are upgraded in a floatation cell, the product usually contains over 80% water. In the plants, the large volume of the water can be removed in three steps. In the first step, slurry is thickened to 35% to 75% solid contents in a large settling tank in which the free water is removed from the top and recycled back to the plant. In the second step, the thickened pulp is subjected to mechanical dewatering processes, such as centrifugation and filtration to further dewater the liquid from the filter cake. In the last step, the dewatered product is thermally dried in the thermal units to obtain significantly low moisture content of a final product [1,3,5,14].

In fact, moisture content of the cake is dependent on several parameters. These include mineral type, particle size, surface characteristics of the materials, applied pressure, cake thickness, clay content, surface oxidation, etc. For example, sulfide mineral concentrates can typically contain 10% to 20% moistures by weight as these products are dewatered in an appropriate filtration unit. For coal, the residual moistures are in the range of 20% to 30% by weight. For clay, PCC and talc, it is even higher because the surface characteristics and size of the clean particles are different (e.g., surface area is very high) [2,7-14].

a) Surface Characterization of Particles

Coal is a heterogeneous material possessing several functional groups on its structure. These include carbon (C-C, C=O-C, CH_3), oxygen (O, OH), sulfur (S), nitrogen (N) and other inorganic compounds (e.g. silicate, CaO, MgO, metal oxides, etc.), which are varied depending on the coal ranks. Thus, in order to understand the surface phenomena of coal, one should determine the chemical characteristics of the particle surface since every surface species responds differently to the chemical used for dewatering, flotation, flocculation and coagulation aids. It is also determined that coal surfaces are generally basic, which comes predominantly from aromatic, aliphatic and heteroatomic entities that may present a wide variety of polar and non-polar sites on the surface [2,13-18].

It is generally known that oxygen affinity on coal (or mineral) surface is high both in air and aqueous media for oxidation. This affinity is much higher for low rank coals (lignite and sub-bituminous coals) and very low for the bituminous coal and anthracite. Since a coal sample is freshly ground in a ball mill, new surface will be moderately hydrophobic (contact angle is in the range of 20 to 70°). After a period of time, oxygen or hydroxyl species (-OH, -COOH, =C=O, -O-) in water form on the surface and make the particles more hydrophilic. Thus, it may affect surfactant adsorption on the surface, and the separation efficiency is decreased [2,12,18,19].

When a charged solid is immersed in water, oppositely charged ions come to the charged surface in the solution, and then balance the total electrical charges of the system. Oppositely charged spices are attracted to the surfaces and form a dense layer around the particles. The same type of particles in the solution can be stabilized by formation of the *electrical double layer* since they are similarly charged and repel each other.

According to the electrical double layer theory, the ions in the double layer form two regions: Stern layer and Gouy layer. The Stern layer consists of inner and outer Helmholtz planes. The adsorbed unhydrated ions remain in the inner and more weakly adsorbed hydrated ions stay in the outer Helmholtz planes. The Gouy layer, which is also known as a diffuse layer, includes different electrically charged planes. Also, the surface potential Ψ_0 is reduced as the distance from the particle surface (e.g. diffuse layer) increases. Schematic representations of the electrical double layers are given in Figure 1.2 [2,12,19-23].

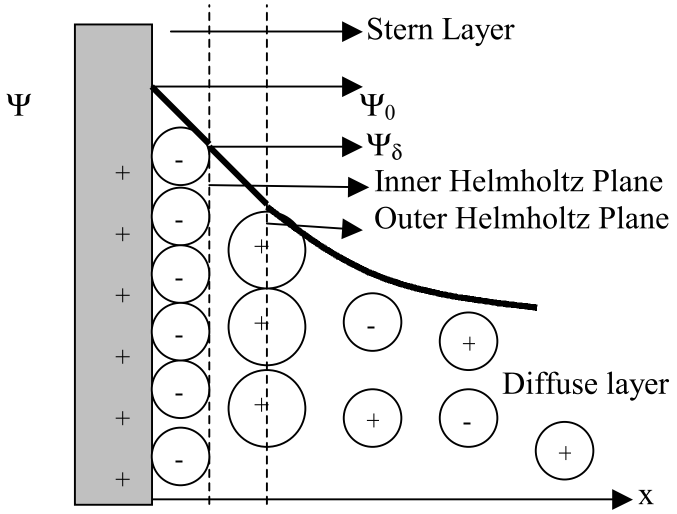
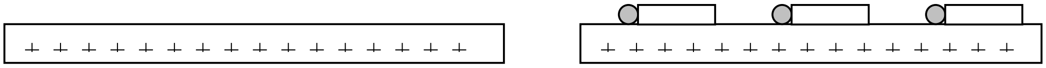


Figure 1.2 Schematic illustration of the electrical double layer

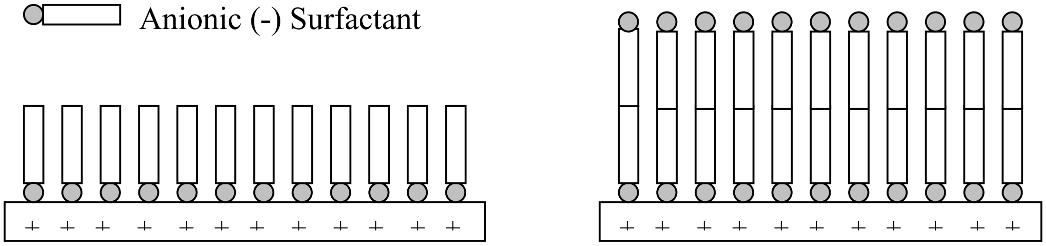
It is known that when the surface potential in water are the same sign with the surfactant molecules, there exists a repulsive force between the particles and the surfactant molecules. This repulsion then stabilizes the additives in the solution, which means that there may not be an adsorption on the coal or mineral surface. However, when the counter ions are presented between the particle surface and head of surfactants, the adsorption occurs in two ways: ion exchange and ion pairing. In the ion exchange, surfactant molecules place on the charged side of the particles that has not been occupied by the counter ions. In the second case, the surfactant molecules displace the charge of the same counter ions (or hydroxyl molecules) and remains on the surface [7,19,23].

Based on the surfactant concentrations, the surface of the particles consists of a neutralized monolayer or reversed secondary bilayer (Figure 1.3). It is known that less surface coating causes less hydrophobic surfaces (Figure 1.3 b), while higher surfactant concentration depicts neutralized surface charge (Figure 1.3 c). This means that a close packed monolayer is formed on the surface by the surfactant molecules. However, if the surfactant concentration is higher than the close-packed monolayer levels, there will be a bilayer orientation or reverse orientation (Figure 1.3 d) which decreases the surface hydrophobicity of the particles. As known, especially head of high hydrophile-lipophile balance (HLB) surfactants adsorb more water and wettability of the particles is increased. Recently, it has been also found that the surfactant adsorption could be dependent on the hydrophobic and acid-base interactions, and these adsorptions will be discussed in detail in the next sections [2,14,19-23].



a) Net positive charged surface

b) Low surfactant concentration (non-neutralized)



c) Surface charges neutralized

d) Reversed bilayer surface charges

Figure 1.3 Schematic illustrations of surface charge due to the layer formations

b) Types of water

Water associated with the fine particles can be categorized as **inherent** and **free water** (or moisture). The inherent moisture is chemically bound to the particles, and it is a part of the substance. This water is removed only by thermal drying methods over 100 °C. It is extensively seen in the structure of the lignite type coal or low rank coals. However, the free water is found on the surface of the particles and can be mostly removed by mechanical methods. Different types of water are present in coal and mineral slurries after cleaning processes. They can be classified as free water, capillary water, and surface water. The ***free water*** occupies the bulk of the slurries and can be easily removed from the bulk under the influence of any forces. For this purpose, screen, thickener, cyclone and centrifugal units can be used to remove this type of water from the fine particles. The ***capillary water*** is trapped in small channels of the filter cake. Removal of the capillary water between the particles requires a more intensive and complex method for complete drainage. The ***surface water*** adhering onto the particle surface as a thin film is held in small intraparticle sites. The quantity of this water is dependent on the particle size and structure of the solid surface. Mechanical and chemical methods can be applied to the slurry to remove the surface water, which will be dealt with in this investigation [2,14, 24-30].

In addition to the moisture in the coal and mineral slurry, there exists a relationship between water and particle. A more detailed presentation of particle-water interaction during the filtration is illustrated in Figure 1.4. Several investigations show that the particle-water interactions can be subdivided into three main states: saturated (capillary) state, funicular state, and pendular state [2,4,5,14,31-36]. The ***saturated state*** (or capillary state) occurs when all interstitial pores and voids (or capillary) of the particle are completely filled with water. The surface tension, capillary radii and contact angle of the system determine the magnitude of capillary forces. If the applied forces, such as vacuum, pressure, gravity, or centrifugal are less than the capillary forces, moisture cannot be displaced from the cake. In contrast, if the applied force is larger than the capillary forces, water can be removed from the capillary channels by means of an air phase; this situation is known as the ***funicular state***. In the ***pendular state,*** if the force is increased more than this pressure of the funicular states, it will lead to a limiting pendular state in which moisture is condensed in lenses shape between the fine particles. It usually corresponds the final moisture contents after the dewatering processes are ended. Figure 1.5 shows a relationship between the pressure and moisture reduction of the fine particles [2,14,31-36].

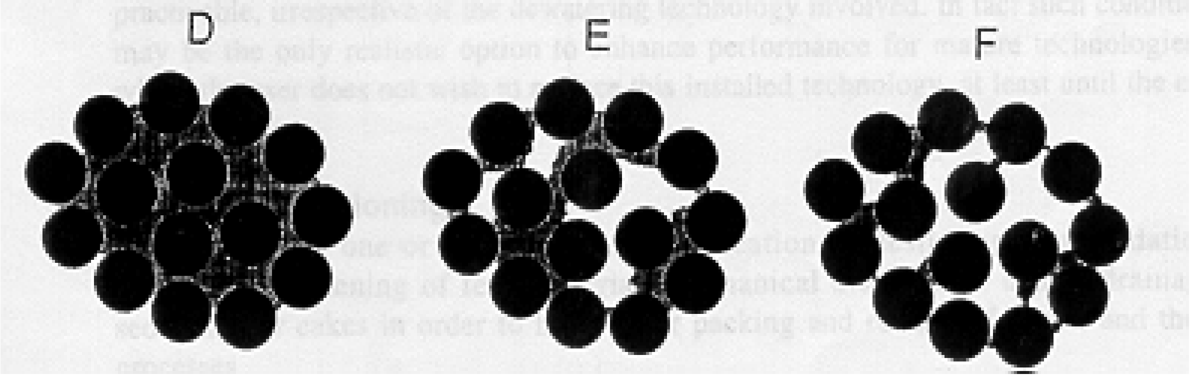


Figure 1.4 Schematic representation of particle-water relationship in the cake structure

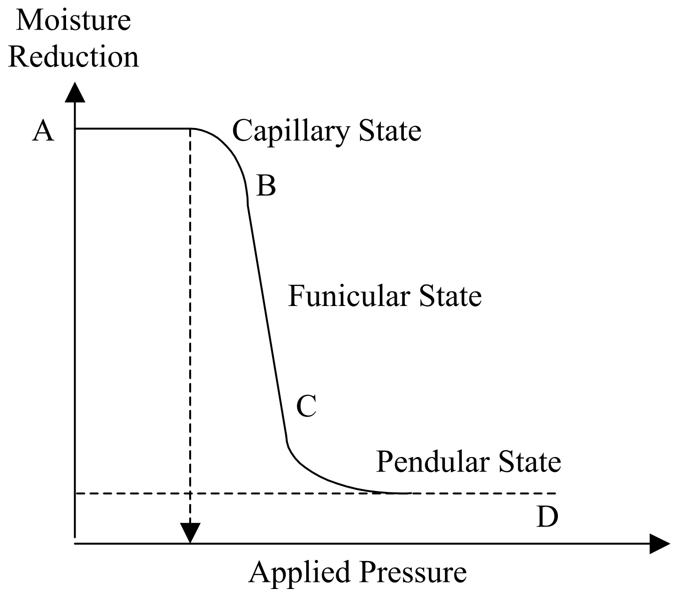


Figure1.5 Relationship between pressure and moisture reduction

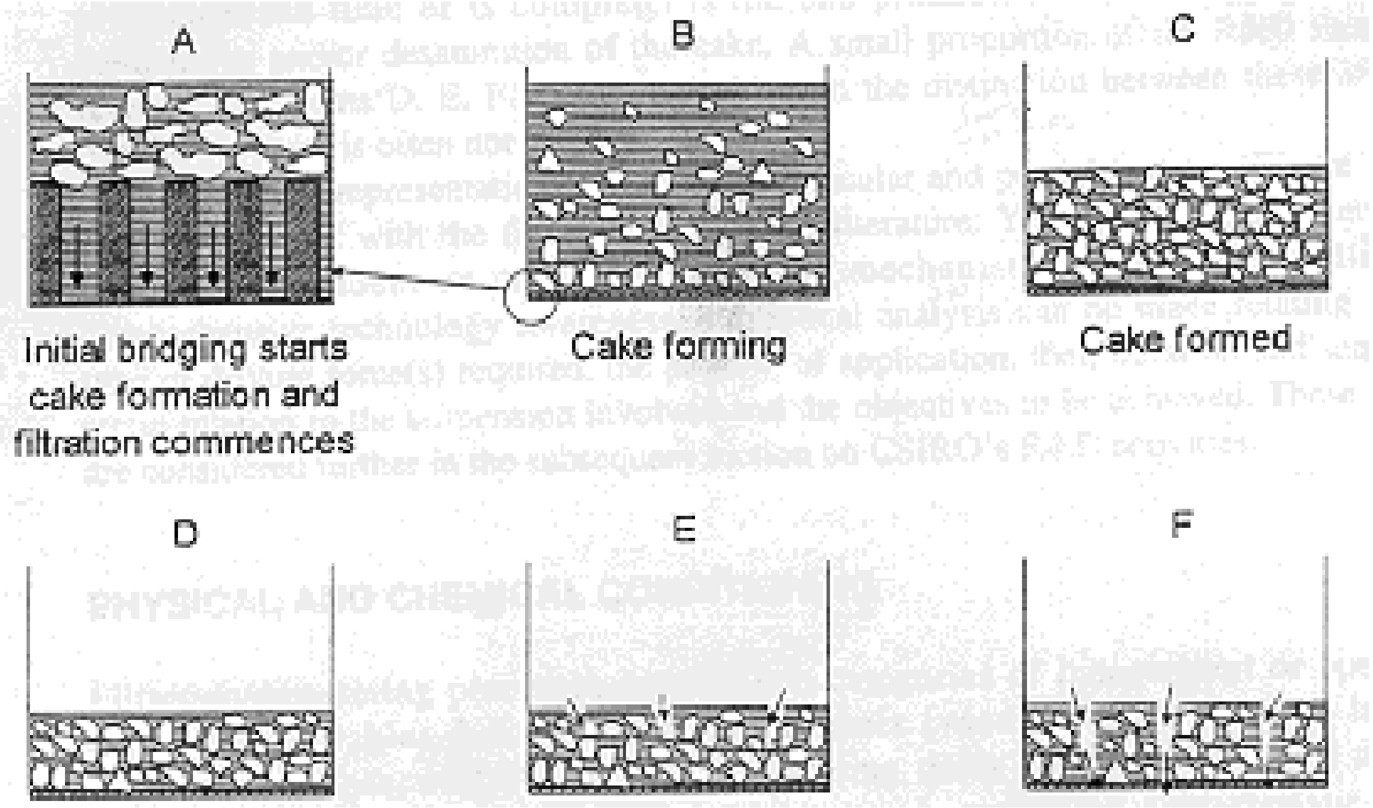


Figure 1.6 Formation of dewatering stages on the filter media

Since vacuum/pressure is applied to the suspension, particles settle on the filter media in the range of particle diameters. During this process, six dewatering stages occur through the end of drying cycle time. These stages are given in Figure 1.6: (A) is an initial bridging cake formation, filtration begins; (B) is cake forming on the filter media; (C) is cake formed; (D) is cake compacted (under the pressures or vacuum); (E) is desaturation with air (air displaces water, air entries into the cake structure); and (F) is air breakthrough (compressed air cracks the cake to make macropores and microprose channels) to drain the more liquid from the cake [2-5,14].

In the pressure or horizontal belt filters (HBF), the filter cake is segregated from large particles at the bottom to fine particles at the top of the cake. This segregation results in a non-uniform formation in the cake with a wide variation of layers. Recognizing that finer particles give higher cake resistance and moisture content than coarser particles. Thus, the fine particle layers can be detrimental for the dewatering processes. For this reason, agitation may be a solution for the segregation so that a uniform cake can form on the filter media [2-5,14,24-30].

In the practical point of view, applied pressure *ΔP* on the cake cannot remove all the water around the particles. Cheremisinoff et al [34] suggested a model (Figure 1.7) that the moisture could be vertically removed from the fine capillaries in the cake. In other words, the moisture located in zones, 2 and 4 can be displaced by the air phase. The other zones, 1 and 3, which are not affected by the air will remain between the particles, and determine the final moisture in the cake. In order to reduce this moisture, adding surfactant molecules can increase the surface hydrophobicity of the particles and decrease the water around the particle zones. It is also possible that the vibration can be a solution for this kind of problem. The significance of the surface treatment and vibration will be discussed in the following sections [2,14,24-28,34-42].

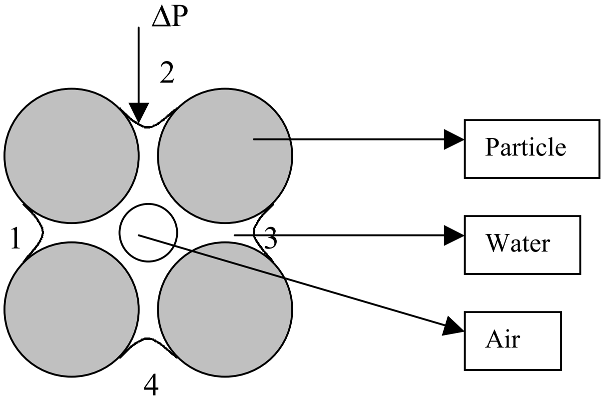


Figure 1.7 Schematic representations of the moisture zones between the particles

c) Chemicals in Dewatering

Several surfactants, polymers and inorganic salts have been utilized as dewatering aids to separate more water from the slurry (or suspension). These chemicals also improve the efficiency of the mechanical filtration systems. It is found that surfactants and polymers have anionic, cationic and nonionic modifications depending on their chemical structures. The adsorption of the chemicals occurs onto the surface because of the intermolecular interactions (or forces) between the surface and the chemicals. The driving forces for the adsorption may be electrostatic, van der Waals, hydrophobic attractive forces and acid-base interactions [12-15,19,23,43-48]. These chemicals can decrease surface tension and viscosity of the fluid and increase contact angle of the particles. The types of chemicals extensively used in solid-liquid separation are given in Table 1.1 [2,12,14,35-40].

Table 1.1 Commonly used solid-liquid separation chemicals in dewatering processes [14]

Flocculation And Coagulation	Salts	Aluminum, copper, ferric sulfates
		Lime
		Soda ash
	Natural Polymer	Gum
		Glues
		Polysaccharides
	Synthetic Polymers	Polyacrylamides (Ionic, cationic, neutral)
Filtration And Centrifugation	Surfactants	Sodium 2- Ethylhexyl Sulfate (anionic)
		Octyl Phenoxy Polyethoxy Ethanol (nonionic)
		1-Hexadecyl Pyridinium Chlorin (cationic)
	Polyelectrolytic Polymer	Polyelectrolytic Polymers

<u>Inorganic salts</u>: These soluble salts (or electrolytes) including aluminum, copper, chromic, ferric and calcium sulfates (or chlorides) affect the surface charge on the fine particles, and cause coagulation in the solid-liquid media by changing the zeta (ζ) potential of the surface. Dosage of the salt concentrations and pH are important parameters to achieve optimum surface conditions. It has been reported that aluminum salts offer the neutralized charge on the clay surface for coagulation process, so filtration selectivity of the nano/micron size particles was increased due to the particle enlargements. In addition, literature studies showed that the electrokinetic behavior of coal was significantly changed in the presence of copper or aluminum ions of 10^{-4} mole/l at different pH values [35]. For copper and aluminum ions, pH values are 6.5

and 7.5, respectively for the dewatering process. The authors [35] assumed that the dominant species on the solid-liquid interface could be hydroxyl species, e.g. $Cu(OH)_2$ and $Al(OH)_3$. From the results, adding metal ions to the solid-liquid media may increase the surfactant adsorption on the surface of coal. Note also that the high valance metal ions strongly depress the double layer of the solid; therefore, the amount of reagent used for dewatering may be substantially decreased due to the coagulation effects on the fine particles [2,14,19, 23,35].

Natural Polymers: These are mostly short chain neutral organic materials, such as polysaccharides, starch, gum, glue and alginates. The glues, gums, and alginates can be more effective in acidic media dewatering, whereas the polysaccharides can be effective in neutral and alkaline media. These flocculants can be utilized in flocculation of ultra fine particles in a suspension [2,12,14,41-45].

Synthetic Polymers: Most of the synthetic polymers including cationic, anionic and neutral groups show longer chain lengths (or higher molecular weight). These are made mainly of polyacrylamide and its derivatives. These polymers are employed to increase the amount of free water in the pulp and to enhance the pulp stability so that lower pressure can be effectively applied to the fine filter media (clay-like minerals) [2,12-14,23,45,46].

The exact mechanism of polymer adsorption on a solid is not well understood, but it is assumed that initial adsorption causes one or more segment formation by strong bonding between the polymer and the surface of solids. This process may be attributed to the entropic adsorption (or physical adsorption). It was reported that the polymer adsorption could exist in two stages: ion or charge neutralization and bridging mechanism. In the later mechanism, one end of the long polymer molecule adsorbs on the particle, while the others move the suspension to bridge the other particle. It is also found that one polymer molecule can remove several thousands of water molecule from the particle surface due to the size of the polymer. As a result, in the presence of polymer, flocculation process spontaneously occur by displacing the water molecules from the slurry [2,12,14,46-51]

Electrostatic and van der Waals interactions between the polymers and particles may cause a bridging formation. It is determined that when polymers adsorb on the surface and neutralize the surface charge, the fine particles come together and settle on the filter medium as a larger particle. This enhances rate of the fine particle filtration. In industrial applications, a 0.1 to 1.0% of polymer is prepared and used for flocculation aids [2,12,14,23,47].

Polyelectrolytic polymer: These types of polymers that are short chain and highly charged are employed with inorganic electrolytes if the solid content of the slurry is lower level. It was reported that this flocculant could have a perfect vacuum filtration characteristic, and produce compact and uniform flocs on the filtration media. Generally, the amount of polymer used as a dewatering aid is in the range of 0.1 to 0.25 kg/ton of dry solid to be able to remove more water from the suspension [2,12,14,35,45].

Surfactants: Several surfactants are used for the controlling the characteristic of the interface between a solid and a liquid. Surfactants that are referred as a surface active agents are classified as nonionic (e.g., -C-O-C-), anionic (e.g., carboxylic) and cationics (e.g., $-N^+(CH_3)_3$) forms [2,7,13,19,23,47]. These surfactants consist of two compounds: hydrophilic head and hydrophobic tail groups. In filtration, these surfactants are added to lower the viscosity and the surface tension of the liquids and increase the contact angle [2,23,47].

Change in the surface chemistry of the particles and filtrate makes the surface more hydrophobic or hydrophilic based on the orientation of the surfactants molecules. It is known that if the amount of chemical is increased or overdosed, it can cause inverse orientation (surfactant head towers to the solution) on the surface and makes the surface hydrophilic, which is not desired for the dewatering of the fine particles. Also, similar observation can be seen on the hydrophobic surfaces (e.g., coal, graphite, talc, molybdenum, etc.). It is determined that surfactant molecules are larger than the water molecules, so the hydrophobic tails (icy structure) of surfactants can squeeze more water molecules adhering on the surface. This process may also increase the entropy of the system for the spontaneous dewetting. Coal is a naturally hydrophobic material, and a nonionic surfactant can be used for surface coating [2,14,19,20,23,47]. More detailed information of the surfactant adsorption will be given in the next sections and chapters.

As mentioned, polymers, surfactants and electrolytes are extensively used to remove the process water from the solid before the thermal drying. For chemical dewatering, amount of chemicals, solubility of the reagents, contact angle, surface tension, zeta potential, conditioning time, agitation of the slurry, process water quality (water hardness), pH variation, ash content, process water contamination, surface oxidation and vibration can be important parameters to obtain a lower moisture content product form the filter cake [2,12,14,42,45-58].

1.2.2 Dewatering Theory

1.2.2.1 Filtration Theory

Mechanical dewatering is kinetically described as a process concerned with the flow of water through the porous cake media created by a bed of particles. Darcy (in 1856) was the first investigator to derive the rate equation for the process [2,12,14,45]:

$$\frac{dV}{dt} = K\frac{A}{\eta}\frac{\Delta P}{L}, \qquad [1]$$

in which V is the volume of fluid, t is the time, ΔP is the pressure drop across the cake surface, L is the cake thickness, A is the cross-sectional area of the cake, η is the viscosity of water, and K is the rate constant known as permeability. Equation [1] suggests that the rate of dewatering is proportional to the pressure gradient and the cross-sectional area, and is inversely proportional to the viscosity.

The process of filtration is often related to the flow of liquid through a bundle of capillary tubes. In this case, one can use the Poiseulle's equation (1846):

$$\frac{dV}{dt} = \frac{\pi r^4}{8\eta}\frac{\Delta P}{L} \qquad [2]$$

where r is the radius of the capillary [1,2,14,45].

By combining Equations [1] and [2], Kozeny (in 1927) obtained the following relationship:

$$\frac{dV}{dt} = \frac{A\varepsilon^3}{kS(1-\varepsilon)^2}\frac{\Delta P}{L} \qquad [3]$$

where ε is the cake porosity, which is defined as the volume fraction of the void space in the filter cake, S is the specific surface area of the particles per unit volume, and k is a constant which is referred to as Kozney constant. Theoretically, k should be 2 for an ideal filter cake that is a porous medium made of capillary tubes of radius r. In the experiments, k is found to be approximately 5 for filter cakes made of simple monodisperse solids [8]. For many industrial filter cakes formed in the presence of flocculants, k is often greater than 5 and can be as large as several thousands [2,5-10,14,45].

From Equations [1] and [3], one can obtain the following relationship:

$$K = \frac{\varepsilon^3}{kS^2(1-\varepsilon)^2} \quad [4]$$
$$= 1/\alpha$$

where α is referred to as specific cake resistance. Equation [4] suggests that cake permeability decreases with decreasing ε and S, both of which decrease with decreasing particle size. Thus, the rate equation derived based on the Darcy's law (Equation [1]) provides an explanation for the difficulty in dewatering fine coal and mineral particles [2,14].

Equation [1] suggests that the flow of filtrate versus time should be linear. However, practically all filtration experiments show parabolic behavior. Figure 1.8 shows the results of typical batch filtration experiments [2]. The main reason for the discrepancy is that the rate equation based on Darcy's law disregards distribution of pore sizes, *i.e.*, there exists a range of pore sizes (and also shapes) in a porous bed [9]. According to the Laplace equation (the implications of which will be discussed in the following section), the water in larger pores will be more easily removed than the water in smaller pores. Thus, the larger pores should determine the initial dewatering rate, while the finer pores determine the water retention (final cake moisture) [2,14,45].

From the Figure 1.8, it is seen that after a certain level of moisture reduction in the cake, there exists a limitation on the moisture reduction, which is also called irreducible saturation S_∞. This value varies depending on the applied pressure, filter medium, cake thickness, particle type and size, specific gravity, cake porosity ε, shape of the particles, surface oxidation, viscosity, surface hydrophobicity and water contaminations. The following equations are considered for the saturation S of the cake [2,42,45,51-58].

$$S_\infty = 0.155(1+0.031\, N_{cap}^{-0.49}) \quad [5]$$

at which N_{cap} is capillary number. This number varies using filtration and centrifugation techniques. For the filtration processes:

$$N_{cap} = \frac{\varepsilon^3 d^2(\rho g L + \Delta P)}{(1-\varepsilon)^2 L\gamma}, \qquad (10^{-5} < N_{cap} < 0.14) \quad [6a]$$

where g is gravitational acceleration, d is particle diameter, L is cake depth, γ is surface tension.

For the centrifugal filtration:

$$N_{cap} = \frac{\varepsilon^3 d^2 \rho N^2 r)}{(1-\varepsilon)^2 \gamma}, \qquad (0.14 < N_{cap} < 10) \qquad [6b]$$

at which N is number of revolution per minute and r is radius of centrifugal basket . For the cake porosity;

$$\varepsilon = \frac{v_0}{V + v_0} \qquad [7]$$

where V and v_0 are volume of the solid and void space, respectively. For the irreducible saturation, one can write the amount of moisture remaining in the cake is called residual saturation S_R at the end of the dewatering period:

$$S_R = \frac{S - S_e}{1 - S_e}, \qquad [8]$$

However, this value can be changed based on the dewatering and particle conditions as mentioned [2,13,14,51-56].

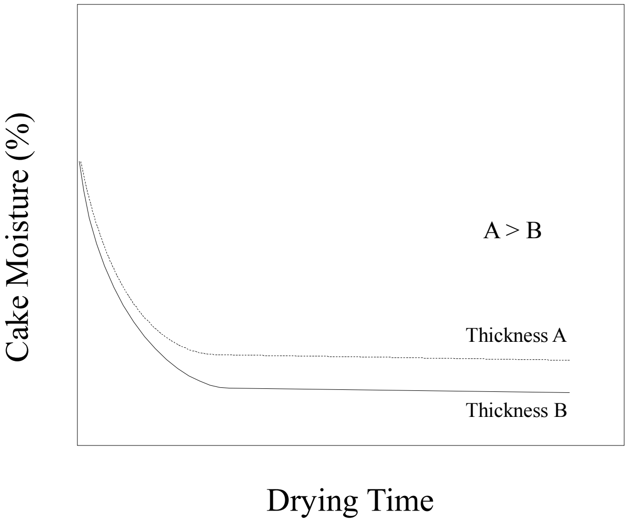


Figure 1.8 Typical results of dewatering tests, which show that cake moisture decreases rapidly at the beginning and then tapers off with increasing drying cycle time. The latter is due to the difficulty in removing the moisture from the capillaries of smaller radii. The situation gets worse with increasing cake thickness.

Laplace Equation: In order to remove the water from a capillary with radius *r*, it is necessary that the applied pressure will be larger than the capillary pressure, *p*:

$$p = \frac{2\gamma_{23}\cos\theta}{r} \; , \qquad [9]$$

which is well known Laplace equation. Here, γ_{23} is the surface tension of liquid, and θ is the water contact angle. One can see that p value decreases with decreasing γ_{23}, increasing θ, and increasing r [1-12,45]. This model is preferred to use for the cake filtration in these studies.

Various chemicals (or dewatering aids) are added to coal and mineral slurry to control these parameters so that p can be significantly reduced. One group of reagents that are most widely used is surfactants. It is reported that the main purpose of using these reagents is to reduce the γ_{23}. Consider a case of filtering fine coal slurry at a vacuum pressure of 22-inches Hg (0.735 atm or $0.745\text{x}10^5$ Pa). Assume that $\theta=45^o$ for the coal, which is typical of many high-volatile bituminous coals mined in the U.S, and that no dewatering aids are used, i.e., $\gamma_{23}=72$ mN/m. Substituting these numbers into Equation [9] and solving it for r, one obtains $r=1.4$ μm. The water in the capillaries of smaller radius will have pressures higher than the vacuum pressure and, therefore, cannot be removed. When γ_{23} is reduced to 40 mN/m by surfactant addition, however, the critical capillary radius at which water can be reduced by vacuum suction is reduced to 0.76 μm. It is seen that the enlargement of the capillary diameter is one of the key parameter for removing more water in the bundle of capillary tubes [2, 6,11-19,45].

Thus, it is possible to reduce the final cake moisture using surfactants. However, the amount of surfactants needed to obtain $\gamma_{23}=40$ mN/m is excessive. When sodium dodecylsulfate (SDS) and dodecylammonium hydrochloride (DAH) are dissolved in distilled water, for example, approximately $6\text{x}10^{-3}$ M of the reagents are needed, as shown in Figure 1.9 [6].

Recently, Singh [11] compared the performance of SDS and DAH as dewatering aids for fine coal. The author showed that the former is more effective than the latter for the following reason. Coal particles can be negatively charged in water; therefore, DAH^+ ions adsorb on the surface, resulting in a decrease in the surfactant concentration in solution and, hence, higher surface tension. The anionic surfactant, SDS, on the other hand, does not adsorb on coal and, therefore, can reduce the surface tension more effectively. Sulfosuccinate is one of the most widely used dewatering aids for coal, probably for the same reasons [2,11-14,23,45].

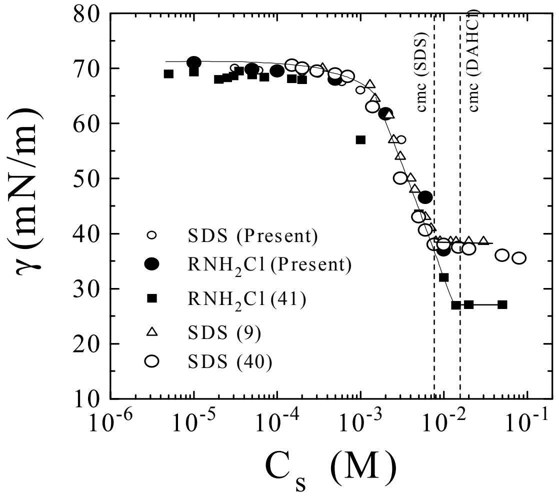


Figure 1.9 Changes in the surface tension (γ) of water as a function of surfactant concentration in moles/liter [6]

It should be noted that sulfosuccinate is also used as a wetting agent for coal in mineral processing plants. The reason is that surfactants with high hydrophile-lipophile balance (HLB) numbers such as sulfosuccinate, SDS and DAH decreases the water contact angle of coal and increases its wettability. Figure 1.10a shows that SDS addition decreases the contact angles of surfaces with different hydrophobicities [6]. The decrease in contact angle can be attributed to the inverse orientation of the surfactant molecules on the surface. In this mode of orientation, the non-polar hydrocarbon tails touch the hydrophobic surfaces, while the polar heads point toward the aqueous phase, thereby rendering the surface hydrophilic. Figure 1.10b shows a similar set of contact angle measurements conducted using DAH. With very hydrophobic surfaces, the trend is the same as with SDS in that the surfactant addition decreases the contact angle. With weakly hydrophobic surfaces, however, the DAH addition increases the contact angle at low concentrations. Once the contact angle reaches 85-90^{o} at 10^{-5} M, however, it begins to decrease again with further additions of the cationic surfactant [6,11,12,45,47].

Thus, the use of high HLB surfactants can reduce the final cake moisture by virtue of lower γ. However, it can also decrease *θ*, which is detrimental for the chemical dewatering process. Virtually, all of the dewatering aids used in industry today are high-HLB surfactants. In this regard, it is not surprising that many dewatering aids actually increase the cake moisture due to the opposite orientation [6,11,14,23,45].

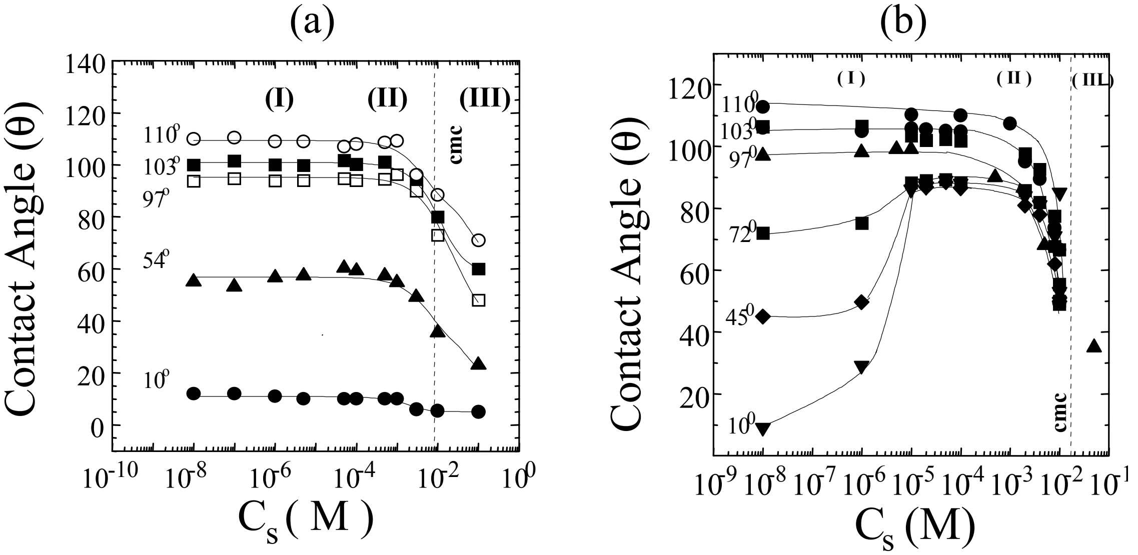


Figure 1.10 Changes in the water contact angles on the surfaces of various hydrophobicities as a function of the concentration of a) an anionic surfactant (sodium dodecylsulfate) and b) a cationic surfactant (dodecylaminium hydrochloride) [6].

Various flocculants (polymers) are used as dewatering aids. As mentioned, the role of these reagents is to increase the effective size of the particles in the filter cake so that the pore radius r can be increased. This will greatly reduce the capillary pressure p and, hence, increase the filtration rate. However, most of the flocculants cause θ to decrease and at the same time create micro-pores within large flocs, both of which contribute to increased final cake moisture. In many plants, it was reported that the flocculants increased the solid liquid separation, but also increased the moisture contents of filter cake due to the trapped water formation between flocs [1,2,14].

1.2.2.2 Centrifugation Theory

Suppose that an aqueous suspension of particles is introduced to a batch centrifuge whose wall is made of a porous medium. The particles will settle quickly on the medium and form a cake since they are heavier than water, while the water forms an annular layer over the cake. As centrifugation continues, water flows through the cake, resulting in a decrease in the thickness of the water layer. The initial dewatering process, in which water flows through the cake while the cake is submersed under it, is referred to as *filtration*. Eventually, the thickness of the water layer becomes zero. The process of dewatering beyond this point is referred to as *drainage* [2,14,42]. For the reasons given below, the drainage process is much slower than the filtration process. Therefore, the control of the rate of drainage is critical in achieving low cake moistures [47-68].

In centrifugal dewatering, there are two driving forces for moving water through the pores of the cake, one resulting from any difference in pressure at the boundaries, and the other from the centrifugal action. During the filtration period, when the annular water layer has a finite thickness, the pressure drops across (ΔP) the cake is determined by the following relationship [2]:

$$\Delta P = \tfrac{1}{2}\rho\omega^2\left(r_S^2 - r_0^2\right), \qquad [10]$$

where ρ is the density of the liquid, ω the angular velocity, and r_0 and r_S are the radial distances to the free water on the cake surface and to the cake surface from the rotational axis of a centrifuge, respectively. The pressure drop can be substituted to Darcy's equation (Equation [1]) to predict the rate of filtration. One can see that dewatering rate should increase with ω and the thickness (r_S-r_0) of the water over the cake [2,14,45].

Note that P_S and, hence, ΔP become zero when the free water disappears from the surface of the cake, i.e., $r_{S=}r_0$, and the thickness of water becomes zero. At this point and beyond, i.e., during the drainage period, the only driving force for the flow of water through the cake is the centrifugal force. This will greatly reduce the rate of dewatering. Common practice of overcoming this fundamental problem is to increase the centrifugal force, which entails high energy consumption and maintenance requirements.

Zeitsch developed a model based on filtration first principles to predict the rate of dewatering during centrifugal filtration and drainage. According to this model, the pressure ($P_{(r)}$) along the radial distance, r, of a centrifuge can be predicted by the following equation [2,12,45,60,63]:

$$P_{(r)} = \frac{\ln(r_b/r)}{\ln(r_b/r_s)}P_S + \frac{\rho\omega^2 r_b^2}{2}\left[\frac{\ln(r_b/r)}{\ln(r_b/r_s)}\left(1-\frac{r_s^2}{r_b^2}\right)-\left(1-\frac{r^2}{r_b^2}\right)\right] \qquad [11]$$

where r_b is the radial distance to the base of the filter cake. Thus, r_b-r_0 is the cake thickness.

Figure 1.11 shows a plot of Equation [11], in which P is plotted vs. r. The calculations were carried out at water thicknesses of 0, 0.5 and 1 cm with the following boundary conditions: diameter of the centrifuge (r_b) is 0.36 m, cake thickness (r_b-r_0) is 0.03 m and the angular velocity (ω) is119 rad/s. It shows that the larger the thickness of the layer of water over the cake surface and the higher the P_S (the pressure at the cake surface) exists. It also shows that P_S becomes lower than the ambient pressure at water thicknesses below 0, i.e., during the drainage period, which may be the fundamental reason that centrifuges can not produce a lower moisture content than the vacuum or pressure filters at finer size [2,14,42,45,69-78].

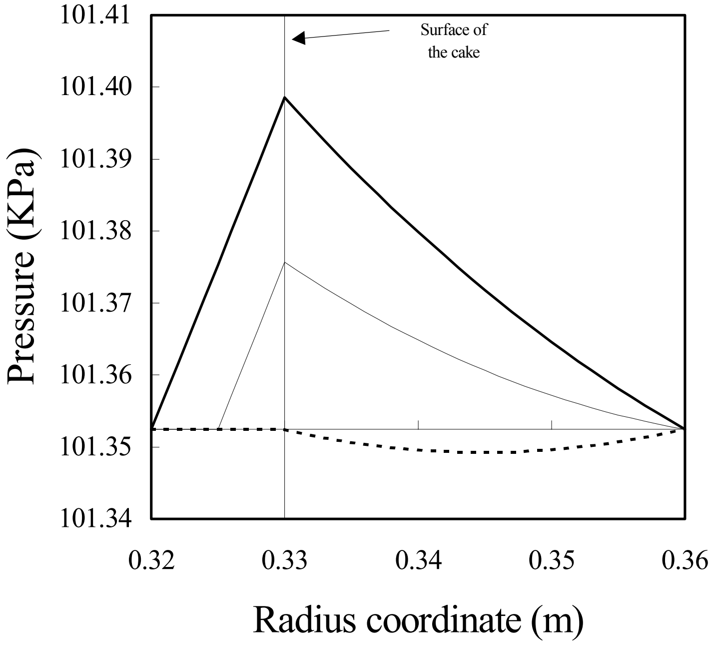


Figure 1.11 Changes in pressure across the filter cake formed on a centrifugal filter

1.2.3 Surface Chemistry

1.2.3.1 Acid-Base Interactions in Filtration

Many of the surface related processes are dependent on the interfacial surface tension between solids and liquids, such as water, organic and inorganic materials that have different interfacial energy levels in the interfaces. These interactions are based on chemical bonding, types of the materials, temperature and pressure. To understand the material surfaces, the surface energy (or surface tension) components of the solid and liquid can be experimentally measured using a new technique (or formula) [79-85]. These components that are called Lifshitz-van der waals γ^{LW}, Lewis acid γ^{+} and Lewis base γ^{-} energies are directly related to the surface of solids and contact angle of the solid/liquid/air interface. The obtained parameters are used to explain the hydrophobic interaction, hydrophilic repulsion, and also the adsorption mechanism of a system existing in the interfaces [79,82].

The surface energies are of technical interests for separation processes, such as flotation, filtration, oil agglomeration, flocculation, coagulation, and the other chemical (e.g. colloid chemistry, painting, detergent, textile, etc.) and hot metallurgical processes. Thus, it would be useful to know surface characteristics of materials when a solid surface interacts with another surface in the presence of liquids. The surface adsorption process is based on the surface thermodynamic theory. This provides the natural and quantitative definitions of hydrophobicity and hydrophilicity of the materials in the form of free energy. From these definitions, it can be understood which properties of the materials and of the liquid media are responsible for the spontaneity of the ongoing processes [45,79,89]. In this section, the surface energies of liquid and solid based on acid-base interaction, wetting, de-wetting, and their contact angle effects are thermodynamically reviewed, and spontaneity of the system (or surfactant adsorption onto solids) is evaluated using solid and liquid components.

a) *Adsorption Phenomena of Acid-Base Interaction*

It is known that the acid-base interaction takes place if complementary surfaces are available: acidic sides interact with basic sides. Literature studies showed that silica, mica, talc, coal, clay and nylon have basic surface characteristics due to the oxygen components in their structures, so acidic surfactants can be favorable for the adsorption on these materials. Since the surface energy of the substances is specified for each material, then the processes are determined to be either thermodynamically spontaneous or not for further operations [79,85-90].

As known, hydrophobic and hydrophilic interactions are very important for the surface related processes based on the surface free energy. For example, if the free energy ΔG of a particles immersed in a liquid media (water) is positive, the surface of the particles can be hydrophilic (it loves water or wetting occurs). However, when the ΔG is negative at the same conditions (contact angle is higher than 90°), surface of the particles will be hydrophobic and water does not spread on the surface of the particles. This means that dewetting takes place on the surface or dewatering of the fine particles spontaneously occurs. Generally, it is assumed that water wets the surface of the hydrophilic solid material, but it does not wet the hydrophobic material due to the lower energy of the particle surface. Also, kinetics of the adsorption processes of the surfactants can vary with the magnitude of total free energy. It is known that a fast process is preferred and usually used in industrial applications [6,13,19,79].

Recently, it has been determined that acid-base interaction is an important part of the surface adsorption. In this process, a basic component, such as a carbonyl group, does not interact with another basic group, and also the same situation exists between acidic groups ($CHCl_3$). van Oss et. al. observed that hydrogen bonding (e.g. $Cl_3C\text{-}H\text{---}OH_2$) is the most common type of molecular interaction that leads an acid-base component of the free energy of the adhesion and of the interfacial tension between two phases in aqueous media. For example, in silica flotation the basic mineral surface may need an acidic reagent to make the surface more hydrophobic for the separation process [79,84,87].

b) Theory

The historical background of the free energy of solids and liquids have been found and given in the references [19,23,79,84]. Machalski et al and van Oss et al state that in the non-covalent interactions between the particles, Brownian movement, electrostatic interactions, and interfacial interactions are the main interaction in a liquid system. In the thermodynamic explanation of the surface phenomena (hydrophobic-hydrophilic interactions, etc.), only the interfacial interactions are relevant and have been used to determine the surface characterization of the particles. This relationship can be attributed to the contact angle and surface tension of particles and liquids to lead the occurrence of cohesion and adhesion. The free energy of cohesion (or work of cohesion) W_{coh} is also related to the surface tension (γ_l) of the same liquid:

$$\Delta G = -W_{coh} = -2\gamma_l \qquad [12]$$

The surface free energy, contact angle, acid-base interactions, and heat of immersion in the interface vary thermodynamic criteria of surfactant adsorption on material surfaces. As known, **free energy** ($\Delta G_i = \frac{dG_{dis}}{dA}$) of the immersional wetting of solid surface is determined by the following equations at a solid/liquid/vapor system [48-50]:

$$\frac{dG_{dis}}{dA} = \Delta G_i = \gamma_{sl} - \gamma_{sv} < 0, \qquad [13]$$

at which A is the surface area, γ_{sl} is solid-liquid and γ_{sv} is solid-vapor interfacial tensions.

The solid-liquid interfacial tension at the triple point may be expressed by using **Young`s** equation (developed in 1805) in the absence of the spreading pressure. The schematic illustration of a water droplet on a solid is shown in Figure 1.12 [2,14,19,20,23,45,79,84].

$\gamma_{lv} \cos\theta = \gamma_{sv} - \gamma_{sl}$, or

$$\cos\theta = \frac{\gamma_{sv} - \gamma_{sl}}{\gamma_{lv}}, \qquad [14]$$

where θ is contact angle formed by a liquid droplet on the smooth solid surface.

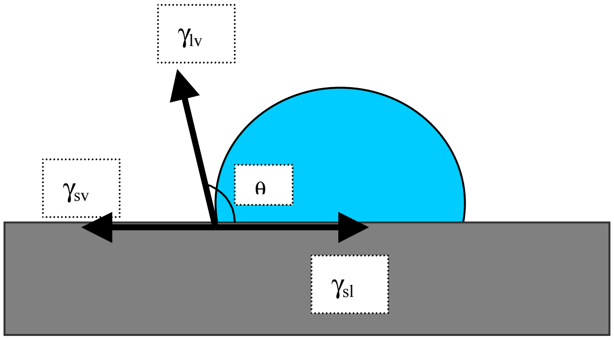


Figure 1.12 The schematic illustration of solid/liquid/air interface

Substituting Equation [14] into [13] for air in water system, one may obtain the following relationship for dewatering [84]:

$$\Delta G = \gamma_{lv} \cos\theta < 0 \qquad [15]$$

which suggests that ΔG becomes negative, i.e. dewatering becomes spontaneous, when θ exceeds 90°. The same conclusion can be seen in Lablace equation [9], suggesting that the capillary pressure becomes negative at an obtuse contact angle [2,19,84].

The process of flotation is also based on hydrophobizing of coal and mineral particles. Appropriate collectors are used to render the surface hydrophobicty so that air bubbles can attach the solid surface by displacing water molecules. For the process of bubble-particle adhesion (or formation of a three-phase contact) to be spontaneous, θ should be larger than 0° (see $\Delta G = \gamma_{lv}(\cos\theta - 1)$). It is clearly seen that the hydrophobcity requirement for flotation is much less than for dewatering. Thus, one can see why dewatering of fine coal and mineral concentrates is thermodynamically more difficult. This is because the floated products are simply not hydrophobic enough for efficient dewatering, which occurs over 90° contact angles [2,19,48,84].

The work of adhesion (W_{adh}) between the solid and liquid, which is also known as a negative of the Gibbs free energy of the adhesion, can be expressed by the **Dupre** equation.

$$W_{adh} = -\Delta G = \gamma_{lv} + \gamma_{sv} - \gamma_{sl}, \qquad [16]$$

In the combination of the Equations [12] and [14], solid-liquid work of adhesion can be expressed by the **Young – Dupre** equation [19,79,87].

$$W_{adh} = \gamma_{lv} (\cos\theta + 1), \quad [17]$$

The Young-Dupre equation implies that the work of adhesion between solid and liquid can be simply calculated from the contact angle and liquid surface tension.

The spreading (S_{ls}) process can also be analyzed using of **Harkins** equation by subtracting the work of cohesion (Equation [12]) from that of adhesion (Equation [16]).

$$S_{ls} = W_{adh} - W_{coh}$$

$$S_{ls} = (\gamma_{lv} + \gamma_{sv} - \gamma_{sl}) - (2\gamma_{lv}),$$

$$S_{ls} = \gamma_{sv} - (\gamma_{lv} + \gamma_{sl}), \quad [18]$$

By substituting the Young equation into the Equation [18], one can obtain the flowing expression.

$$S_{ls} = \gamma_{lv} (\cos\theta - 1), \quad [19]$$

According to the Harkins theory, the spreading phenomena spontaneously occur if the spreading coefficient has positive values. Also, when the work of cohesion is larger than that of adhesion, the solid surface becomes hydrophobic, which means water does not wets over the solid surface. In addition, the other explanation is that since $\gamma_{sv} > \gamma_{lv,}$ spreading can be favorable [19,23,45-50,79].

The relationship between intermolecular force and spreading is examined with a model developed by **Fowkes**. The author suggests that in the surface free energy of the solid and liquid there is an attraction arising from the different intermolecular interactions that cause surface free energy. Fowkes equation in determining surface tension of a phase *i* is given in the form of:

$$\gamma_i = \gamma_i^d + \gamma_i^p \quad [20]$$

where γ_i^d is apolar surface tension component (London-van der Waals dispersion force) and γ_i^p polar surface tension of the same phase, which is also related to acid-base interactions. The Fowkes approach between two interacting surfaces, such as solid and liquid, is written for the determination of the interfacial surface tension [19,23].

$$\gamma_{sl} = \gamma_s + \gamma_l - 2(\sqrt{\gamma_s^d \gamma_l^d}), \quad [21]$$

Fowkes considered here that only apolar dispersion interaction was important in the interface for the work of adhesion. However, this approach may fail in calculating interfacial surface tension if there exist a hydrogen bonding, metallic interactions, dipolar and induction interactions [13].

van Oss and Good explained that the surface tension γ_{ij} of phase *i* and *j* (e.g., different solids or liquids) might be written as below [48]:

$$\gamma_{ij} = \gamma_{ij}^{LW} + \gamma_{ij}^{AB} \qquad [22]$$

where γ_{ij}^{LW} is Lifshitz-van der Waals component (apolar or non-polar surface tension component), which always occurs everywhere in a substance and γ_{ij}^{AB} is polar acid-base component of the surface tension. The polar surface can be monopolar or bipolar. In the monopolar interaction, the acid-base interaction will be zero; therefore, the total free energy is the same as apolar free enegry. As mentioned, the γ_{ij}^{LW} component of the interfacial tension, also known as Good and Girifalco and Fowkes equation, can be expressed [14,19,20,23,48]:

$$\gamma_{ij}^{LW} = \left(\sqrt{\gamma_i^{LW}} - \sqrt{\gamma_j^{LW}}\right)^2 \qquad [23]$$

at which *i* and *j* stand for surface tension component of different materials. van Oss and Good showed that acid-base interfacial tension was related to the surface tension component given by:

$$\gamma_{ij}^{AB} = 2\left(\sqrt{\gamma_i^{+}} - \sqrt{\gamma_j^{+}}\right)\left(\sqrt{\gamma_i^{-}} - \sqrt{\gamma_j^{-}}\right) \qquad [24]$$

In this equation, Lewise acid is an electron acceptor, while Lewise base is an electron donor. If the Equations [23] and [24] are substituted into the Equation [22], one can obtain a useful equation [48]:

$$\gamma_{ij} = \left(\sqrt{\gamma_i^{LW}} - \sqrt{\gamma_j^{LW}}\right)^2 + 2\left(\sqrt{\gamma_i^{+}} - \sqrt{\gamma_j^{+}}\right)\left(\sqrt{\gamma_i^{-}} - \sqrt{\gamma_j^{-}}\right) \qquad [25]$$

which deals with that the apolar component is always positive, while the polar component can be positive or negative which is crucial for the total free energy of the system.

The interaction energy between materials *i* and *j* in vacuo is given by the Dupre equation. For the different surfaces, free energy of the apolar system may be:

$$\Delta G_{ij} = -2\sqrt{\gamma_i^{LW}\gamma_j^{LW}} \qquad [26]$$

which is one of the valuable relationships for the surface chemistry.

For acid-base interactions between the polar materials *i* and *j*, van Oss and Good (1988) have expressed that [40,48,79,84]:

$$\Delta G_{ij}^{AB} = -2\sqrt{\gamma_i^{+}\gamma_j^{-}} - 2\sqrt{\gamma_i^{-}\gamma_j^{+}} \qquad [27]$$

In the form of free energy, one can also write the following mathematical equality.

$$\Delta G_{sl} = \Delta G_{sl}{}^{LW} + \Delta G_{sl}{}^{AB} \qquad [28]$$

By combining the Young and Dupre equations, ΔG_{sl} may be as below [48,79,84]:

$$-\Delta G_{sl} = \gamma_{lv} (\cos\theta + 1) \qquad [29]$$

which is identical to Eqquation [17].

Substituting Equations [22] and [23] into Equation [24], one of the most relevant relationship exists [13,48-50,79,84,87]:

$$(1 + \cos\theta)\gamma_{lv} = 2(\sqrt{\gamma_s{}^{LW}\gamma_l{}^{LW}} + \sqrt{\gamma_s{}^{+}\gamma_l{}^{-}} + \sqrt{\gamma_s{}^{-}\gamma_l{}^{+}}), \qquad [30]$$

which determines surface free energy components of solids, e.g. $\gamma_s{}^{LW}$, $\gamma_s{}^{+}$ and $\gamma_s{}^{-}$ or that of liquids. In order to determine these values, it is necessary to measure contact angle of three different liquids of known components ($\gamma_l{}^{LW}$, $\gamma_l{}^{+}$ and $\gamma_l{}^{-}$) on a solid substrate. By solving three equations with three unknowns, solid or liquid parameters can be theoretically found. From the three parameters of surface tension, one can find the surface tension of a solid as follows [48,49,79,84, 87]:

$$\gamma_s = \gamma_s{}^{LW} + 2\sqrt{\gamma_s{}^{+}\gamma_s{}^{-}} \qquad [31]$$

c) Mostly Used Liquids and Solids

Liquids in Contact Angle Measurements: For the contact angle measurements, the most important parameter is the surface tension of the liquid that should be higher than the solid in order to obtain a contact angle on the solid/liquid/vapor interface. Otherwise, liquid spreads over the solid surface and the contact angle will be zero, which means that surface components can not be predicted. van Oss et. al found that if an organic or inorganic solid has a 45 mN/m surface tension, a liquid used in contact angle tests must be at least 40 mN/m or more [79-88].

In the literature, there are several apolar and polar liquids employed in this purpose. α-bromonaphthalene (γ_i = 44.4 mN/m) and diiodomethane (methylene iodide) (γ_l = 50.8 mN/m) are frequantly used apolar contact angle liquids. Also, other alkanes having a lower surface tension than the previous liquids do not have any acid-base interaction and γ_i is always equal to $\gamma_l{}^{LW}$.

These liquids can be directly used to receive the Lifshitz-van der Waals surface tension (γ_s^{LW}) of a solid [19,84,87].

The most commonly utilized polar liquid for contact angle measurement is water. Apart from its general availability and low cost, water has a higher surface energy (γ_w = 72.8 mN/m) than many solids, so it can be used on several solid surfaces for contact angle measurements. The high γ_w value of water comes from its hydrogen bonding, which corresponds 70.1% total cohesion energy, while 29.9% is for the polar side of acid-base interaction. In the polar side, acidic γ_w^+ and basic γ_w^- sides of water are equal to each other as 25.5 mN/m [13,42-44].

In addition to water, three other high energy bipolar liquids used for contact angle measurements are formamide, glycerol and ethylen glycol having 58 mN/m, 64 mN/m and 48 mN/m surface tensions, respectively. Several apolar and polar liquids and their surface tension parameters are given in Table 1.2 [84].

Table 1.2 Surface tension components of the selected liquids at 20 °C in mN/m

LIQUIDS	γ_l	γ_l^{LW}	γ_l^{AB}	γ_l^+	γ_l^-
Hexane	18.40	18.40	0	0	0
Carbon Tetrachloride	27.0	27.0	0	0	0
Methylene Iodide	50.8	50.8	0	0	0
Benzene	28.85	28.85	0	0	2.7
Chloroform	27.15	27.15	0	3.8	0
Ethanol	22.4	18.8	2.6	0.019	68
Ethylene Glycol	48	29	19	1.92	47.0
Glycerol	64	34	30	3.92	57.4
Formamide	58	39	19	2.28	39.6
Water	72.8	21.8	51.0	25.5	25.5

Solids in Contact Angle Measurements: The surface of a material can be either apolar or polar based on the chemical structure of the substance. Important apolar materials are teflon, polypropylene, polyester and polyethylene, which are polymeric substances. For these substances, LW type energy is favorable between atoms and molecules. The polar part of a substance can be an electron donor or electron acceptor with monopolarity and bipolarity forms. The electron donicity is largely a consequence of oxygen atoms in the form of oxides and hydroxides on the material. It was reported that surface oxidation or hydration changed the surface parameters of the solid. To find out the polar surface tension of a substance, one should measure both the LW and AB interactions for the surfaces [79, 83-88].

From the practical point of view, properties of the high energy bipolar liquids, such as formamide, glycerol, ethylen glycol, and other polar and apolar liquids can be determined from the contact angle measurement on known solid surfaces [46]. These substances that have a lower surface tensions than the liquid surface tensions can be polyethylen oxide, teflon, nylon, mica, glass, talc, etc. The important issue here is that the solid surface should be smooth and clean for contact angle measurements. It is known that surface roughness and contamination are detrimental for determining surface parameters of the liquids and can give incorrect calculation. Frequently used polar and apolar solids and their surface tension parameters are given in Table 1.3 [79].

Table 1.3 Surface tension components of the selected solids at 20 °C in mN/m

SOLIDS	γ_s	γ_s^{LW}	γ_s^{AB}	γ_s^{+}	γ_s^{-}
Teflon	17.9	17.9	0	0	0
Polyethylene	33.0	33.0	0	0	0
Polyethylene Oxide	43.0	43.0	0	0	64.0
Nylon	37.7	36.4	1.3	0.02	21.6
Talc	36.6	31.5	5.1	2.4	2.7
Muscovite (mica)	43.2	36.5	6.8	0.2	57.7
Calcite Crystal	57.0	40.2	16.8	1.3	54.4
Dolomite Plate	42.5	37.6	4.9	0.2	30.5
Zirkonia (coarse)	41.2	34.8	6.4	1.3	7.8
Silica glass	49.8	34.0	15.8	1.0	64.2
[1]Montmorillonite (clay)	59.9	43.6	16.3	1.8	36.8
Coal	39.8	39.8	0	0	2.5

[1] Wicking contact angle method used for the powder materials

1.2.3.2 Hydrophobic forces in filtration

It is assumed that the process of dewatering relies on the replacement of the capillary water by an air phase. However, complexity of the capillary water replacement makes this assumption extremely more difficult since several effects including surface hydrophobicity and surface tension exist in the dewatering process [45,48,87-95]. The surface hydrophobicity that may be controlled by the contact angle is the major interests to determine capillary water behavior in a filter cake.

Role of the surface forces was first considered by Derjaguin and Duhkin [90]. In their studies, three different surface forces, such as van der Waals force, double layer force and structural forces were mentioned as a particle was immersed into water. However, the same authors did not consider the attractive forces that were related to the surface hydrophobicity, which plays a major role in bubble-particle interactions. Blake and Kitchener [91] gave some evidence of the attractive force existing in bubble-particle interactions by using film stability measurements on a mathylated silica-air bubble system. In this investigation, it was expressed that there were some forces (electrostatic and dispersion) between substances. The investigators also suggested that there might be an additional attractive force that could play a role for stability of the surface chemistry processes [91,96-102].

In 1982, Israelachvili and Pashly [92] reported a hydrophobic interaction obtained using mica surfaces to clarify the net attractive force. It was shown that this force was higher than the predicted ones (e.g., electrostatic and van der Waals forces). The measurement was conducted on the particle-particle interaction, and it may not be suitable for bubble-particle interaction. This may be the key point for the flotation and filtration mechanisms. In order to find out the bubble particle interactions, Ducker et al used an atomic force microscopy (AFM) to measure the surface forces between bubbles and particles, and found that there existed a net attractive force [93,94]. In addition, Flinn et al carried out a surface force measurement at Virginia Tech by simulating a glass sphere as an air bubble [95]. Several other papers have also dealt with the hydropbicity, colloidal particle interaction and their role on the flotation processes [81,96-103]].

a) Classical DLVO Theory

In the 1940s, the classical DLVO theory, named after the contribution of the authors Derjaguin, Landau, Verwey and Overbeek, was considered the colloidal stability of fine particles. This theory only states a total interaction force *F* which consists of ion-electrostatic force F_e and London-van der Waals force F_d given below [84,92-99]:

$$F = F_e + F_d, \qquad [32]$$

The theory can be used for a weak hydrophobic force at a lower contact angel θ (~20°). For the electrostatic repulsive force between a sphere and a flat smooth surface, this approximation can be expressed for only lower surface potential [84]:

$$F_e = 4\pi R\varepsilon\varepsilon_0\kappa\psi_0^2 e^{-\kappa H} \qquad [33]$$

at which R is the radius of the sphere, ε is dielectric constant of the medium, ε_0 is permittivity of the free space, κ is reciprocal of Debye length, Ψ_0 is surface potential, and H is separation distance.

For the London van der Waals attractive force, a similar expression may be given:

$$F_d = \frac{-AR}{6H^2} \qquad [34]$$

where A is Hamaker constant for a substance. For the direct force measurements between two surfaces (**1** and **2**) in water **3**, one can write the geometric mean of the Hamaker constant:

$$A_{132} = \sqrt{A_{131}A_{232}} \qquad [35]$$

It is found that this constant is always positive for two identical surfaces attracting each other in a liquid media. In contrast, it may be negative if there are dissimilar bodies [88-95,100-105].

b) Extended DLVO Theory

The classical DLVO theory does not count hydrophobic, hydration, steric repulsive and depletion forces, which can be important parameters for colloidal stability. After Israelachvili and Pashly [92], several investigations have been focused on the extended DLVO theory. Yoon et al determined that the hydrophobic force F_h is the major parameters for particle-particle and bubble-particle interactions [81,88,89,96]. It is assumed that the same phenomena may occur during filtration, flotation, coagulation, flocculation and other wetting/dewetting processes. When the hydrophobic forces are measured at a higher contact angle, Equation [32] may be extended to [84,87,90-101]:

$$F = F_e + F_d + F_h, \qquad [36]$$

which is known as the extended DLVO theory. In the literature, there are several mathematical representations of the hydrophobic forces [89-96]. The measured hydrophobic forces (e.g., θ = 60s) are most commonly described by an empirical relationship [84]:

$$\frac{F_h}{R} = C_0 \exp\left(\frac{-H}{D_0}\right) \qquad [37]$$

Since a stronger hydrophobic force is measured between the surfaces which means the surface is formed a nanosize close-packed monolayer by surfactant molecules and the contact angle becomes over 90°, it is often suggested to use a double-exponential function for the representation of the magnitude of the surface forces [84,87,90]:

$$\frac{F_h}{R} = C_1 \exp\left(\frac{-H}{D_1}\right) + C_2 \exp\left(\frac{-H}{D_2}\right) \qquad [38]$$

at which C_0, C_1 and C_2 are related to interfacial tension at the solid/liquid interfaces and D_0, D_1 and D_2 are referred to as decay lengths. A power law can also describe the higher hydrophobic forces using the equation [84,87]:

$$\frac{F_h}{R} = \frac{-K}{6H^2} \qquad [39]$$

which is the same form of the dispersion forces. Advantage of this equation is that it better describes the suggested force and easily fits to the theory. The value of hydrophobic force constant K is directly related to Hamaker constant A. One can equate it as geometric mean:

$$K_{132} = \sqrt{K_{131}K_{232}} \qquad [40]$$

These values can be determined by conducting force measurements between the surfaces, which have the same contact angles [84,87,95,104].

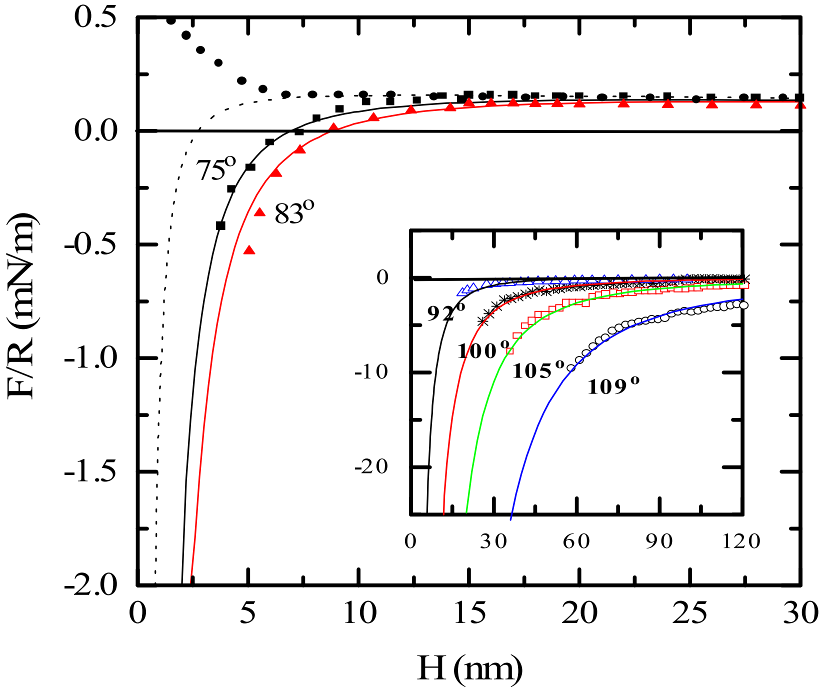


Figure 1.13 Hydrophobic forces of silanated silica plate and glass sphere at high contact angles. The contact angle values on the surfaces were obtained using octadecyltrichlorosilane (OTS). The dashed line represents the classical DLVO fit at zero contact angle with $A_{131} = 8\text{x}10^{-21}$, Ψ_1=-60 mV and κ^{-1}=94 nm. For the hydrophobic forces, a power law was used for the extended DLVO fits.

According to the Derjaguin approximation, the force can be converted into energy form [82,87,95]. Figure 1.13 shows the form of energy as a function of separation distance. It is seen that the force measurement conducted on a silica surfaces at zero contact angle and even at 75° and 83° corresponds the repulsive force which may be attributed to the hydration of the silica surface. However, when the surfaces are coated by a certain amount of surfactant to form a close packed monolayer increasing the contact angle over 90°, a positive net attractive forces can be obtained which is not considered in the classical DLVO theory [84,87,94-99]. Table1.4 shows the change of the surface force parameters as a function of contact angles. It is clearly seen that at a 109° contact angle, almost all the force parameters are exponentially improved due to the strong hydrophobic forces between the particles [87,100-107].

Table 1.4 Surface force parameters on the symmetric interactions as a function of θ

Contact Angle (θ°)	H_j (nm)	C_2 (mN/m)	D_2 (nm)	K_{131} (10^{-18} J)		F_{ad}/R (mN/m)
				Equilibrium	Jump	
81	6.30	-9.0	2.0	0.07	0.20	4.63
92	19.6	-12	10	3.2	5.82	45.1
100	15.5	-9.0	24	12.5	9.94	38.6
109	45.5	-83	32	270	340	144

<u>Electrolyte Effects on Hydrophobic Forces</u>: It was found that addition of electrolyte can destabilize the particles in a suspansion. For this reason, a certain amount of salt is added to the system to decrease the repulsive forces created by electrostatic and hydration forces in water. Based on the valance, the electrolyte decreases the double layer thickness and possibly increases the adsorption of the ions into the Stern layer. According to the Schulze-Hardy rule, the effect of the valance changes coagulation of fine colloidal particles by an order of magnitude (z^{-6}). In this model, it is assumed that surfactant dosages in which a hydrophobic layer is formed on a material surface may be decreased, as well.

As has been stated, dewatering of the fine particles is spontenious if the contact angle is 90° (wettability/dewettability boundary is existed) or over by using large amount of low HLB non-ionic surfactants. Therefore, it may be a solution to reduce the total surfactant consumption in the dewatering process using high valance electrolytes. In addition, pH of the aqueous solution can change the surface forces of the substrates. Ducker et al determined that the measured force between the silica glass and silicon wafer plate was increased by decreasing the pH value (HCl), and thus decreased by increasing pH (NaOH) at 10^{-3} M NaCl [86,93-97].

Acid-Base Interaction on the Hydrophobic Forces: As previously stated, the acid-base interaction may occur since dissimilar surfaces are introduced in the system. Hydrogen bonding is the most common type of this interaction. Pazhianur and Yoon [107] have reported that the acid-base interaction conducted on silanated silica surfaces could vary hydrophobic forces. From the tests, the value of the basic side γ^-_s was higher than that of the acidic side γ^+_s at a lower contact angle (50°), which was due to the basic characteristics of the silica surface. It was also found that i) the values of γ^-_s, γ^+_s and γ_s^{AB} decreased with increasing hydropobicity of the surface, ii) the values of γ_s^{LW} reduced as a function the contact angle, and iii) the contact angle might be dependent on the acid-base parameters. It was assumed that the values of London van der Waals surface tension γ_s^{LW} were always constant for the material. However, decrease in γ_s^{LW} was due to the fact that the silica surface was well coated by the surfactant molecules (octadecyl silane chains), and the surface could not be the solid surface. In addition, it is also assumed that the values of γ_s^{LW} and γ_s^{AB} never becomes zero for any substances. Figure 1.14 shows the change in surface parameters as a function of contact angle [84-99].

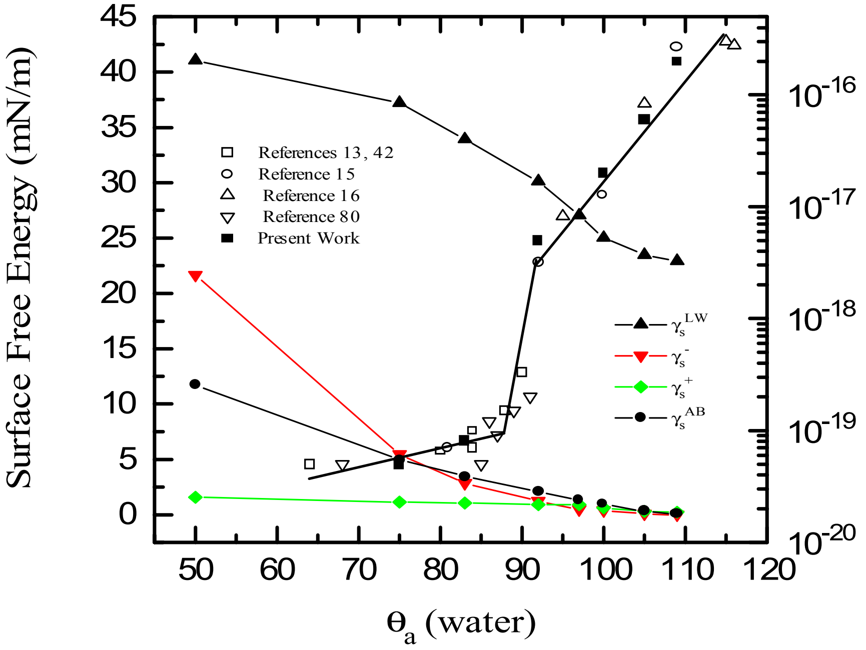


Figure 1.14 Effects of acid-base interaction on the surface free energy

Like flotation, dewatering is also a three-phase (solid-liquid-air) operation system when the vacuuming is started through the cake. As previously stated, flotation occurs if contact angle is higher than zero, while dewatering needs at least 90°, according to the Laplace equation. At that high contact angle, dewettability of the particle exists on the surface, which means that dewatering spontaneously takes place. Therefore, one can see that the extended DLVO theory is more suitable on dewatering than on flotation according to the high hydrophobic force formation on the particles to be dewatered [45,87,104-107].

1.3 SOLID-LIQUID SEPARATION TECHNIQUES

1.3.1 Sedimentation Techniques

In the early stages of dewatering process, sedimentation of the fine particles occurs by gravitational or centrifugal forces to increase the solid contents of the slurry. This process is conducted on the suspension in large capacity thickeners or centrifuges by adding flocculant or coagulants to separate a large volume of free water. The settling velocity of fine particles in the thickeners is slower than in the centrifuges due to the fact that the centrifuges have higher gravitational effects on the fine particles. The thickened product is then introduced to mechanical filtration or centrifugation to reduce the total moisture content of the cake before the thermal dryers [2,14,21,42,45,47,69,108].

1.3.2 Filtration Techniques

The dewatering performance of fine coal and mineral particles are associated with the chosen filtration techniques. Each of the technique is composed of various units, which are applicable for selected materials to improve dewatering capacity. In this section, some of the dewatering techniques and their characteristics that are also used in the present work are being discussed [2,14,42,108].

a) Vacuum Filtration

There are several types of vacuum filters used for dewatering fine particles, three of which are rotary drum, rotary disc and horizontal belt filter (HBF). The *drum filter* is the most widely used continuous vacuum filter for fine coal and mineral particles. It consists of a cylindrical drum submerged into a slurry tank in which the material in suspension is agitated by a mixer. The drum surface is divided into compartments, each of which is provided by a number of drain sectors. A filter cloth is tightly wrapped around the drum surface and rotates with the drum together. The speed of the drum can be changed from 0.1 to 3 rpm. When the drum is in the slurry tank, cake starts forming - called cake formation time, whereas when it is on the air, derange stage starts - called drying cycle time. It has various types of discharge mechanisms including fixed knife, air blow cycle, belt-type drum filter, and endless spinning arrangements. When the cake is removed from the drum surface, belt is cleaned with wash water for the next cycle. Applied vacuum pressure, rotation speed and submergence control the performance of the drum filter. A schematic illustration of a pilot drum filter is shown in Chapter 4 [2,14,42,45,47,108].

The *disc filter* has a similar operating principle with the drum filter. The difference is that the disc filter consists of a number of vertical discs connected to a horizontally rotating shaft. These discs divided into several sectors and covered with filtering mediums are immersed into the slurry tank to gradually form the cake. In this process, the cake thickness is dependent on the solid content of the slurry. After the cake is formed and dewatering is completed, then the cake is removed with a scraper blade or an air blow back system. It was reported in many plants that the disc filter cost per unite area was lower than the drum filter; however, the cake washing could not be possible in the disc filters [14,47,108].

The *horizontal belt filter* has an endless perforated rubber belt on which a filter cloth is placed. The belt is slipped onto a smooth tray so that a vacuum can be applied from the bottom of the cake. In this system, the slurry inlet is at one end and the cake discharge is at other end of the belt. During the vacuuming period, the filtrate is collected in a vacuum box and continuously pumped to the outside by a prestatic pump. Application of the HBF is specially increasing in coal and mineral industries due to the low cost and handling of dilute slurry in the plants without thickening operation. However, this filter gives higher moisture content than the other vacuum filters, and it can have a leakage problem under the vacuum pressures. A schematic presentation of a small scale HBF is given in Chapter 4 [2,14,45,108].

b) Pressure Filter

The pressure filter works under air or hydraulic pressures. It has advantages over the vacuum filter due to the vertical incompressibility of the solids. Filter press and chamber press are the most frequently used pressure filters. In these units, high pressure creates a better washing rate and lowers moisture contents from the filter cake. Conversely, the continuous discharge of the cake from the inside of the chamber can be difficult, so it is usually maintained as a batch unit. In order to eliminate this problem and increase the capacity of the pressure filter, two parallel filters are performed in the plants. More clearly, while one unit is filtering the suspension in a chamber, the other unit is discharging the cake that has been already formed [2,14,47,108].

The *filter press* consists of two major elements: plate and frame separated by a filter cloth. A hydraulic pressure prevents the leakage and tightly closes the plates. The suspension is introduced to the empty frames, and then the pressure is applied to the slurry by means of pistons. When the filtration period is ended, the cake remaining in the frames is discharged one by one releasing the applied pressure. Finally, the frames of the filter press are closed to repeat the cycling operations [2,14,47,108].

The second pressure filter – *chamber press* - is similar to the filter press; the only difference is that the filter elements consist of drilled filter plates in the center. The filtration chambers are combined by a hole covered by the filter cloth. The slurry is poured into channels of the filter, and the pressure is then applied to gradually deposit the cake on the surface of the chamber. These filters significantly lower the moisture content of the cake and decrease the cost of the thermal drying units [2,47,108].

1.3.3 Centrifugation Techniques

It is known that the centrifugal machines create high gravity forces for the purpose of the solid-liquid and liquid-liquid separations. The important advantages of the machine are that coal and mineral particles are dewatered in a short time and continuously discharged by scrapers. The disadvantages of the unit are that it has a high maintenance cost due to the inside wearing of the cylindrical basket and other working elements and losing of the fine particles through filtrate. This technique mainly developed for the coal and mineral industry is efficient method especially for coarse (37.5 mm x 0.5) and fine coal (0.5 mm x 0) dewatering. In the coarse coal dewatering, *perforated basket* centrifuges are usually performed in the preparation plants. In the recant application, a vibrating type of the perforated basket is preferred to obtain a lower moisture content of a product. For the fine size, bowl centrifuges are usually utilized as a dewatering machine. These techniques are divided into two main units: solid bowl centrifuge and screen bowl centrifuge [2,14,42,45,47,108].

The cylindrical *solid bowl centrifuge* has two rotating units including an outer solid bowl and inner bowl, both of which have slightly different speeds that are controlled by a centrifuge motor. During the rotation stage, a stationary pipe that is placed into the centrifuge bowl feeds the slurry, and then solid is settled on the bowl surface. After the settling of the fines on the surface of the centrifuge, a helical screw conveyor continuously discharges the solid from the machine. The effluent in the centrifuge is moved to a large end of the cone in which it is removed through effluent ports. A schematic illustration of Bird solid bowl centrifuge is shown in Figure 1.15 [2,14,45,108].

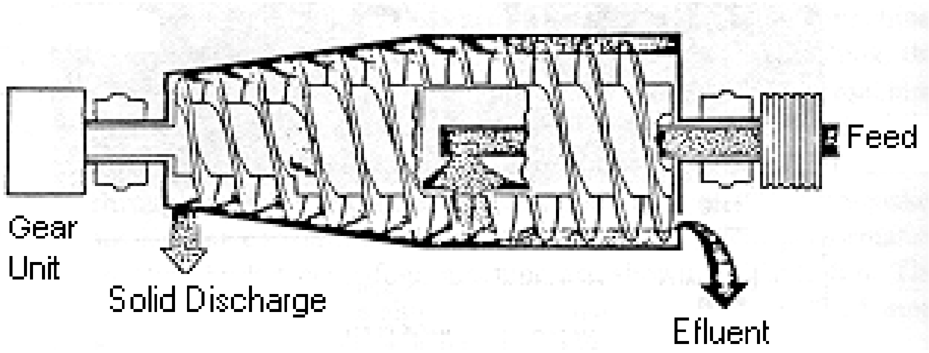


Figure 1.15 Bird solid-bowl centrifuge used for solid-liquid separation

The *screen bowl centrifuge* has a similar design and operation of the solid bowl centrifuge. The difference is that the screen bowl centrifuge incorporates a fine size screen in the bowl so that the screen permits water to pass through the effluent tank. A screw conveyor continuously discharges the settled particles from the machine. The screen surface gives an additional dewatering for the cake prior to the thermal dryers. It is reported that moisture content and ash content of the product is 3 to 6% lower than the other dewatering machines. The low ash content can be attributed to the removal of clay-like particles into the effluent, while the low moisture content can be attributed to the fine particle losing from the cake. One of the principal advantages of the screen bowl filter is that a dilute flotation slurry can be directly fed to the centrifuge without thickening. A Bird screen bowl centrifuge is shown in Figure 1.16 [2,14,45,108].

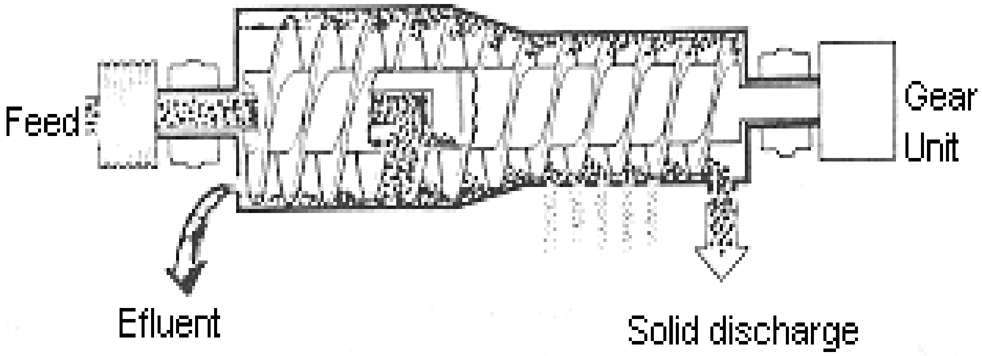


Figure 1.16 Bird screen-bowl centrifuge used for solid-liquid separation

1.3.4 Thermal Drying

Thermal drying is the last operation performed on the dewatered particles prior to marketing. This decreases the cost of the transportation for especially oversea shipment. In the practical point of view, the moisture content of a product can be around 5% by weight due to the fact that dust losses can be a problem if the moisture is lower than this level. In the industrial application, rotary thermal dryers, in which hot gasses or air are introduced, are usually used. For these dryers, the cylindrical body of the unit is given a slight slope so that particles movements occur from feed to discharge end by the gravity effects. In addition to that, fluidized bed and flash dryers can also be used for the same purposes [2,14,42,47].

In the thermal drying, heating of the particles can be direct or indirect. In the direct method, the hot gas passes through the fine particles inside the dryers and removes the moisture out of the unit. This method is most commonly preferred method for fine particle drying. In the second one, the fine particles in the chamber of the dryer are externally heated by hot gas. It is preferred if the product is not to be contaminated by the environment [42,47,108].

1.4 RESEARCH OBJECTIVES

The objective of the current project (or thesis) was to develop advanced fine coal and mineral dewatering processes that can greatly assist in the greater utilization of fine particles. To meet this objective, novel dewatering technologies have been developed at Virginia Tech. These include i) novel dewatering aids and ii) a novel centrifuge.

The new technologies were tested on batch and pilot scales units. The scope of the present tests were:

i) Testing of dewatering aids on various bituminous coal and mineral fines using laboratory-scale batch dewatering devices, which included Buchner funnel filter and an air pressure filter,

ii) Testing selected dewatering aids on a variety of coal fines using pilot-scale mechanical dewatering devices, which included a vacuum disc filter, a horizontal belt filter and two drum filters,

iii) Testing the novel centrifuge on a laboratory-scale in bench mode on a variety of bituminous coal and mineral fines,

iv) Conducting continuous tests on selected filtration units in a plant set-up, in which coal samples are floated and subsequently dewatered with and without using selected novel dewatering aids for an extended period of time,

v) Making technical and economic evaluations on the basis of the test result obtained in the present work,

vi) As a result of the tests, developing conceptual Proof-of-Concept (POC) plant designs that will allow testing some of the advanced dewatering technologies in large scale at industrial sites.

1.5 REPORT ORGANIZATION

The dewatering results of the present work have been reported in Chapters 1 to 6. Each chapter consists of an introduction, experimental (sample and method), results and discussions, summary and conclusions and reference sections. In Chapter 2, results of batch filtration tests using vacuum and air pressure filters conducted on coal and mineral samples are discussed in the presence and absence of dewatering aids. The dewatering aids used for fine coal and mineral particles were controlled by changing the amount of chemical dosages. Hydrophobicity, surface tension, contact angle, coagulation and vibration of the cake were considered for the high moisture reductions. The other filtration variables, such as pressure, conditioning time, drying cycle time, cake thickness and particle oxidation were also considered for the dewatering of the fine particles.

In Chapter 3, dewatering tests were conducted on the same samples by using novel centrifugal filtration techniques: G-force combined with air or vacuum pressures. The slurry sample was thickened in a funnel and used for the centrifugal tests. The experimental tests were conducted at different G-Forces, spine time, cake thickness, air/vacuum pressure. The results showed that in the presence of air in the centrifugal bask, a drastic moisture reduction was obtained from the fine cake.

Chapter 4 exhibits effects of the dewatering chemicals on the fine coal samples in the pilot plant scale. Disc, belt and drum filters were used to be able to compare the batch scale test results and the pilot plant test results together. In addition, plant processing, sample analysis, economical and technical approaches of the dewatering processes were evaluated

Chapter 5 deals with the surface chemistry of filtration, which is based on the fundamental of the filtration processes. It consists mainly of the surface characterization of coal samples, contact angle measurements, acid-base interactions of solids and liquids, zeta potential, surface image analysis and surface area tests. In addition, carbon coating on a silica plate using palsed laser deposition (PLD) for reagent adsorption, Langmuir-Blodgett (LB) tests for surfactant film deposition, FTIR, x-ray photoelectron microscopy (XPS) studies, atomic force microscopy (AFM) and dewatering kinetic tests were conducted on the samples.

Finally, Conclusion and Future Work are given in Chapters 6 and 7, and the Appendices are shown at the end of the chapters.

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