

## CHAPTER 2

### FILTRATION

#### 2.1 INTRODUCTION

*General Background:* High quality material production has been increased for technological and economical reasons. For coke production or power station use, coal should be required to meet properties of low moisture, ash and sulfur content and high calorific values. To obtain the high quality products, removal of the sulfur and other gangue minerals in coal requires fine grinding to liberate the particles before separation process. Also, similar effect occurs for mineral ores that are used for several industrial applications [1,2]. Besides, fine particle production can be increased during the run-of-mine (ROM) production. The pulverized fine ores and coal are then separated using appropriate methods.

One of the most widely used methods of separation is forth flotation. In this method, the fine particles are mixed with water to form a slurry before surfactant addition. However, higher-rank coals, such as bituminous and anthracite coals which are naturally hydrophobic as mined may not need collectors. When these materials are not sufficiently hydrophobic, appropriate surfactants known as collectors are added to enhance their hydrophobicity for flotation. The hydrophobized (or naturally hydrophobic) particles are then collected by the air bubbles introduced at top of the flotation cell, while hydrophilic particles are not collected by air bubbles and exit from the bottom of the cell. As a result, the valuable and seldomly tailing products are dewatered for next processes [1-11].

As known, the fine particles have larger surface area to adsorb more water in filter cake, so it is extremely difficult to dewater such fine particles in current dewatering machines, such as drum, disc, horizontal belt and pressure filters. The difficulty in dewatering fine materials may be explained from the first principles of filtration law, which deals with small size capillary tubes formed in the cake where water cannot be removed easily during the vacuum or air pressure. Water can be removed only when the pressure drop applied across the filter cake exceeds the pressure of the water present inside the capillaries. In addition to that, cost of dewatering fine coal (0.5 mm x 0) is approximately 3 to 5 times higher than that of coarse particles, and these make the fine particle processing impossible in the plants [1,2,9].

*Theory:* The pressure  $\Delta p$ , in the capillary of radius,  $r$ , can be calculated using the Laplace equation [1-10].

$$\Delta p = \frac{2\gamma_{23} \cos \theta}{r}, \quad [1]$$

in which  $\gamma_{23}$  is the surface tension at the water **3** and air **2** interfaces, and  $\theta$  is the water contact angle of the inner walls of the capillary. This equation is considered to use for the cake filtration of the present studies.

In the Laplace equation, three are ways of achieving low cake moistures during filtration. These include i) contact angle increase ii) capillary radius enlargement, and iii) surface tension lowering. Various dewatering chemicals are used to control these parameters. According to the Equation [1], when the water contact angle on the substrate is less than  $90^\circ$ , the process is no longer spontaneous which means that an extra pressure may be needed to remove the water in the capillary. In other words, energy must be supplied to the system to displace the surface water. The Laplace equation shows that the free energy requirement is reduced by lowering the surface tension and by increasing the contact angle. Of these two variables, control of the contact angle is a more powerful means of reducing cake moisture, particularly if it can be increased above  $45^\circ$ . As an example, consider a case where one can increase the contact angle from  $45^\circ$  to  $85^\circ$  using appropriate surfactants. This will reduce the energy requirement by 8.1 times due to the logarithmic function of the contact angle. Likewise, the critical capillary radius ( $r_c$ ) will also be reduced by 8.1 times. Consider a case, where the surface tension is lowered from 70 to 40 mN/m. This will reduce the energy requirement and  $r_c$  by only 1.8 times. Note also that lowering the surface tension to lower levels may require a large amount of surfactant, which can cause harmful effects, such as hydrophobic dampening (due to the inverse orientation) and frothing problems. However, when the contact angle is  $90^\circ$  where the dewettability of the particle starts, extra pressure may not be needed to remove the capillary water in the cake [6-15].

The contact angle is the most widely used measurement technique for particle hydrophobicity (water-hating property). In order to determine the contact angle, a drop of water is placed on a smooth surface of interest and the angle is measured through the aqueous phase. Thus, the term contact angle used in these tests refers to the water contact angle, which decreases with increasing the surface hydrophobicity. According to the Equation [1], a filter cake consists of smaller capillary radii, makes it more difficult to remove the water from the cake. At a given

pressure drop across the filter cake, the water trapped in the capillaries cannot be removed. Hence, the moisture of a filter cake can be determined by the amount of the trapped water in the capillaries that are smaller than critical capillary radius [15-23].

Various dewatering chemicals are used to control the parameters of the Laplace equation. One group of reagents is the surfactants that can lower the surface tension. Most of the dewatering aids used for this purpose are ionic surfactants with a high hydrophile-Lipophile balance (HLB) numbers. Sodium laurylsulfate and sodium dioctylsulfosuccinate, whose HLB numbers are 40 and 35.3, respectively, are typical examples [2]. It is suggested that the former is an ideal dewatering aid for coal because it does not adsorb on the surface, which in turn allows for the reagents to be fully utilized for surface tension lowering. In addition, investigations show that a method of spraying the chemicals through the cake may help to remove the supernatant process water in the cake [3]. This method, which is referred to as torpedo-spray system, ensures even distribution of the dewatering aid without becoming significantly diluted by the supernatant water [3, 11-16].

It has been determined that free energy  $\Delta G$  values are useful parameters to better understand the dewatering, coagulation, flocculation and flotation processes of the fine particles. For dewatering of the fine particles, one can write the following equation used for a single particle [15]:

$$\Delta G = \gamma_{lv} \cos\theta \quad [2]$$

at which  $\gamma_{lv}$  is air-water surface tension. It suggests that  $\Delta G$  becomes negative (or dewatering becomes spontaneous) as  $\theta$  exceeds  $90^\circ$ . The same conclusion can be seen from the Laplace equation, which suggests that the capillary pressure of the cake becomes negative at contact angle higher than  $90^\circ$  [7-12].

The process of flotation is also based on hydrophobizing of mineral particles, and used following relation [15,24-30]:

$$\Delta G = \gamma_{lv}(\cos\theta-1) \quad [3]$$

According to the Equation [3], bubble-particle adhesion for a flotation process spontaneously occurs if  $\theta$  is larger than  $0^\circ$ . From the later equation, it is clearly seen that the hydrophobicity requirement for dewatering is higher than for flotation. Hence, it may be concluded why dewatering of fine particles is more difficult than flotation of the same particles. The reason is that the floated product is not hydrophobic enough to dewater in the first hydrophobization step

of the flotation process. Therefore, a second step will be necessary for the hydrophobicity enhancement. The initial hydrophobization step may be omitted if the particulate material is naturally hydrophobic or has been sufficiently hydrophobized in an upstream process using a less amount of reagents. For dewatering process, higher dosages (5 to 10 times more in comparison with flotation) of surfactant additions can be needed for the second hydrophobization to become thermodynamically spontaneous filtration [1,10-17].

Previous Work: From the literature reviews, it should be noted that high HLB *surfactants* have been used as wetting agents for hydrophobic materials, such as coal, talc, sulfur and molybdenum. Recognizing that dewatering is essentially a de-wetting process. It is well known that high HLB surfactants adsorb on hydrophobic non-wetting surface with inverse orientation, i.e., with hydrocarbon tails in contact with the surface and the polar heads pointing toward the aqueous phase. Thus, high HLB surfactants can lower the surface tension, but they can also dampen the hydrophobicity and decrease the contact angle. The high HLB surfactants used as dewatering aids can actually cause an increase in moisture content [9,15,18-26].

In addition to the surfactants, various *polymeric flocculent* have been successfully employed as dewatering aids for a long time [1,9,23]. The role of these reagents is to increase the effective size of the nano/micro size particles in the suspension due to the bridging formation between particles and polymer molecules. This will be greatly reduce the capillary pressure, and hence, increase the filtration rate. However, most of the flocculants used as dewatering aids are hydrophilic. Therefore, their adsorption dampens the hydrophobicity of the mineral or coal concentrates that are mainly hydrophobic by virtue of collector adsorption or by nature. As a result, the method of using polymeric flocculants for dewatering has limitations. It has been reported that flocculants are capable of reducing dewatering rate but not necessarily the final cake moisture [4,30-39].

Various *electrolytes* can be used to coagulate the particles to be filtered, and improve dewatering of ultrafine materials (clay, aluminum ore, PCC). Also, it was found that fine coal dewatering could be considerably enhanced in the presence of divalent and trivalent cations. Investigators suggest that this process can be the case of lowering the surface charges of the substances [1,5,23,40-43].

Recently, it was found that a method of using non-ionic (or natural) low HLB surfactants (mono-unsaturated fatty esters) and water soluble polymers (polymethylhydrosiloxanes) as

hydrophobizing agents were conducted on coal and mineral particles to increase the contact angle above 80° and, thereby, facilitate dewatering processes [6]. The fatty esters were used for particulate materials in the presence and absence of butanol as a carrier solvent. These include coal, clay, sulfide minerals, phosphates, metal oxide minerals, industrial minerals, and waste materials, most of which are hydrophilic without suitable pretreatment [6,44-50]. The use of the low HLB surfactants may be able to increase the contact angles of the minerals that are already hydrophobic, but not for the hydrophilic particles.

There are several other researches that show methods of using low HLB surfactants as dewatering aids. HLB numbers in the range of 6 to 12 of surfactants were used as a dewatering aid to lower surface tension of the liquid. These are the reaction products of one mole equivalent of a primary alcohol containing 6 to 13 carbons with 2 to 7 mole equivalents of ethylene oxide. It was pointed out that these reagents did not adsorb on the surface of the particles in the slurry [7, 8,14]. The other research deals with a nonionic surfactant made of a polyoxyethylene of a hexitol anhydride partial long chain fatty acid ester, functioning alone or as a solution in light oil. This surfactant was used for sulfide mineral filtration and removed 2 to 3% moisture in comparison with the base line [9,27,51-58].

It has also determined that sulfosuccinate, polyoxyalkylene, polyethylen glycol ether, mixed hydroxyether, diesel, kerosene, butane, C<sub>8</sub> to C<sub>20</sub> carbon chain length fatty acids, fatty acid precursors, such as esters or amids and fatty acid blends have been used for flotation, agglomeration, filtration and defoaming aids. These reagents were used alone or in conjunction with hydrocarbon alcohol containing 6 to 24 carbon atoms for dewatering of coal and mineral particles. They reduced the total moisture contents and increase the dewatering kinetics [1,6-16].

A new dewatering method was developed at Virginia Tech and used successfully in a lab unit scale for the dewatering of fine coal particles. The method uses liquid butane to displace process water from the surface of particles. The authors showed that the moisture content of the fine coal could be as low as 1% by weight. It was also pointed that the large amount of spent butane could be economically recovered and recycled for the next cycle [15].

*Novel Dewatering Chemicals:* In this section, various non-ionic surfactants developed at Virginia Tech were used as dewatering aids. The novel reagents increased the contact angle closer to or above 90° and capillary radii and decreased the surface tension so that the efficiency of the dewatering fine particles was greatly improved. The non-ionic surfactants may be useful to

obtain nanosize monolayers on the particle surface for hydrophobicity improvements. Part of the surfactants may adsorb in between the sparsely populated hydrocarbon tails and thereby increase the hydrocarbon chain density on the surface, which is conducive to hydrophobic enhancement. Some of the surfactants may adsorb on top of the first monolayer of hydrophobes, which should also increase the hydrophobicity. Since the more hydrophobic moiety of a low HLB surfactant is attracted to the hydrophobes on the surface via hydrophobic interaction, the more polar part of the molecule may be exposed to the aqueous phase. However, such an orientation should not dampen the hydrophobicity significantly, because the polarity of the head group of the low HLB surfactants is much lower than that of high HLB surfactants.

In addition, the low HLB surfactant on the less hydrophobic part of the surface may adsorb with their polar parts in contact with the surface, possibly via acid-base interactions. Such an adsorption mechanism will have the hydrocarbon tails point toward the aqueous phase, and thereby convert the less hydrophobic sites to more hydrophobic ones by covering the sites with hydrocarbons. Recently, van Oss and his colleagues determined that acid-base interaction could be a key parameter for surfactant adsorption. In this process, a basic component, such as a carbonyl group does not interact with another basic group, and also the same situation occurs between acidic parameters ( $\text{CHCl}_3$ ). In the acid base interaction, the hydrogen bonding ( $\text{Cl}_3\text{C-H} \cdots \text{-OH}_2$ ) 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. For example, in filtration or flotation processes the basic mineral surfaces may need acidic surfactants for acid-base interaction [26-38].

The non-ionic surfactants used in these tests have HLB numbers lower below 15. These include fatty acid, fatty esters, phosphate esters, hydrophobic polymers, ethers, glycol derivatives, sarcosine derivatives, silicon-based surfactants, sorbitan derivatives, sucrose and glucose esters and derivatives, lanolin-based derivatives, glycerol esters, ethoylated fatty esters, lipids (vegetable oil and animal fats) and their derivatives, and blending of lipids and pure surfactants. The most of these reagents are insoluble in water; therefore, they are normally used in appropriate solvents, which are light hydrocarbon oils and short-chain alcohols whose carbon atom numbers are less than eight. The light hydrocarbons include diesel oil, kerosene, gasoline, fuel oil, petroleum distillate, turpentine, naphthanic oils, vegetable oils, etc.

Lipids are naturally occurring organic surfactant that can be isolated from plants and animal cell (and tissues) by an extraction method. These are hydrocarbon compounds that are named as soybean oil, sunflower oil, corn oil, coconut oil, peanut oil, fish oil, lard oil, etc., so they are insoluble in water, but can be soluble in the organic solvents (light oils and alcohols). The animal fats and plant oils, that is, the former are solids and the later are liquids have similar structures. Both can have oleic acid, linoleic acid and palmitic acid that are main surfactant supplies for dewatering aids.

The light hydrocarbon oils may also be used as hydrophobic enhancing reagents as well. Both the light hydrocarbon oils and short chain alcohol may act as added surfactants that can lower the surface tension of water and increase contact angle. Since the surface tensions of the solvents used in these tests are in the range of 20 to 30 mN/m, this phenomenon can be possible. Thus, the use of a low HLB surfactant in conjunction with a proper solvent addresses two of the three parameters that are important for improving dewatering parameters, namely contact angle and surface tension.

In the present tests, it also seems that the dewatering aids cause particles to coagulate by virtue of increased hydrophobicity. The phenomenon, known as hydrophobic coagulation, should increase the capillary radius and help dewatering kinetics [9,58-69]. Evidence for the hydrophobic coagulation is because of the fact that cake thickness increases by approximately 10-20% in the presence of the dewatering aids. As a result, the novel reagents are capable of controlling all three parameters suggested by the Laplace equation, e.g., contact angle, surface tension and capillary radius, to achieve maximum moisture reduction. High HLB surfactants and polymeric flocculants usually address one, and adversely affect the others, as has been discussed in the early sections.

Even though hydrophobic coagulation causes the capillary radius increase, which is beneficial for dewatering processes, still another method of achieving the same effect can be shown. For this achievement, electrolytes (or salts) are added to coagulate nano and micro size particles by decreasing the surface charges of the fine particle surfaces. It is assumed that the electrolytes may significantly reduce the amount of surfactant requirements [69-72]. Various electrolytes, e.g., Al, Ca, Cr and Cu in conjunction with the novel reagents can be used for this purpose. In general, the higher the valence of the cations, the smaller the amount of the reagents

needed to obtain beneficial effects [23-29,72-76]. The reagents can be added before the dewatering aids shown in the present tests.

In these tests, a method of decreasing the final moisture content by applying vibration was conducted on the samples. It was possible that the vibration improved the transportation of the water that has become labile by increasing the hydrophobicity of the surfaces. The technique can be particularly useful for lowering the moisture of thick cakes (i.g., 0.6-2 inches) [54-58]. The reason can be that during the vibration, the fine particles are vibrated and this may cause the air molecules to pass through the cake by creating more open channels.

In the present study, a new technique is also tested on the cake by spraying the light hydrocarbon oils and short-chain alcohol to further decrease the total moisture in the cake. It is assumed that these reagents reduce the surface tension of the residual water left in the filter cake. This method can be efficient in lowering the surface tension of the water that is most difficult to remove. Spraying low HLB surfactant onto a filter cake is also effective in achieving low cake moistures using very little incremental reagent consumption [15,33,75].

Finally, the low HBL surfactants, metal ions, vibration and reagent spray tests are also effective together on the fine coal and mineral samples to achieve a very low moisture content of a product before thermal drying. The test results of the combined method showed that the moisture reduction was higher than any other processes used for dewatering aid. This product may need very low amount of thermal energy for the upstream processes.

## **2.2 EXPERIMENTAL**

### **2.2.1 Samples**

Several samples were used for dewatering tests of this investigation. These included various coal samples from different sources, sulfide mineral concentrates, clay, talc and silica flour. The first part of the study included the selection, acquisition and shipping of coal and mineral samples (both solid and slurry forms) from industrial sites to the testing facilities at Virginia Tech. For each sample, pertinent information was documented including geographic location, mine site name, sample description and gross sample weight. A limited number of standard analyses (e.g., particle size analysis, density partition analysis, flotation release analysis, etc.) were performed on selected samples to provide baseline data related to a particular sample.

Table 2.1 provides an overview of selected samples used in the dewatering programs. In



general, four different types of coal and several mineral samples were subjected for the dewatering tests. The first coal was feed streams to industrial dewatering equipment such as vacuum disc filters and screen-bowl centrifuges. For laboratory-scale batch dewatering tests, the samples were received in 5-gallon buckets. They were homogenized by agitating the slurry by means of a dynamic mixer to be able to receive a representative sample. While they were being agitated, a volume of the slurry was scooped out of the 5-gallon bucket in a dipper of known volume and used for the dewatering studies.

Table 2.1 Selected Coal Samples Evaluated in the Dewatering Test Program

<b>Company</b>	<b>Mine Name</b>	<b>Geographic Location</b>	<b>Coal Seam</b>	<b>Sample Description</b>	<b>Sample Weight</b>
Massey Coal Services	Goals Coal Co.Inc	Sundial W V	Rum Creek	DMC Product	2x5 gal pails
Massey Coal Services	Marfork Coal Co.Inc	Whitesville, W V	Eagleton	Svedaula Pressure Filter Feed (-325 #)	1x5gal pail
Massey Coal Services	Elk Run Coal Co.Inc	Whitesville, W V	Coalburg	Flotation Feed	1x5gal pail
Red River Coal	Red River Mine	Norton, VA	Dorchester	WOC Product (-60 #)	8 x 55gal drums
Pittston	Moss 3	Dante, VA	Upper Banner	DMC Product (-2 inch)	2 x 55 gal drums
Pittston	Middle Fork Reclamation	Dante, VA	Mixed Refuse	Column Product (-28 #)	2x5 gal pails
Pittston	Meadow River	VA	Swell, Pocahontas	Sized Coal	2x5 gal pails
Coastal	Toms Creek	VA	Jawbone, Kelly	Column Product (-100 #)	2x5 gal pails
Consol	Bailey	Graysville, PA	Pittsburgh	Filter Feed (-28 #)	4 x 55gal drums
Elkview Coal Ltd	Elkview Mine	Sparwood, BC	No. 10	WOC & Flotation Product (-28 #)	2 x 55 gal drums

It was found that the performance of the novel dewatering aids tested in the present work deteriorated with time. In general, the performance became seriously deteriorated in two weeks depending on the sample conditions after a sample was taken from an operating preparation plant. This was attributed to the superficial oxidation of the surface of the particles, which is based on the sulfide minerals (pyrite, markacite) contents in coal structure, process water quality, coal rank, etc. To overcome this problem, some of the samples were wet ground in a ball mill for a few minutes to regenerate a fresh unoxidized surface. In most cases, grinding for a short period restored the performance of the novel dewatering aids. When a coal sample was ball mill ground, the pulverized coal was subjected to a flotation using a Denver D-12 laboratory flotation

machine. This was done to ensure that the sample to be used for dewatering tests would have the same chemistry as the normal flotation products. The flotation was carried out using kerosene as collector and MIBC as frother. Thus, the coal samples pulverized for a short period and floated, which represent the second type of samples used in the present work.

The third type of coal samples were cyclone overflows from operating coal preparation plants that have been floated to remove the ash-forming minerals. Again, the flotation step was necessary to ensure that the samples used for dewatering tests were similar to those produced in industry. Finally, the fourth type of coal sample used in the present work was obtained as dense-medium cyclone (DMC) products. Because of their large particle size, these products could be stored for an extended period with a minimal oxidation. They were pulverized in a hammer mill as needed, and then subsequently wet ground in a ball mill to produce fine coal samples with fresh unoxidized surface. In most cases, the ball mill product was subjected to flotation using appropriate chemicals to ensure that the surface chemistry of the fine coal samples thus were the same as that produced by flotation in an operating plant.

In this investigation, the mineral samples were also subjected for dewatering tests using similar test procedures as explained above. These samples were received from the preparation plants located in different countries and used as it was or after treatment (flotation). It was seen that some of the mineral samples were superficial oxidized during the transportation, so these were re-ground and floated with standard flotation reagents before the tests.

## **2.2.2 Method and Procedures**

### *a) Equipment*

The filtration equipment used in this study consisted of laboratory-scale apparatus that are listed below:

- Buchner funnels with porous glass frit of different porosity and diameters
- 3-inch diameter pressure filter

*Buchaner funnels* were used for testing various dewatering chemicals in these experiments. The bulk of the tests were conducted using 2.5-inch diameter Buchner funnels with medium porosity (~40  $\mu\text{m}$ ) glass frit as a filter medium. The height of each funnel was 3-inches. They were purchased from Fisher Scientific. In a given experiment, a known volume of coal slurry was poured into a funnel and vacuum was applied to form a cake on the filter medium. The

volume and diameter of the Buchner filter determined the cake thickness. Therefore, the height of the funnel was extended up to 8 inches when it was desired to form a thick cake. Some of the tests were conducted using Buchner funnels with coarse fabric filters, which were provided by EIMCO. It was found that there were not much differences between the funnels with glass frit or fabric medium in terms of final cake moisture or dewatering rate, as the resistance from the medium were small as compared to the resistance from filter cake.

Figure 2.1 shows the apparatus used for the Buchner funnel filtration tests. Most of the tests were conducted using 2.5-inch diameter funnels with medium porosity glass frit. Buchner funnel tests have advantages over the standard filter leaf tests in that cake thickness is determined by the amount of a sample used in each experiment. A Buchner funnel was mounted on a vacuum flask, which in turn was connected to a larger vacuum flask to stabilize the vacuum pressure. A known volume of a slurry sample was poured into the funnel before opening the valve between the two flasks to subject the slurry to a vacuum pressure. In each experiment, the cake thickness, vacuum pressure, and cake formation time were recorded.

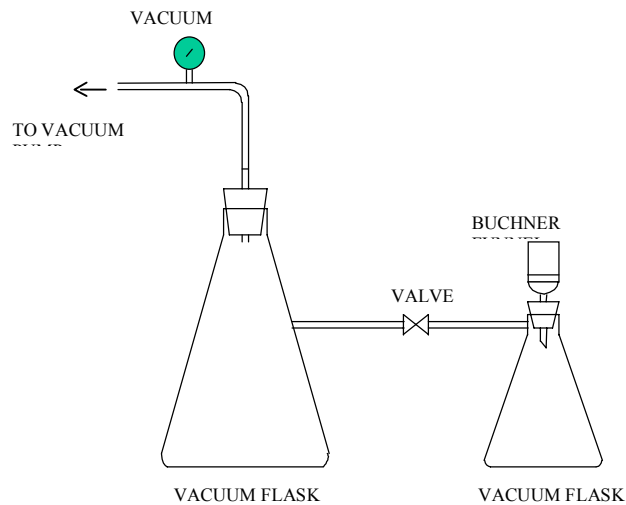


Figure 2.1 Experimental setup for laboratory vacuum filtration tests.

A Pressure Filter was designed and constructed at Virginia Tech for the present studies. It was made of a Plexiglas cylinder with dimensions of 2.5 inches in diameter and 8 inches in

height. As shown in Figure 2.2, the bottom of the pressure filter was made of perforated Plexiglas frit, on which a fabric filter medium was placed. The top of the filter was covered with a Plexiglas lid. Compressed air was injected to the top portion of the pressure filter so that the slurry introduced to the chamber was subjected to a desired pressure. The pressure was varied in the range of 100 to 400 kPa. The laboratory-scale batch units (i.e., Buchner filter and pressure filter) were setup in the Holden Hall laboratory.

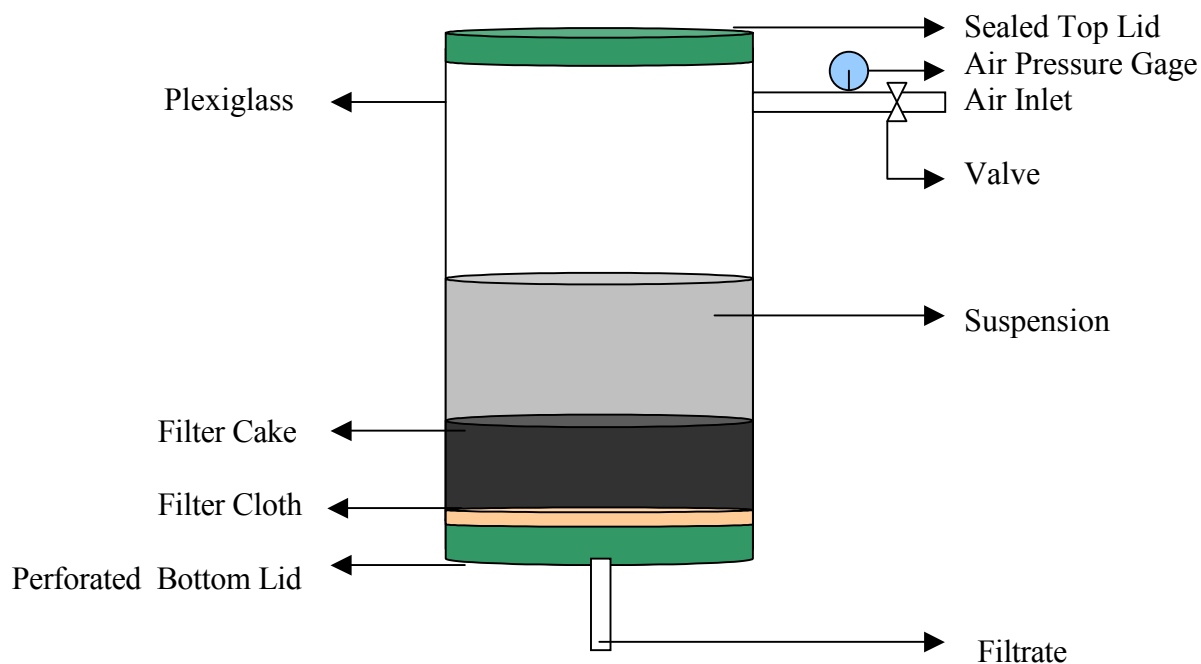


Figure 2.2 A schematic representation of the 2.5-inch diameter pressure filter.

In this study, various dewatering aids were tested on a variety of different coal and mineral samples. The objectives of the study were i) to identify the best possible reagents and combinations thereof for different samples, and ii) to identify the conditions under which a given dewatering aid can give the best performance. To meet these objectives, a series of laboratory dewatering tests were conducted using these Buchner funnels and pressure filters.

A volume of coal or mineral slurry was transferred to a 250-ml flask, to which a known amount of a dewatering aid (or a mixtures thereof) was added by means of a Microliter syringe. The flask was attached to a mechanical shaker for a given period of time to allow for the reagent to adsorb on the surface of the particles to be dewatered. After the conditioning time, the slurry was transferred to a Buchner funnel (or a pressure filter). Filtration was commenced when a vacuum was applied to the slurry. The time it took for bulk of the water to pass through the

filtering medium is referred to as *cake formation time*. After the cake formation, the vacuum pressure was kept on for a desired period of time to remove the residual water trapped in the capillaries formed between the particles in the cake. After this period, which is referred to as *drying cycle time*, part of a representative filter cake was removed, weighed, and dried for overnight in a convention oven. The sample was weighed again after the drying, and the moisture content was calculated from the difference between the dry and wet weights.

## 2.3. RESULTS AND DISCUSSIONS

### 2.3.1 Dewatering Tests on Coal Samples

#### 2.3.1.1 Low HLB Surfactants (Pure Reagents)

The first group of reagents used in the present work was nonionic surfactants with HLB numbers of less than 15. Most of these reagents are insoluble in water; therefore, they were used as solutions in appropriate solvents. Table 2.2 shows the results obtained with sorbitan monooleate (Span 80) whose HLB number is 12. For one part of the dewatering aid, two parts of solvents were used. Reagent dosages shown in the tables refer to the active ingredient only. The tests were conducted using a 2.5-inch diameter Buchner funnel at 25-inch Hg vacuum pressure with 2 minute drying cycle time and 0.45-inch cake thickness. The experiments were tested on a Pittsburgh coal sample. It was a DMS product, which was pulverized to -0.5 mm and then floated in a Denver laboratory flotation cell using 1 lb/ton kerosene and 75 g/ton of MIBC. Diesel oil and kerosene gave the best results, which may be the chain length of these oils. In general, mineral oils gave considerably better results than butanol for all the tests. As shown, approximately 50% moisture reductions were obtained at higher reagent dosages.

Table 2.2 Effects of Using Sorbitan Monooleate with Various Solvents for the Vacuum Filtration of a Pittsburgh Coal (0.5 mm x 0) Sample

Reagent Dosage (lbs/ton)	Cake Moisture (% wt)				
	Diesel	Kerosene	Fuel Oil	Gasoline	Butanol
0	25.7	25.7	25.7	25.7	25.7
1	15.1	15.0	16.6	16.3	17.2
3	13.8	13.7	14.8	14.5	15.8
5	12.5	13.4	14.2	14.2	15.3

According to the Laplace equation, achieving the low cake moistures during filtration is based on the surface tension lowering, capillary radius enlargement, and contact angle improvements. These chemicals probably control these parameters and give such a high moisture reductions. As known, the Span 80 used as dewatering aids is nonionic surfactant with a HLB numbers 12, and always offers high moisture reduction when it is dissolved in diesel and kerosene [3,11-16].

Table 2.3 shows the results obtained on a bituminous coal sample from Elkview Mine, British Columbia, Canada. The coal sample was a 0.21 mm x 0 flotation product, which was received as a slurry. It was oxidized during transportation; therefore, the sample was wet-ground in a ball mill for 1.5 minutes and re-floated using 1 lb/ton kerosene and 75 g/ton MIBC before filtration. A 2.5-inch diameter Buchner funnel was used at a vacuum pressure of 25 inch Hg and 2 min drying cycle time. The tests were conducted using ethyl oleate as a low HLB surfactant. It was used as a 33% solution in diesel oil. At a 5 lb/ton ethyl oleate, the moisture reductions were 71.3 and 57.4% at 0.25 and 0.5 inches of cake thicknesses, respectively.

In addition to that, the dewatering kinetics of the sample was also increased two - six times higher because of the surface hydrophobicity of the coal particles. For example, the base tests and 5 lb/ton reagent tests gave 47 seconds and 13 seconds cake formation times, respectively. It was determined that the reagent addition increased the contact angle; therefore, the higher the contact angle, the higher the surface hydrophobicity, and the larger the capillary tubes could occur in the cake. It will be seen in the next tests that when the chemical is added to the slurry, the cake formation time is always 2 to 6 times faster, which means that the capacity of the filtration machines can be increased in the order of magnetite [6-15-18].

Table 2.3 Effects of Using Ethyl Oleate for the Filtration of a 0.21 mm x 0 Elkview Coal Sample at 200 kPa of Air Pressure

Reagent Dosage (lbs/ton)	Moisture Content (%wt)	
	Cake Thickness (inch)	
	0.25	0.50
0	24.0	26.3
1	10.3	15.2
3	7.8	12.6
5	6.9	11.2

Phosphate esters constitute an important group of low HLB surfactants. Table 2.4 shows the results obtained with tridecyldihydrogen phosphate (TDDP) as a dewatering agent using the 2.5-inch diameter pressure filter at 200kPa air pressure. The coal sample was received as a 0.21 mm x 0 in size flotation product. By the time the sample was received, it had been superficially oxidized. Therefore, it was refloatated using 1 lb/ton kerosene and 75 g/ton MIBC. At a 5lb/ton TDDP and 0.25 inches cake thickness, the moisture was reduced from 25.8 to 5.8%, which represents a 77.5% reduction. The moisture was reduced to below 10% even at a thicker cake thickness of 0.5 inches.

The tests results indicted that the use of phosphate ester which is an acidic reagent decrease the cake moisture contents to sufficiently low levels for the thin and thick cakes. In these studies, it was pointed out that the reagent adsorption was also dependent on the acid-base interactions. Coal surface consists mainly of basic characteristics due to the oxygen formation in its structure. In this system, there may be an acid-base interaction between the surface and reagents, and it may form a surfactant coverage on the particle surface. This may be another reason for lowering the moisture contents [5,16,25,29].

Table 2.4 Effects of Using TDDP on the Filtration of an Elkview Coal at 200 kPa Air Pressure

Applied Pressure (kPa)	Reagent Dosage (lbs/ton)	Moisture Content (%wt)	
		Cake Thickness (inch)	
		0.25	0.50
200	0	25.8	27.1
	1	9.3	12.0
	3	7.4	10.4
	5	5.8	9.8

The effectiveness of TDDP as a dewatering aid is due to the fact that it enhances the hydrophobicity of coal particles to be dewatered. Table 2.5 shows the contact angles measured on a Pittsburgh coal sample, along with the results of the Buchner filter tests conducted on the same coal sample and the surface tensions of the filtrate. The filtration tests were conducted at

25-inch vacuum pressure, 2 minute drying cycle time, and 0.45-inch cake thickness. The sample was a dense-medium product, which was crushed and ground to obtain a 0.5 mm x 0 fraction. The fine coal sample was floated using 1 lb/ton kerosene and 100 g/ton MIBC.

Table 2.5 Effects of TDDP on the Surface Chemistry Parameters for the Filtration of a Pittsburgh Coal Sample

Reagent Type	Reagent Dosages (lb./ton)	Contact Angle (Degree)	Filtrate Surface Tension (mN/m)	Cake Formation Time (sec)	Moisture Content (%wt)
None	0	12	71	56	28.4
Kerosene	1	40	70	47	25.3
	1	74	67	23	16.2
TDDP	2	84	65	17	14.0
	3	90	61	14	12.8
	5	92	57	13	11.9

As shown, the reagent addition caused a substantial increase in contact angle measured using a ring method (Sigma70) and a decrease in surface tension, both of which are conducive to improved dewatering. At a 5 lb/ton reagent, the contact angle increased from 12 to 92°, and the moisture content was decreased from 28.4% to 11.9%. This is the result of the second hydrophobization effects on the dewatering of the fine coal particles. According to the Laplace equation, the capillary pressure should become negative at contact angle above 90°. This could be a clear evidence of the contact angle enhancement that during the tests the applied pressure was significantly dropped, and cake formation time was also decreased from 54 second to 13 seconds in the presence of the reagent [6,10,11,16].

It may be noteworthy that at 1 lb/ton kerosene the moisture was reduced from 28.4 to 25.3%, which is far less than the cases of using mixtures of TDDP and diesel oil. Even when the dosage of kerosene (or any other mineral or vegetable oil) was increased, the moisture reduction did not exceed more than 5%. When the kerosene dosage was increased to very large amounts, moisture content actually increased, because water is trapped within the flocs of coal created in the presence of large amounts of oil.

Yoon et al. found that the hydrophobic forces obtained from the AFM force measurement



were substantially increased in the presence of the surfactant addition to the glass shaper and silica plate since the contact angle was increased above 90° where the filtration spontaneously occurs. These tests were conducted to solve the mechanism of the flotation in which three phases exist in the solid/liquid/vapor interface [6,15,18,33,75]. It is known that the chemical dewatering also consists of three phase separations during the drying cycle time. Therefore, it can be concluded that this hydrophobic force may be used to solve the mechanisms of the chemical dewatering.

Table 2.6 shows the results of the pressure filter tests conducted on the Blackwater coal sample from Australia. The sample was a 0.6 mm x 0 flotation product. By the time the sample was received, it was oxidized; therefore, it was wet ground in a ball mill and floated using 1 lb/ton kerosene and 75 g/ton MIBC. The results in Table 2.6 show that moisture can be reduced to less than 10% with thin cake. Even at 0.85 inch thickness, nearly 50% moisture reductions could be achieved at 200 kPa air pressure. These tests indicate that the reagents work well on the hydrophobic surface with vacuum and air pressure since the air phase displaces the water molecules left in the cake [16].

Table 2.6 Effects of Using Sorbitan Monooleate for the Filtration of a Blackwater Coal (0.6 mm x 0) Sample at Different Air Pressures

Applied Pressure (kPa)	Reagent Addition (lb/ton)	Cake Moisture (%wt)		
		Cake Thickness (inch)		
		0.25	0.50	0.85
100	0	27.5	29.5	30.1
	1	17.3	21.6	22.5
	3	12.8	15.8	18.4
	5	9.4	14.6	16.7
200	0	24.5	26.2	27.8
	1	13.2	14.6	19.4
	3	8.4	11.9	16.4
	5	7.9	10.5	14.2

Effects of Vibration The primary role of low HLB surfactants is to help destabilize and ‘liberate’ the water molecules adhering to the surface of the coal particles to be dewatered by further increasing the particle hydrophobicity, but it plays no part in transporting the liberated water through a filter cake. The transportation problem becomes more serious with thicker cakes. In the present work, filter cake was subjected to vibration as a means of assisting the transportation of the liberated water. Placing an ultrasonic probe at the bottom part of the Buchner funnel created the vibration. Table 2.7 shows the effects of vibration when using sorbitan monooleate as a dewatering aid. The tests were conducted on a bituminous coal from Massey Energy-West Virginia at 2 minutes of drying cycle time. The coal sample was a spiral product wet-ground in a ball mill, and floated using 1 lb/ton kerosene and 125 g/ton MIBC. As shown, very low levels of cake moistures were obtained by combining the methods of using low HLB surfactants and mechanical vibration.

Table 2.7 Effects of Ultrasonic Vibration on the Vacuum Filtration of a Bituminous Coal (0.6 mm x 0) Using Sorbitan Monooleate on Massey Coal

Reagent Addition (lb/ton)	Cake Moisture (% wt.)			
	0.25 Inch Cake		0.5 Inch Cake	
	w/o Vibration	W/ Vibration	w/o Vibration	W/ Vibration
0	25.5	19.2	26.4	21.7
1	15.2	10.3	17.7	12.1
2	12.3	8.5	16.5	10.3
3	12.2	6.4	15.6	9.2
5	11.5	5.5	15.2	8.5

Keller et al showed that applying a vertical vibration through filter cake could decrease the moisture content of fine particles [54]. It was pointed out that during the vibration, the air molecules might open the blinded capillaries in the cake, and cause more water reduction from the cake. Also, several other papers conducted on fine calcite, silica and clay minerals illustrated that the vibration helped decrease overall moisture content in the range of 2 to 5% [54-57]. The mechanism of vibration was not completely understood; however, it is assumed that during the

vibration of the fine coal particles compressed air may break the water film between the fine particles and take the water out of the cake. Alternatively, vertical movements may increase the cake thickness, and make the cake more porous, which means that the formation of porosity may increase the moisture reductions.

Reducing Surface Tension As suggested by the Laplace equation (Eq. [1]), surface tension lowering is useful in decreasing capillary pressure and, hence, improving dewatering kinetics and reduction. Conventional wisdom is, therefore, to add surfactants to a feed slurry before it enters a filter. However, the bulk of the water present in the feed stream is easily removed at the beginning of a filtration process. It may be stated, therefore, that much of the surfactants added to the feed stream are wasted and do not contribute to reducing the final cake moisture. A more effective method of using a surfactant may, therefore, be to add some surfactant when it is needed most, i.e., during the drying cycle time. Some of the water trapped in finer capillaries could then be removed during drying cycle time. To demonstrate this, a series of experiments were conducted in which different surface tension lowering reagents were sprayed onto the filter cake at the end of cake formation time [15-23].

Table 2.8 shows the results obtained by spraying approximately 2-4 lb/ton of butanol, ethanol, and diesel oil at the beginning of 2 min drying cycle time. The surface tensions of *n*-butanol and ethanol are 20.6 and 22.8 mN/m, respectively, at 20°C. The surface tension of diesel oil is also low (~26 mN/m) like most other hydrocarbon liquids. Therefore, spraying these reagents should lower the surface tension of the water remained in filter cake and help reduce the more moisture. The tests were conducted with a Buchner funnel filter on the 0.6 mm x 0 bituminous coal sample from Middle Fork Pond Recovery Facility, Pittston Coal Company, Virginia. Two sets of tests were carried out using sorbitan monooleate and TDDP dissolved 33.3% in diesel as dewatering aids at a 0.45-inch cake thickness 25-inch Hg vacuum pressure. Approximately 2.5 lb/ton of butanol was sprayed on the cake when using the former, while the amount of ethanol and diesel oil were sprayed when using the latter. As shown, the spray technique further reduced the cake moisture substantially. Also, further increase in dosages of the spray did not significantly change the moisture reductions.

The results of these tests confirmed that there was a correlation between moisture content and surface tension of the cake. From the experimental results, the spraying plays very important role on the efficiency of the moisture reduction. It is seen that alcohol gives higher moisture

reduction than light oils, which may be due to the solubility and viscosity of the former spraying reagents. As known, butanol is more soluble and has lower viscosity than diesel, so it substantially decrease the water surface tension in the capillary radius of the cake as soon as the spraying was applied on the cake surface [15,18,29].

Table 2.8 Effects of Spraying Different Reagents Over Middlefork Filter Cake When Using Sorbitan Monooleate and TDDP as Dewatering Aids

Reagent Dosage (lbs/ton)	Moisture Content (% wt.)					
	Sorbitan Monooleate		Tridecyldihydrogenphosphate (TDDP)			
	No Spray	Butanol Spray	No Spray	Diesel Spray	Ethanol Spray	Butanol Spray
0	23.1	18.1	22.3	20.7	20.1	17.4
1	13.8	8.3	12.4	11.9	11.4	7.3
2	12.2	7.1	11.8	10.0	9.5	6.2
3	10.1	6.1	10.3	8.5	8.1	5.2
5	9.7	5.6	10.0	7.7	6.9	4.8

Increasing Cake Thickness It has been shown that applying vibration and spraying surface tension lowering reagents can facilitate the transportation of the capillary water. These techniques can be used to obtaining low cake moistures at high cake thicknesses. To demonstrate this, the height of the 2.5-inch diameter Buchner funnel was extended to 6 inches so that 300 ml of coal slurry (18% solids) could be used in each test. This allowed the cake thickness to be increased up to 1.2 inches. The coal sample used in these experiments was a DSM product from Massey Energy-WVA, which was crushed and wet-ground in a ball mill to -0.6 mm and floated using 1 lb/ton kerosene and 100 g/ton MIBC. The tests were conducted at varying amounts of TDDP, 25 inch Hg, and 5 min drying cycle time. As shown in Table 2.9, the combined use of i) a low HLB surfactant dissolved in diesel, ii) butanol spray, and iii) mechanical vibration achieved very low moistures at a cake thickness as large as 1.2 inches.

Table 2.9 Effects of Using TDDP Reagent, Butanol Spray, Vibration, and a Combination Thereof at 1.2-inch Cakes Thickness on a Massey Coal

Reagent Dosage (lbs/ton)	Moisture Content (%wt)			
	None	Spray	Vibration	Spray and Vibration
0	25.6	22.4	22.2	20.0
1	18.2	14.3	14.5	12.3
2	15.8	12.0	12.7	10.1
3	14.9	11.0	10.8	8.8
5	14.7	10.8	10.6	8.1

It was already stated that the reagents, vibration and spray were individually used to achieve low cake moisture from the fine particles. When the cake thickness is increased over 0.5 inch, the moisture reduction can not be as high as the thin cake (0.2-0.5 inch). In these tests, the moisture reduction was decided to increase up to 50% on the thick cake. For this reason, these three methods were simultaneously conducted on the sample to take advantage of the individuals. At the end of the dewatering stages, a 68% moisture reduction was obtained from the thick cake (1.2 in.), which is the cake thickness of the industrial application. This result indicates that further decreasing of the dewatered product causes lower energy to the thermal dryers [15,58,59,70]

Minimizing Reagent Consumption The Laplace equation (Eq. [1]) suggests that the capillary pressure can be reduced by i) decreasing surface tension ( $\gamma$ ), ii) increasing capillary radius ( $r$ ), and iii) increasing contact angle ( $\theta$ ). As discussed earlier, the major role of the nonionic surfactants tested in the present work is to increase contact angle  $\theta$  which is also based on the wettability and dewettability conditions. It has been found, however, that the use of the novel dewatering aids also causes a decrease in  $\gamma$ , as shown in Table 2.5, and an increase in  $r$ . Evidence for the latter is given by a decrease in vacuum pressure when a novel dewatering aid is added, which can be attributed to hydrophobic coagulation at higher contact angle. It was shown that hydrophobic particles coagulate with each other. Thus, an increase in particle hydrophobicity by the use of the novel dewatering aids should entail particle size enlargement and, hence, a decrease in capillary pressure [18,29,33,77].

Particle size can be enlarged by adding coagulants (or flocculent), thereby, further decrease the capillary pressure when zeta potential of the particles are zero. Therefore, a series of Buchner filter tests were conducted in the presence of various inorganic electrolytes. Similar experiments with polymeric flocculants were not conducted as these reagents are known to decrease hydrophobicity of the particles. Table 2.10 shows the results obtained with a bituminous coal sample (0.2 mm x 0) from Massey Energy using TDDT in the presence of  $Al^{3+}$ ,  $Cr^{3+}$ , and  $Cu^{2+}$  ions. In each experiment, the coal sample was conditioned with an electrolyte for 5 minutes and then conditioned with TDDP dissolved in diesel oil (1:2 ratio) for 2 minutes. The tests were conducted at a 25-inch Hg vacuum pressure with 2 minutes of drying cycle time, 0.4 inches cake thickness. The results show that the use of the electrolytes substantially decreases the amount of the novel dewatering aid required. For example, 3 lb/ton the reagent was required to achieve 16.0% cake moisture. In the presence of 20 g/ton  $Al^{3+}$  or  $Cr^{3+}$  ions, however, only 0.5 lb/ton TDDP was required to obtain 16.3% cake moistures. Divalent cations are not as efficient as the trivalent cations, which agrees well the Schultze-Hardy rule [29-33,77].

Table 2.10 Effects of Using Electrolytes for the Filtration of Massey Bituminous Coal Sample (0.2 mm x 0)

Reagent Dosage (lb./ton)	Moisture Content (% wt.)			
	None	$Al^{3+}$ (20 g/ton)	$Cr^{3+}$ (20 g/ton)	$Cu^{2+}$ (50 g/ton)
0	28.1	23.2	23.0	23.4
0.25	22.5	18.2	17.6	18.4
0.5	20.6	16.3	16.0	17.2
1	19.3	15.4	15.2	16.2
2	17.2	14.2	14.7	15.4
3	16.0	13.6	14.2	15.3
5	14.6	13.5	13.8	14.8
pH	7.5	5.5-7.5	5.5-7.5	4.5-6.5

It has long been known that a small amount of suitable electrolytes (e.g. salts) could coagulate the nano/micro size colloids, which had been already made stability in the aqueous media. The classical DLVO theory provides a quantitative explanation for this type of

coagulation. As known, coal surface is negatively charged in water due to the OH<sup>-</sup> tendency on the surface [5,29,77]. Therefore, Al<sup>3+</sup> ions or its hydroxyl species may go onto the fine coal particles and decrease the zeta potential of the particles ( $\xi = 0$  mV) at neutral pH. The test results indicate that when the potential of the surface becomes zero by adding metal ions, these fine particles can be coagulated in the suspension, so they settle on the filter media behaving as large particles. In the cake, these large particles can increase the capillary radius of the cake, and improve the dewatering performance of the fine particles. It was also observed that very low levels of surface contamination (polymer, clay content, water hardness, impurity ions and surface oxidation) suddenly changed dewatering capacity.

Table 2.11 Effects of Using Electrolyte, Regent Spray, and Vibration on the Filtration of a Moss 3 Coal (0.6 mm x 0) at 1-inch Cake Thickness Using Sorbitan Monooleate as a Dewatering Aid

Reagent Addition (lb./ton)	Moisture Content (% wt.)			
	HLB Reagent Only <sup>1</sup>	<sup>2</sup> Al <sup>3+</sup>	<sup>2</sup> Al <sup>3+</sup> and Spray <sup>3</sup>	<sup>2</sup> Al <sup>3+</sup> , Spray <sup>3</sup> and Vibration <sup>4</sup>
0	25.2	22.8	21.0	18.7
0.25	20.1	18.0	16.7	14.2
0.5	18.7	15.2	13.6	11.7
1	16.2	14.3	12.5	10.2
2	15.3	13.6	11.7	9.5
3	14.7	13.2	10.6	8.2
5	13.8	13.0	10.3	7.4

Table 2.11 shows the results obtained using different amounts of sorbitan monooleate, 20g/ton AlCl<sub>3</sub> (5x10<sup>-5</sup> M/L), 2-4lb/ton butanol spray, and vibration. The tests were conducted on a bituminous coal sample using the 2.5-inch diameter Buchner funnel with a 6-inch height at 25-inch Hg vacuum pressure, and 2 min drying cycle time. The cake thicknesses were approximately 1-inch, and the coal sample was a DMC product from West Virginia, pulverized in a hammer mill, wet-ground in a ball mill to -0.6 mm, and floated using 1 lb/ton kerosene and 100 g/ton MIBC. The results showed that very low levels of cake moisture could be achieved at an industrial cake thickness by using a combination of different methods. This includes i) the use

of a low HLB surfactant to destabilize (or liberate) the surface water, ii) the use of a coagulant to increase the capillary radius, iii) the addition of a short-chain alcohol to reduce the surface tension of the capillary water, and iv) the vibration of the filter cake to facilitate the transport of the destabilized surface water. For example 14.2% cake moisture can be achieved using only 0.25 lb/ton sorbitan monooleate, 20 g/ton aluminum chloride, 2 to 4 lb/ton butanol, and mechanical vibration.

It was demonstrated that diameter of the particle, surface tension of the capillary water and particle movements during the tests could decrease the moisture content to very low levels where thermal dryers could be replaced. The important indication was that when these methods were employed together on the fine particle cake, the moisture reduction was enhanced far from the one method. In this test, the parameters of the Lablace equation were changed to be able to achieve very low moisture content of product, which is a real challenge in this field. To date, there has not been any information on combining the dewatering parameters using a single unit. In addition, the combination of the methods gave high dewatering kinetics, which would be beneficial for industrial applications.

Further examples of the effect of pure reagents on the dewatering of coal samples are given in Appendix A.

#### *1.3.1.2 Natural Products*

Several organic chemicals have been used for many applications including food, detergent, machine, chemistry, metallurgy, paper and paint industries. The important parts of the organic substances consist of the lipids that are naturally occurring hydrophobic materials. Animal fats and vegetable oils are the most widely occurring lipids isolated by extraction with nonpolar organic solvents. The major chemical components are triacylglycerols, which are the triesters of glycerols with three long-chain carboxylic acids. As stated in the early sections, they can be found in various vegetable oils (e.g., soybean oil, peanut oil, olive oil, linseed oil, sesame oil), fish oil, butter, lard and tallow. The triacylglycerols may be viewed as low-HLB surfactants with one slightly polar group and three nonpolar hydrocarbon chains. In this section, the results obtained using lipids as dewatering aids are presented.

*Buchner Funnel Tests with Different Lipids* The lipids are insoluble in water; therefore, they are used as solutions in appropriate solvents, such as light hydrocarbon oils and short-chain



alcohols. Since some of these solvents are also insoluble in water, they may be referred to as ‘carriers’. Table 2.12 shows the results obtained using several different carriers. The tests were conducted on a coarse DMS product from the Bailey plant, Consol Energy - Pittsburgh. It was pulverized by means of a jaw crusher, a roll crusher, wet-ground in a ball mill to -0.5 mm, and then floated with 1 lb/ton kerosene and 0.2 lb/ton MIBC. The flotation product was conditioned for 2 minutes in Elenmeyer flasks with different amounts of soybean oil dissolved in diesel oil, kerosene, Fuel oil No. 4, gasoline, and butanol. The ratio between the soybean oil and the carriers were 1:2 by volume. The filtration tests were conducted using a 2.5-inch vacuum filter at 0.45-inch cake thickness, 2-minute drying cycle time, and 25-inch Hg vacuum pressure. It was observed that the light oils submitted better results than butanol.

The idea of using the neutral oils is that the pure reagents (e.g. Span 80, TDDP, EGMO, PMHO) are three to seven times more expensive than the lipids. The test results indicated that the natural product would slightly give low moisture reduction in the plant condition. The reasons are that the lipids possess a chemical structure that consists mainly of three tails on one head and also slightly basic characteristic. Therefore, the surfactant coverage on the surface may not be good as the pure reagents that have one tail on one head of the surfactant molecule. In addition, it was concluded that when the quality of the sample (lesser oxidation, water hardness, clay content and other contamination) was increased, the moisture reduction was also decreased.

Table 2.12 Effects of Using Soybean Oil as a Dewatering Aid in Various Solvents on the Vacuum Filtration of a Pittsburgh Coal Sample (0.5 mm x 0)

Reagent Dosage (lbs/ton)	Cake Moisture (% wt)				
	Diesel Oil	Kerosene	Fuel Oil No. 4	Gasoline	Butanol
0	25.1	25.1	25.1	25.1	25.1
1	16.8	17.0	17.5	17.6	19.8
3	14.3	14.4	15.4	16.1	18.6
5	13.7	13.5	14.7	14.8	17.1

A series of Buchner funnel filtration tests were conducted on a bituminous coal sample using soybean oil and diesel oil individually, and compared the results with those obtained using a 1:2 mixture of the two. The tests were conducted on a bituminous coal sample from Blackwater

Mine, Australia. It was a flotation product received in the form of slurry. The coal sample was superficially oxidized as received; therefore, it was wet-ground for 1.5 minutes and re-floated using 1 lb/ton kerosene 0.2 lb/ton MIBC. The filtration tests were conducted at a 25 inch Hg vacuum pressure, 0.45-inch cake thickness, and 2 min drying cycle time. The results are given in Table 2.13.

Table 2.13 Synergistic Effect of Using Soybean Oil and Diesel Oil for the Vacuum Filtration of a Blackwater Coal Sample (0.85 mm x 0)

Reagent Addition (lb/ton)	Moisture Content (% wt.)		
	Soybean Oil	Diesel Oil	Combination <sup>1</sup>
0	25.8	25.8	25.8
1	20.2	22.5	17.1
2	19.6	20.8	15.5
3	20.5	20.1	14.3
5	21.5	19.7	13.7
7	20.9	19.9	14.4

<sup>1</sup>1 part soybean oil mixed with 2 parts of diesel oil by volume; The reagent dosages for the combination refer to soybean oil alone.

At a 1 lb/ton, soybean oil reduced the cake moisture from 25.8 to 20.2%, while diesel oil reduced it to 22.5%. At higher dosages, no further improvement in moisture reduction was obtained. Using 1:2 mixtures of the two oils gave greater degrees of moisture reductions. In this case, the reagent dosages given in the fourth column of Table 2.13 refer to the dosages of soybean oil (active ingredient) alone rather than the sum of the two oils. One may, therefore, compare the performance of the mixture at a 1 lb/ton with that obtained with 3 lb/ton of soybean oil alone or diesel oil alone. Even then, the soybean oil-diesel oil mixtures outperformed either soybean oil or diesel oil individually. For example, the use of 1 lb/ton soybean oil and 2 lb/ton diesel oil mixture gave 17.1% moisture, while 3 lb/ton of soybean oil alone and diesel oil alone gave 20.5 and 20.1% cake moistures, respectively. Thus, there exists a synergistic effect of using the mixtures of two. The synergism increased with increasing reagent dosage. As shown in Table 2.13, continued increases in the dosages of soybean oil alone and diesel oil alone did not significantly decrease the cake moisture, while an increase in the dosages of the soybean oil-

diesel oil mixtures substantially improved the moisture reduction. At a 3 lb/ton soybean oil as an active ingredient, the cake moisture was reduced to as low as 14.3%. From a practical point of view, diesel oil is substantially cheaper than soybean oil; therefore, one may consider using the mineral oil as a low-cost facilitator, which can greatly enhance the performance of the lipid, i.e., soybean oil.

Table 2.14 Effects of Using Different Vegetable Oils for the Vacuum Filtration of Elkview Coal

Reagent Addition (lb/ton)	Moisture Content (% wt.)		
	Sesame Oil	Peanut Oil	Corn Oil
0	22.7	22.7	22.7
0.5	15.0	15.2	16.3
1	13.4	13.0	14.8
2	11.2	12.2	13.5
3	10.6	11.2	13.1

Table 2.14 shows a set of vacuum filtration tests conducted on a bituminous coal sample (0.6 mm x 0) from Elkview Mine, British Columbia, Canada. The sample was floated using 450 g/ton kerosene and 120 g/ton MIBC. The tests were conducted using a 2.5-inch diameter Buchner funnel at a 25 inch Hg of vacuum pressure with 2 min drying cycle time and 0.4 inch of cake thickness. Three different vegetable oils were used as dewatering aids, and the results are compared. These oils were used as 25% solutions in kerosene. Both sesame oil and peanut oil reduced the cake moisture by nearly 50% at a 2 lb/ton of reagent addition.

Table 2.15 shows the results of the vacuum filtration tests conducted on a Pittsburgh coal sample using a lipid of animal origin (fish oil) as a dewatering aid. It was used as a 1:2 mixture by volume with diesel oil. The coal sample was a dense-medium product, which was pulverized, ball-mill ground and screened at 0.5 mm. The screen underflow was floated using 1 lb/ton kerosene and 100 g/ton MIBC before filtration. The filtration tests were conducted using a 2.5-inch diameter Buchner funnel at a 25-inch Hg of vacuum pressure and 0.45 inch of cake thickness. At a 3 lb/ton of fish oil, moisture was reduced from 28.2 to 15.4%.

Table 2.15 Effects of Kerosene and Fish Oil on the Contact Angle of a Pittsburgh Coal Sample, Filtrate Surface Tension, and the Final Cake Moisture

Reagent Type	Reagent Dosages (lb./ton)	Contact Angle (Degree)	Filtrate Surface Tension ( $\mu\text{N/m}$ )	Cake Formation Time (sec)	Moisture Content (%wt)
None	0	12	71	61	28.2
Kerosene	1	44	69	50	24.9
	2	73	65	24	18.4
Fish Oil	1	86	62	15	16.2
	2	89	63	13	15.4
	3	91	56	12	15.5

Also shown in Table 2.15 are the equilibrium contact angles of the Pittsburgh coal sample treated under different reagent conditions. In the absence of the reagent, the coal sample gave a contact angle of  $12^\circ$  using Sigma70 measurement technique, which should give rise to a relatively high capillary pressures and, hence, a high cake moisture. At a 1 lb/ton kerosene, contact angle increased to  $44^\circ$ . According to the Laplace equation, the increase in contact angle from  $12^\circ$  to  $44^\circ$  should reduce the capillary pressure by 1.36 time, which may be responsible for the modest reduction in cake moisture from 28.2 to 24.9%. In the presence of fish oil, contact angle increased close to  $91^\circ$ . At a 2 lb/ton reagent addition, it increased to  $86^\circ$ , which should reduce the capillary pressure by 14 times as compared to the case of untreated coal. Such a large decrease in capillary pressure may be responsible for the substantial decrease in moisture (from 28.2 to 16.2%). Table 2.15 also shows the cake formation times and surface tensions of the filtrates. It is seen that the cake formation time is decreased approximately five times. The decrease in surface tension and cake formation time with increasing reagent addition may be another reason for obtaining the lower cake moisture. Thus, the use of a lipid as a dewatering aid not only increase the contact angle, but also decreases the surface tension of water, both of which contribute to the substantial reduction in moisture.

Pressure Filter Tests A flotation product from Peak Downs Mine, Australia, was received in the form of slurry. The sample was superficially oxidized during transportation. It was, therefore, wet-ground in a ball mill for 1.5 minutes and re-floated using 1 lb/ton of kerosene

and 0.2 lb/ton MIBC. The flotation product was conditioned with the fish oil to enhance its hydrophobicity. The lipid was used as a 33.3% solution in diesel oil. The conditioned coal sample was subjected to a series of filtration tests using the 2.5-inch diameter pressure at 200 kPa air pressure and 2 min drying cycle time. The results are given in Table 2.16. At a 0.25-inch cake thickness and 5 lb/ton fish oil, the moisture was reduced from 23.4 to 9.4%, which represents a 59.8% moisture reduction. At lower reagent dosages and higher cake thicknesses, the moisture reduction became less substantial.

Table 2.16 Effects of Using Fish Oil on the Filtration of a Coal Sample (0.6 mm x 0) from the Peak Downs Mine, Australia, at 200 kPa of Air Pressure

Reagent Addition (lb/ton)	Moisture Content (% wt.)		
	Cake Thickness (inch)		
	0.25	0.50	0.85
0	23.4	25.8	26.7
1	14.8	16.2	18.8
3	10.1	13.7	17.2
5	9.4	12.4	15.6

It is pointed out that these test results are identical to those obtained in the previous results using Buchaner vacuum filter. What is changed is the direction of the air flow from the top of the cake to the bottom side. Therefore, it can be concluded that vacuum or pressure can be used on the fine coal dewatering to obtain the similar moisture reductions. As known, the air phase is the key point for the chemical dewatering to displace the capillary water in the cake.

A flotation product (0.85 mm x 0) from Massey Energy –West Virginia was used for pressure filtration tests at 200 kPa air pressure and 2 min drying cycle time. The coal sample was wet-ground in a ball mill for 1.5 minutes to remove superficial oxidation products and re-floated using 1 lb/ton kerosene and 100 lb/ton MIBC. The results obtained using varying amounts of coconut oil as dewatering aid are given in Table 2.17. The coconut oil was used as a 1:2 mixture with diesel oil. The moisture reductions were 64.7, 58.5, and 51.2% at 0.2, 0.4 and 0.8 inches cake thicknesses, respectively.

Table 2.17 Effects of Using Coconut Oil for the Filtration of a Bituminous Coal at 200 kPa of air Pressure

Reagent Addition (lb/ton)	Moisture Content (% wt.)		
	Cake Thickness (inch)		
	0.2	0.4	0.8
0	21.8	23.4	24.8
1	12.4	14.2	16.2
2	10.1	11.9	14.5
3	9.0	10.4	12.8
5	7.7	9.7	12.1

Table 2.18 shows another set of pressure filtration tests conducted using lard oil, a low-cost lipid of animal origin. A clean spiral product was wet-ground in a ball mill. The fines fraction (0.85 mm x 0) was floated using 1 lb/ton kerosene and 0.2 lb/ton MIBC as a means of initial hydrophobization. The hydrophobicity of the flotation product was enhanced using a lipid of animal origin (lard) and then subjected to the filtration tests. Two sets of tests were conducted at a 100 and 200 kPa of air pressures. Varying amounts of the lipid were used as 25% solutions in diesel oil. The tests were conducted using a 2.5-inch diameter filter at 2 min drying cycle time. As shown in Table 2.18, lard oil works well as a dewatering aid. The moisture reduction improves with increasing reagent dosage and air pressure. Moisture reductions of 50 to 60% were obtained at lower cake thicknesses and at the higher air pressure. Even at the thicker cake, moisture reductions approaching 50% were obtained at higher reagent dosages.

Table 2.18 Effects of Using Lard Oil for the Filtration of a 0.85 mm x 0 Massy Coal Sample at 100 and 200 kPa of Air Pressures

Applied Pressure (kPa)	Reagent Addition (lb./ton)	Moisture Content (% wt.)		
		Cake Thickness (inch)		
		0.2	0.4	0.8
100	0	24.6	26.4	27.1
	1	14.0	16.3	19.1
	3	12.3	14.1	15.2
200	0	22.4	24.1	25.4
	1	10.8	12.6	14.3
	3	8.7	10.8	12.8

Another set of pressure filtration tests was conducted using a mixture of a lipid and a low-HLB surfactant. One part by volume of sunflower oil was blended with one part of sorbitan monooleate (Span 80) and four parts of diesel oil, and the blend was used as dewatering aid. A DMS product from Massey Energy was crushed, ground, and screened to -0.6 mm, and floated with 1 lb/ton kerosene and 100 g/ton MIBC. The flotation product was used for the filtration tests employing the 2.5-inch diameter pressure filter at 150 kPa air pressure at 2 min drying cycle time and 0.5 inches cake thickness. The results are given in Table 2.19, in which the results obtained with the reagent blend are compared with those obtained with its individual components. As shown, sunflower oil gave considerably inferior results to those obtained with sorbitan monooleate. However, the results obtained with the blend were comparable to those obtained with sorbitan monooleate. Thus, blending a lipid with a low HLB surfactant provides a means of reducing reagent costs, as the former is substantially cheaper than the latter.

Table 2.19 Effects of Using a Sunflower Oil-Sorbitan Monooleate Blend for the Filtration of a Bituminous Coal Sample at 150 kPa Air Pressure

Reagent Addition (lb/ton)	Moisture Content (% wt)		
	Sunflower Oil	Sorbitan Monooleate	Combination
0	25.7	25.7	25.7
1	16.2	13.4	13.0
2	14.2	10.3	10.4
3	12.0	9.5	9.3
5	11.7	9.0	8.7

Table 2.20 shows the results of the pressure filtration tests using soybean oil as dewatering aid. The tests were conducted on the Elkview flotation product. The sample was re-floated using 1 lb/ton kerosene and 75g/ton MIBC as a means of regenerating fresh hydrophobic surface. As seen, 50% moisture reductions could be achieved at a lower cake thickness, higher pressure, and/or a high reagent dosage.

Table 2.20 Results of the Pressure Filtration Tests Conducted on the Elkview Flotation Product Using Soybean Oil

Applied Pressure (kPa)	Reagent Dosage (lbs/ton)	Moisture Content (%wt)	
		Cake Thickness (inch)	
		0.25	0.50
100	0	28.4	30.8
	1	16.7	20.4
	3	13.8	18.3
	5	13.2	17.1
200	0	23.6	26.1
	1	14.3	16.7
	3	11.7	14.7
	5	10.3	13.5

Table 2.21 shows the results obtained using fish oil as dewatering aid. It was used as a 33.3% solution in diesel oil. Dewatering tests were conducted on the 0.6 mm x 0 flotation product from Peak Downs Mine-Australia using the 2.5-inch diameter pressure filter at 100 and 200kPa air pressures and 2 min drying time. The coal sample was superficially oxidized; therefore, it was wet-ground in a ball mill for 1.5 minutes and floated with 1 lb/ton kerosene and 0.2 lb/ton kerosene prior to the filtration tests. At a 0.25-inch cake thickness and 5 lb/ton fish oil, the moisture was reduced from 23.4 to 9.4% with a 59.8% moisture reduction. At lower reagent dosages and higher cake thicknesses, the moisture reduction became less substantial. This was most probably due to the trapped water among the particles, or efficiency of the air pressure through the capillary tubes in the larger cakes.

Table 2.21 Effects of Using Fish Oil on the Filtration of a Coal Sample (0.6 mm x 0) from the Peak Downs Mine, Australia, at 200 kPa of Air Pressure

Reagent Addition (lb/ton)	Moisture Content (% wt.)		
	Cake Thickness (inch)		
	0.25	0.50	0.85
0	23.4	25.8	26.7
1	14.8	16.2	18.8
3	10.1	13.7	17.2
5	9.4	12.4	15.6



To better understand the mechanism of the fine particle dewatering, the Laplace equation has usually been used for the chemical filtration of the cake. If one looks at this formula, it is seen that the surface tension, contact angle and diameter of the capillary tube are the major parameters. In the presence of the pure or natural reagents, these parameters were changed to improve the moisture reductions. The effects of the lipid additions on the pressure filter tests are also seen at higher contact angles (or higher hydrophobic forces). Therefore, it is concluded that the air pressure is as effective as the vacuum pressure due to the fact that it gave 40 to 60% moisture reductions on the dewatering of the fine coal particles.

Effects of Vibration Although the results obtained using lipids as dewatering aids, their effectiveness decreased with increasing cake thickness. This is due to the difficulty in transporting the water molecules liberated by the dewatering aids through filter cake. One solution to the problem would be to apply a mechanical vibration to the filter cake during drying cycle time.

Table 2.22 Effects of Vibration on the Filtration of a Virginia Coal Using Sunflower Oil as a Dewatering Aid

Reagent Addition (lb/ton)	Cake Moisture (% wt.)			
	Cake Thickness (inches)			
	0.2		0.4	
	w/o Vibration	w/ Vibration	w/o Vibration	w/ Vibration
0	19.6	16.1	22.6	19.2
1	12.5	10.7	14.3	10.7
2	10.2	7.3	12.6	9.2
3	9.6	6.0	12.0	8.3
5	8.2	4.8	11.7	7.7

Table 2.22 shows the results obtained with and without using vibration when sunflower oil was used as dewatering aid for the filtration of a coal sample (0.6 mm x 0) from Virginia. The reagent was used as a 33.3% solution in diesel oil. The coal sample was a dense-medium product, which was crushed, ground and floated using a 1 lb/ton kerosene and 0.2 lb/ton MIBC. The filtration experiments were conducted using a 2.5-inch diameter Buchner funnel at 25-inch Hg vacuum pressure. An ultrasonic probe was placed at the conical part of the Buchner funnel

during the 5 minute drying cycle time. When the vibration was applied without the dewatering aid, the cake moisture was reduced from 22.6 to 19.2%. When 2 lb/ton of the dewatering aid was used in conjunction with the vibration, the cake moisture was reduced to 9.2% at 0.4-inch cake thickness. At 5 lb/ton, the moisture was reduced to as low as 7.7%.

In the literature, there are several applications of the vibration on dewatering and screening of the fine particles [54-57]. It was reported that a vertical vibration through filter cake reduced the moisture content of the fine particle [54]. The reason of using the vibration can be the increase of the free water in the capillary tubes so that compressed/vacuum air can remove water from the cake. It was seen that applying a vertical vibration was also improved the moisture reduction using natural lipids.

*Effects of Butanol Spray* A series of dewatering tests were performed by spraying butanol directly onto a filter cake during drying cycle time. Approximately 3 lb/ton of the reagent was added immediately after cake formation. The surface tension of butanol is 20.6 mN/m at 20°C, which is much lower than that of water. Therefore, the role of butanol may be to reduce the surface tension of the water trapped in the finer capillaries. The coal sample used in this example was a Middle Fork-Virginia dense-medium product, which was crushed, ground, and floated using 1 lb/kerosene and 0.15 lb/ton MIBC. The flotation product was conditioned with varying amounts of a lipid (sunflower oil) prior to filtration. The filtration tests were conducted using a 2.5-inch diameter Buchner funnel at 25-inch Hg vacuum pressure, 2-min drying cycle time, and 0.45-inch cake thickness.

Table 2.23 Effects of Combining the Techniques of Using Sunflower Oil and Butanol Spray to Achieve Deep Moisture Reductions at 0.45-inch Cake Thickness

Reagent Dosage (lb/ton)	Moisture Content (%wt)	
	w/o Spray	w/ Spray
0	22.2	18.0
1	15.3	11.2
2	13.2	9.4
3	12.7	8.3
5	12.5	7.6

As shown in Table 2.23, the spray technique reduced the cake moisture by 3 to 5% beyond what can be achieved using the lipid as a hydrophobicity-enhancing reagent. Thus, the technique of using lipids and butanol spray provides a means of achieving deep moisture reductions. Any other surface tension lowering reagents may be sprayed in place of the butanol used in this example.

*Thick Cake* Table 2.24 shows the Buchner funnel filtration tests conducted on a DMS product from the Middle Fork-Virginia coal preparation plant. It was crushed, ground, and screened to obtain a 0.6 mm x 0 fraction, which was floated using 1 lb/ton kerosene and 0.2 lb/ton MIBC. The flotation product was filtered at 0.67-inch cake thickness and 5 min drying cycle time. As shown, the cake moisture obtained using both  $Al^{3+}$  ions and a lipid (sunflower oil) are much lower than the case of using the latter alone. Consequently, the amount of sunflower oil needed to achieve a given level of cake moisture was reduced substantially in the presence of  $Al^{3+}$  ions. For example, a 5 lb/ton of sunflower oil was needed to achieve 12.3% cake moisture in the absence of  $Al^{3+}$  ions. In the presence of  $Al^{3+}$  ions, however, only 0.5 lb/ton sunflower oil was needed to achieve 12.6% cake moisture. When a 2 lb/ton butanol was sprayed, dewatering became even more effective. The amount of sunflower oil needed to achieve 12.3% cake moisture was further reduced to 0.25 lb/ton, as shown in the third column of Table 2.24.

Dewatering became even more efficient when filter cake was vibrated during the 5 min drying cycle time. As shown in the last column of Table 2.24, the cake moisture was reduced to 10.3% at 0.25 lb/ton sunflower oil. At higher dosages of sunflower oil, single digit cake moistures were obtained. As a result, proper combinations of: i) using the dewatering aids, ii) conditioning the slurry with trivalent (or divalent) cations, iii) spraying appropriate surface tension lowering agent(s) during drying cycle time, and iv) applying mechanical vibration during drying cycle time, can help achieve deep levels of moisture reduction using small amounts of lipids as dewatering aids. From the results, it is concluded that a 5 lb/ton reagent, 20 g/ton Al ion ( $7 \times 10^{-5}$  M/L), 3 lb/ton butanol spray and mechanical vibration can decrease the moisture to the pendular levels where moisture content cannot be decreased more than this level by chemical-mechanical methods. In other words, thermal drying can be applied to remove the moisture at the pendular stage.

Table 2.24 Effects of Combining the Techniques of Using Sunflower Oil, Al<sup>3+</sup> Ions, Butanol Spray, and Vibration to Achieve Deep Moisture Reductions at a 0.67-inch Cake Thickness

Reagent Addition (lb./ton)	Cake Moisture (% wt.)			
	None	Al <sup>3+</sup> Ion	Al <sup>3+</sup> ions and Butanol Spray	Al <sup>3+</sup> ions, Butanol Spray and Vibration
0	23.8	20.4	18.8	17.0
0.25	17.1	14.3	12.3	10.4
0.5	16.3	12.6	10.7	8.7
1	14.4	11.7	9.5	7.5
2	13.7	11.2	9.1	7.1
3	13.1	10.9	8.8	6.8
5	12.3	10.8	8.5	6.2

van Oss [27] and Ducker [79] found that electrolyte addition (e.g., NaCl) was decreased the repulsive forces between the particles and increased the surface hydrophobicity of the particles. After the certain salt addition to the suspension, critical coagulation concentration occurs between the particles and the system will not be longer stabilized. In addition to the coagulation and particle enlargement effects with metal ions, Al ions may also increase the surface hydrophobicity of the coal used in this study by decreasing the repulsive forces and improve the moisture reduction [5,6,10,11,27,79].

Further examples of the effect of lipid reagents on the dewatering of coal samples are given in Appendix B.

### 2.3.1.3 Modified Natural Products

As shown in Sections-a and -b, the performance of the naturally occurring lipids is slightly inferior to that of the low HLB surfactants. A likely reason may be that tryacylglycerols that constitute lipids may be too large for the proper surface coverage on coal particles. As discussed earlier, lipid molecules may be considered as low-HLB surfactants with three hydrocarbon tails. Therefore, dewatering tests were conducted after breaking the lipids molecules into smaller ones so that they can form a well coated hydrophobes and, hence, render the surface more hydrophobic. One method of breaking the molecules is transesterification, in

which a lipid reacts with an alcohol in the presence of a catalyst such as  $H^+$  or  $OH^-$  ions. To expedite the reaction rate, the reaction may be carried out at a slightly elevated temperature, e.g., in the range of 40 to 80°C. The reaction product, containing fatty esters and glycerols, may be used without purification to minimize reagent costs.

Table 2.25 Results of the Filtration Tests Conducted on a Meadow River Coal Sample (0.5 mm x 0) Using Sunflower Oil with and without Modification

Reagent Dosage (lbs/ton) <sup>1</sup>	Moisture Content (%wt)	
	Un-modified	Modified
0	22.6	22.6
1	16.3	13.5
2	14.4	11.0
3	13.8	10.6
5	13.3	9.9

<sup>1</sup>not including diesel oil.

Sunflower oil was transesterified by mixing with ethanol at an approximate molar ratio of 1:3, and agitated on a hot plate for one hour after adding acetic acid (2% by volume) to the mixture. The reaction product was used as a dewatering aid without purification. The modified sunflower oil was used as a dewatering aid without purification in a series of vacuum filtration tests. In each experiment, one part of the modified sunflower oil was dissolved in three parts of diesel oil before use. All test were conducted using a 2.5-inch diameter Buchner funnel at 2 min drying cycle time, 0.4-inch cake thickness, and 25-inch Hg vacuum pressure. The filtration tests were conducted on a Meadow River coal sample from Virginia. It was freshly pulverized and floated using 1 lb/ton kerosene and 0.2 lb/ton MIBC prior to the filtration tests. The pulp density of the flotation product was 16.9%. The results given in Table 2.25 show that the modified sunflower oil gave considerably better results than the case of using the naturally occurring lipid without modification. The reagent dosages given in the table represent only the amount of the active ingredient (modified sunflower oil) used in each experiment and do not include the amount of the solvent (diesel oil) used. The results given in Table 2.25 show that the modified sunflower oil gave considerably better results than the case of using the naturally occurring lipid

without modification.

Further testing was carried out on using safflower oil with and without transesterification. A volume of safflower oil was mixed with a volume of ethanol at molar ratio of approximately 1:3 and, then, agitated on a hot plate in the presence of 1 to 5% by volume of acetic acid. The acyl groups of the triacylglycerols present in safflower oils contain 70-80% oleic and linoleic acids and 6-7% palmitic acid. The modified safflower oil was used as a dewatering aid without purification. The filtration tests were conducted using a 2.5-inch diameter Buchner filter at 2 min drying cycle time and 0.4 to 0.5 inch cake thicknesses. The tests were conducted on a coal sample from the Middle Fork coal preparation plant, Virginia. It was pulverized, wet-ground in a ball mill, and floated using 1 lb/ton kerosene and 0.2 lb/ton MIBC. In each experiment, one part of the modified safflower oil was dissolved in two parts of diesel oil. The results given in Table 2.26 show that lower moisture filter cakes can be obtained when the safflower oil was broken into smaller molecules before using it as a dewatering aid.

Table 26      Results of the Vacuum Filtration Tests Conducted on a 0.5 mm x 0 Middle Fork Coal Sample Using a Modified Safflower Oil

Reagent Dosage (lbs/ton)	Moisture Content (%wt)	
	Unmodified	Modified
0	19.3	19.3
1	13.3	10.7
2	12.2	11.3
3	12.7	10.6
5	11.3	10.3

A lard oil was modified and used as a dewatering aid. A volume of lard oil was mixed with ethanol at an approximate molar ratio of 1:3, and agitated on a hot plate for one hour after adding acetic acid (~2% by volume) to the mixture. The product, containing methyloleate, methylpalmitate, methylstearate, and glycerol, was used as a dewatering aid without purification in a series of vacuum filtration tests. The tests were conducted on the Meadow River-Virginia coal sample, which had been pulverized and ground in the same manner as above. As it can be seen from Table 2.27, the results show that the use of the modified lard oil reduced the cake

moistures substantially below the values obtained using the lard oil without modification.

Table 2.27 Results of the Filtration Tests Conducted on a 0.5 mm x 0 Meadow River Coal Sample Using a Modified Lard Oil

Reagent Dosage (lbs/ton)	Moisture Content (%wt)	
	Unmodified	Modified
0	21.5	21.7
1	16.9	14.4
2	16.6	12.4
3	16.2	10.7
5	15.7	9.9

The use of modified and unmodified reagents gave a clear moisture differences on the cake. These test results proved that the hypothesis of the modification (breaking the tails of the surfactant to make a well surface coverage on the particles) could be true on the dewatering of fine particles. Also, acid base property of the modified reagent could be changed by adding acetic acid, and this could give better dewatering results. However, more detail studies should be conducted on the modification of the lipids and the other surfactants used in the present study using surface measurement techniques, e.g. vibrational spectroscopy (infrared, Raman, electron energy loss) [29,51,53]. This will give the level of a surface formation (or oily droplet spreading) on the surface for the further decisions.

#### *2.3.1.4 Comparison with Conventional Dewatering Aids*

The dewatering aids were conducted in this tests included i) low-HLB surfactants, ii) naturally occurring lipids, and iii) modified lipids. It would be of interest to compare the results obtained using some of these reagents with those obtained using conventional dewatering aids. Therefore, a series of Buchner funnel filter tests were conducted on a fine coal sample prepared from a coarse DMC product. It was a bituminous coal from Red River Coal Company, Virginia. The sample was crushed, wet-ground in a ball mill, and floated using only 100 g/ton MIBC. Part of the tests was conducted on the froth product immediately after the flotation, and part of the tests were conducted after aging the coal sample for one week.

Table 2.28 compares the results obtained using Span 80, a low-HLB surfactant, with those obtained using diesel oil. The low-HLB surfactant was used as a 33.3% solution in diesel

oil. The reagent dosages given in the table for Span 80 represent only those of the active ingredient. As shown, diesel oil works reasonably well by itself when the coal sample was fresh. The cake moisture was reduced from 22.4% with no reagent to 17.0% at a 3 lb/ton reagent addition. At a 5 lb/ton, it increased slightly to 17.9%. The increase in moisture with increasing diesel oil dosage can be more clearly seen with the aged coal sample. It is assumed that coal particles are coagulated in the presence of the oil, and the resulting coagula may entrap water within its fine structure. On the contrary, Span 80 was able to reduce the cake moisture substantially even with the aged coal sample. However, its performance deteriorated considerably, which might be due to the trapped water in the flocculated the particles for Span 80, as well.

Table 2.28 Effects of Aging a Red River Coal Sample (0.6 mm x 0) for Using Span 80 and Diesel

Reagent Addition (lb/ton)	Diesel		Span 80	
	Fresh	Aged	Fresh	Aged
0	22.7	24.4	22.7	24.4
1	20.2	24.6	14.6	22.0
2	18.9	25.3	12.2	16.7
3	17.0	26.2	10.8	14.2
5	17.9	26.8	13.8	19.2

When the low-HLB surfactant (Span 80) was used in conjunction with diesel oil, the moisture was reduced to 10.8% at a 3 lb/ton and then to 10.3% at 5 lb/ton. Thus, the effectiveness of using a low-HLB surfactant as dewatering aid is not due to the diesel oil that was used as solvent or carrier. As has already been noted, the novel dewatering aids could be used with any other solvent, including short-chain alcohols that do not have as much hydrophobizing effect as diesel oil. In fact, some of the low-HLB surfactants can be used without any solvent, provided that a longer conditioning time is employed.

Table 2.29 shows the results obtained using Superfloc 16 diluted 0.5% in water. The moisture was reduced to 18% at 40 g/ton reagent addition, and then increased at higher dosages. The increase in moisture at high dosages can be attributed to the entrapment of water within flocs, as is the case with diesel oil. With the aged coal sample, the performance of the flocculant



deteriorated significantly.

Table 2.29 Effects of Aging a Red River Coal Sample (0.6 mm x 0) for Using Superfloc 16

Reagent Addition (g/ton)	Superfloc 16	
	Fresh	Aged
0	22.7	24.4
10	19.8	23.2
20	19.2	22.8
40	18.0	22.6
80	19.2	22.9
160	20.8	23.2
320	21.8	24.5

Table 2.30 Comparison the Buchner Filter Tests Conducted on the Middle Fork Coal Sample (0.6 mm x 0) Using High- and Low-HLB Surfactants as Filter Aids

Reagent Dosage (lbs/ton)	Moisture Content (%wt)				
	Reagent Types				
	Diamine	Dodecylamine Hydrochloride	Sun Flower Oil	Span 80	TDDP
0	22.6	22.6	22.6	22.6	22.6
0.5	20.6	19.1	17.1	16.5	16.9
1	20.5	18.6	16.2	15.0	15.3
2	19.7	17.9	14.3	12.6	12.2
3	19.8	17.4	13.2	11.4	11.1
5	20.9	17.1	12.6	10.9	10.2

\* 2.5 inch diameter vacuum filter; 2 min drying cycle time; sample size -600  $\mu\text{m}$ ; sample crushed, ground and floated using 1 lb/ton kerosene and 100 g/ton MIBC and cake thick 0.45 in.

Table 2.30 shows the Buchner filter tests conducted using diamine and dodecylamine hydrochloride as dewatering aids. The moisture reductions achieved using these high-HLB surfactants were reasonable, which may be attributed to the fact that these cationic surfactants are known to adsorb on coal and increase its contact angle (or surface hydrophobicity) considerably. The results obtained using anionic surfactants (not shown here) were not as good

as observed with the cationic surfactants. Also given in the table are the results obtained using three low-HLB reagents, including soybean oil, Span 80, and TDDP. All of these reagents performed substantially better than the high-HLB surfactants.

Further examples of the effect of modified lipid reagents on the dewatering of coal samples are given in Appendix C.

### **2.3.2 Dewatering Tests on Mineral Samples**

As explained in the early section, the surfactant molecules could adsorb on the surface to make the particle more hydrophobic for the high moisture reduction. It was determined that the dewatering aids worked well with hydrophobic coal samples and gave 40 to 70% moisture reduction. In order to confirm reagent effects on the hydrophilic particles, the similar batch dewatering tests were conducted on clean mineral samples (sphalerite, chalcopyrite, galena, talc silica and clay minerals).

As known, fresh surface always gave significantly better dewatering results. Some of the mineral samples were used as received, while most of them were treated if they were superficial oxidized or not hydrophobic enough. For this purpose, the samples were wet-ground in a ball mill for a short period of time (1 to 2 min) to remove the oxide layer of the surface and regenerate fresh surface. The ground particles were then floated using appropriate collectors and frothers. It is assumed that the low HLB surfactants adsorb on hydrophobic surface, but not on the hydrophilic surface. In order to eliminate the problems associated with the oxidation, all tests were also conducted in the same week after flotation tests to obtain consistent dewatering results.

The flotation product was placed in a container and agitated continually. A known volume of the sample and dewatering aids were added to the flask before shaking it for 2 to 3 minutes. The conditioned slurry was then poured into a filter to initiate a filtration test. After a present drying cycle time, the filtered product was transferred from the filter, weighted, dried in an oven for overnight and then re-weighted to determine the cake moisture. During each tests, cake formation time, which is the time to remove bulk of the water from suspension, was recorded. For vacuum filtration tests, a 2.5-inch diameter Buchaner funnel with medium porosity glass frit was used. For pressure filtration, a 2.5-inch diameter air pressure filter with a fabric cloth medium was used to conduct tests under different pressures. It was made of a Plexiglas so

that the events taking place during filtration could be visually seen. In the following sections, dewatering test results conducted on the mineral samples are given.

*Sphalerite*: A series of filtration tests were conducted on a zinc (sphalerite) concentrate (0.105 mm x 0) obtained by flotation method. The zinc sulfide was activated by adding CuSO<sub>4</sub> and then floated using KAX and MIBC in the plant. The sample received from a zinc mine in Sweden was found that it was superficially oxidized during the transportation. Therefore, the sample was slightly ground and re-floated using 50 g/ton of sodium isopropyl xanthate and 50 g/ton of MIBC at pH 9.2 (lime) as a means of regenerating fresh and hydrophobic surface. The filtration tests were conducted using a 2.5-inch diameter pressure filter at 100 kPa air pressure and 2 min drying cycle time. For the test, one part of fish oil was mixed with 2 parts of diesel oil before use. The tests were carried out by varying reagent (fish oil) dosages and cake thickness, and the results are given in Table 2.31. At a 3 lb/ton fish oil, the moisture reductions were 46, 43 and 41% at 0.2, 0.3 and 0.6 inches of cake thicknesses, respectively. Higher reagent additions did not significantly increase the moisture reductions.

Table 2.31 Effects of Using Fish Oil as a Dewatering Aid for the Filtration of a Zinc Concentrate from Boliden at 100 kPa of Air Pressure

Reagent Dosage (lbs/ton)	Moisture Content (% wt.)		
	Cake Thickness (inch)		
	0.2	0.3	0.6
0	13.7	14.6	17.3
1	8.7	9.5	11.8
3	7.4	8.3	10.2
5	7.6	8.2	9.8

Sorbitan monooleate (Span 80) was also used for dewatering of the same zinc (sphalerite) concentrate. The flotation product was subjected to pressure filtration tests using a 2.5-inch diameter filter at 100 kPa of air pressure and 2 minutes of drying cycle time. Cake thickness was also varied by changing the volume of the slurry used in the filtration tests. The results are given in Table 2.32. The %moisture reductions were 64.1, 54.8, and 52.8% at 0.2, 0.3 and 0.6 inches of cake thicknesses, respectively, at a 3 lb/ton sorbitan monooleate.

Table 2.32 Effects of Using Sorbitan Monooleate Mixed with Diesel Oil for the Filtration of a Zinc Concentrate (0.105 mm x 0) at 100 kPa of Air Pressure and at Varying Reagent Addition and Cake Thickness

Reagent Dosage (lbs/ton)	Cake Moisture (% wt.)		
	Cake Thickness (inch)		
	0.2	0.3	0.6
0	14.2	15.5	18.0
1	6.5	8.4	9.1
3	5.1	7.0	8.5
5	4.7	6.6	8.1

According to the Laplace equation, it has been well known that increasing contact angle and capillary radius and decreasing surface tension could reduce the capillary pressure in the cake. The newly developed nonionic surfactants tested in the present work increase contact angle and capillary radius and decrease surface tension of the capillary water in the cake of the mineral sample. These tests indicate that when the reagent dosages are increased in the slurry, it can cause a surfactant coating on the mineral surface. Thus, the nonionic surfactants will increase the hydrophobic forces on the surface, which means that dewetability of the particles is also increased. This can be the reason why reduction in moisture is high at higher contact angle, but lower at lower contact angle (wettability is still favorable) [18,29,33,77]. The obtained results on the zinc sample are comparable with the coal sample results.

Chalcopyrite: Soybean oil was used as dewatering aid for copper (chalcopyrite) concentrate sample (0.150 mm x 0). One part of soybean oil was mixed with 2 parts of diesel oil before use. The sample was a flotation product, which was superficially oxidized during transportation. To obtain a significant fresh surface, the sample was wet-ground in a ball mill and re-floated using 50 g/ton sodium isopropyl xanthate and 50 g/ton MIBC at pH 10.5 (adjusted using lime). The flotation product was subjected to vacuum filtration tests at 25-in.Hg and 2 minutes of drying cycle time. The %moisture reductions given in Table 2.33 were 55, 43, and 43.4% at 0.15, 0.3 and 0.6 inches of cake thickness, respectively. Reagent additions above 3 lb/ton did not significantly decrease the moisture reduction, which may be the existence of the pendular

moisture levels in the cake. These results are similar to those obtained in the plant, where the concentrate was produced, using a high-pressure filter followed by a thermal dryer.

Table 2.33 Effects of Using Soybean Oil as a Dewatering Aid for the Vacuum Filtration of a Copper Concentrate

Reagent Dosage (lbs/ton)	Moisture Content (%wt)		
	Cake Thickness (inch)		
	0.15	0.30	0.60
0	9.8	10.7	12.2
1	5.7	6.7	8.3
2	4.9	6.4	7.2
3	4.4	6.1	6.9
5	4.1	5.8	6.7

Galena: Ethyl oleate was tested as dewatering aid for a lead concentrate (0.074 mm x 0) from a flotation plant in Boliden-Sweden. One part of the surfactant was dissolved in 2 parts of diesel oil by volume before use. The sample, which was received as thickened slurry, was oxidized during the shipment. To generate fresh and hydrophobic surface, the sample was wet-ground for 1.5 minutes and re-floated using 50 g/ton of isopropyl xanthate and 50 g/ton MIBC at pH 9.5 (lime) before filtration tests. A 2.5-inch diameter Buchner funnel was used for filtration at a vacuum pressure of 25-inch Hg and a drying cycle time of 2 minutes.

Table 2.34 Effects of Using Ethyl Oleate Mixed with Diesel Oil as a Dewatering Aid for the Vacuum Filtration of a Lead Concentrate (0.074 mm x 0) Sample at Varying Reagent Dosage and Cake Thickness

Reagent Dosage (lbs/ton)	Moisture Content (% wt.)		
	Cake Thickness (inch)		
	0.2	0.3	0.6
0	9.9	11.5	13.1
1	5.3	5.5	7.8
3	4.3	5.2	6.0
5	4.0	5.1	5.8

The tests conducted at various reagent additions and cake thickness are given in Table 2.34. At a 3 lb/ton ethyl oleate, the cake moisture was reduced to 6% at 0.6 inches of cake thickness. After the 3 lb/ton reagent addition to the slurry, moisture content of the cake stays constant. At such low moisture levels, there is no need to dry the dewatered concentrate by thermal drying before the metallurgical processes.

*Talc:* The dewatering aids given in the present studies worked perfectly with hydrophobic particles. Talc is a naturally hydrophobic mineral that is used for a variety of applications including paper coating (removal of sticky materials from wood pulp), ceramic, polymer composites, paint, etc. The sample used for dewatering tests was received from Luezanac America, and floated using 100 g/ton PPG as a frother at neutral pH just before filtration. The tests were applied using a 2.5-inch diameter pressure filter at 200 kPa air pressure and 2 min drying cycle time. Table 2.35 shows the results obtained from a series of filtration tests conducted using sunflower oil as dewatering aid. The reagent was used as a 1:2 mixture with diesel oil. It is seen that better than 50% moisture reductions were achieved at 0.2 and 0.4 inches cake thicknesses. At a 0.8 inch cake thickness, the moisture was reduced from 28.4% to 16.3% using a 5 lb/ton sunflower oil, which may be the improvement of the particle dewettability due to the second hydrophobization.

Table 2.35 Effects of Using Sun Flower Oil for the Filtration of a Talc (0.15 mm x 0) Sample at 200 kPa of Air Pressure with Varying Reagent Addition and Cake Thickness

Reagent Dosage (lbs/ton)	Moisture Content (%wt)		
	Cake Thickness (inch)		
	0.2	0.4	0.8
0	25.2	26.9	28.4
1	14.2	17.3	18.9
3	12.6	14.7	17.5
5	11.8	13.4	16.3

*Silica:* A set of dewatering tests were conducted on a fine quartz powder obtained from Fisher Chemical Scientific. The tests give evidence that the low HLB surfactants work well

when the particles are reasonably hydrophobic. The use of the surfactant in a manner described in the earlier sections further enhances the hydrophobicity of the particles, which is crucial for spontaneous removal of surface water. The hydrophobicity of the particles produced from flotation is usually not high enough for the spontaneous removal of water. In order to demonstrate these points clearly, a series of dewatering tests were conducted on a 0.038 mm x 0 size silica sample. A 2.5 inch diameter Buchner funnel was used for two sets of vacuum filtration tests at a 25 in.Hg, 2 min drying cycle time, and 0.45 inches cake thickness. The test results are given in Table 2.36.

Table 2.36 Flotation effects on silica dewatering conducted on a silica flour (0.038 mm x 0) using Span 80 dissolved 33.3% in diesel at 25 in.Hg vacuum pressure

Reagent Dosage (lb/ton)	w/o Amine Flotation		w/ Amine Flotation	
	Moisture Content (%wt)	Cake Form. Time (sec)	Moisture Content (%wt)	Cake Form. Time (sec)
0	26.1	158	18.9	27
0.5	22.6	152	11.2	21
1	20.9	167	9.4	20
2	20.7	175	8.4	18
3	20.9	179	8.6	18
5	21.8	181	8.7	20

\* 2.5-inch diameter vacuum filter; 2 min. drying cycle time; Fisher sample floated

The first set of tests were conducted using various amount of sorbitan monooleat (Span 80) dissolved in diesel oil. In the absence of dewatering aid, the cake moisture was 26.1% and the cake formation time was 158 seconds. At a 2 lb/ton Span 80, the moisture was reduced to 20.9% and cake formation time increased to 179 seconds. The moisture reduction was not as good as those obtained in other examples with hydrophobic particles. Probably, the relative small moisture reduction is due to the surface tension lowering of the liquid. The next series of tests were conducted on the silica sample floated using 200 g/ton of dodecylammonium hydrochloride as a collector at pH 9.5 (lime addition). The first hydrophobization by the collector coating

reduced the cake moisture from 26.1% to 18.9% and cake formation time from 158 seconds to 27 seconds. When the low HLB surfactants was added to the flotation product as a second hydrophobization reagent, the moisture was further reduced to 8.4% at a 2 lb/ton Span 80. The cake formation time was lowered to 18 seconds. The improved dewatering brought about by the low HLB surfactants is most likely due to the hydrophobic enhancement.

*Clay:* Kaolin clay is the most difficult mineral to dewater. In the kaolin industry, fine clay is dewatered using drum and high pressure filters, and obtained cake moistures are in the range of 40 to 60%. In addition, part of the filter cake is spray dried in a natural gas flame to obtain a 65 to 75% solid content product before use. The spray drying is costly, but it is the only method to produce high solid content material [1,59,70]. In this example, a series of filtration tests were conducted on a Brazilian clay sample (80% finer than 2  $\mu\text{m}$ ). The clay sample was floated using a 700 g/ton dodecylammonium hydrochloride and 120 g/ton MIBC at pH 9.3 (lime addition) to make the surface hydrophobic called first hydrophobization step. The flotation product was then subjected to vacuum filtration tests using 2.5 inch diameter Buchner funnel at 25 in.Hg, 0.16 inches cake thickness and 3 min drying cycle time. As shown in Table 2.37, the cake moisture was 50.4% and the cake formation time 39.4 minutes when no dewatering aid was used. At a 7 lb/ton Span 80, the moisture content and cake formation time was reduced to 28.6% and 18.4 minutes. These results suggest that the dewatering methods may be able to eliminate the use of spray dryers in the clay industry. With further optimization of the process, the reagent consumption can be reduced to significantly lower levels for the clay dewatering.

Table 2.37 Effect of Span 80 (dissolved 33.3% in diesel) on the dewatering of the Brazilian Kaolin Clay (-2 micron) at 25 in.Hg Vacuum Pressure and 3 min Drying cycle time.

Reagent Dosage (lb/ton)	Moisture Content (%wt)	Cake Form. Time (Min.)
0	50.4	39.5
1	46.2	34.2
2	39.1	26.3
3	33.9	20.2
5	30.2	19.2
7	28.6	18.4

\* 2.5-inch diameter vacuum filter; 3 min. drying cycle time; sample floated using 700 g/ton Dodecylamine and 120 g/ton MIBC at pH 9.3 (lime); and cake thickness 0.36 inches.



#### 4. SUMMARY AND CONCLUSIONS

The filtration tests were conducted on several coal and mineral samples to remove more water from filter cake at different vacuum/air pressure, drying cycle time, cake thickness and chemical dosages. If the samples were superficially oxidized during the transportation or originally hydrophilic, they were floated using appropriate flotation reagents (called first hydrophobization step) before the filtration tests. The newly developed reagents were then added to the slurry to further increase the surface hydrophobicity (or contact angle), which is called second hydrophobization step for the fine particle dewatering.

The first group of reagents used in the present work was Span 80 dissolved in different light oils. The tests were conducted on a Pittsburgh DMC product using a 2.5-inch diameter Buchner funnel at a 25-inch Hg vacuum pressure with 2 minute drying cycle time and a 0.45-inch cake thickness. It was seen that the mineral oils gave considerably better results than butanol. Specially, diesel oil and kerosene gave the best results, and approximately 50% moisture reductions were obtained from the cake at higher reagent dosages.

Phosphate esters (TDDP) constitute an important group of low HLB surfactants for dewatering and flotation. At a 5lb./ton TDDP, 200 kPa air pressure and 0.25 inch cake thickness, moisture of an Australian coal sample was reduced from 25.8 to 5.8%, which corresponds to a 77.5% reduction. The moisture was reduced to below 10% even at a thicker cake thickness of a 0.5 inch.

It was determined that the second step of reagent addition caused a substantial increase in the contact angle and a decrease in surface tension, both of which are conducive to improved dewatering. At a 3 lb/ton TDDP, the contact angle of the coal sample increased from 12 to 90°. According to the Laplace equation, the pressure of the capillary water should become zero at contact angle 90° at which the particles cannot be wetted. The results of the pressure filter tests conducted on the Blackwater coal sample show that moisture can be reduced to less than 10% with a thin cake. Even at a 0.85-inch thickness, nearly 50% moisture reductions could be achieved at a 200 kPa air pressure.

In addition the low HLB surfactants, it was found in this study that metal ions, vibration and butanol spray (surface tension lowering agents) also helped to further reduce the moisture content of the fine particles. The results obtained using different amounts of sorbitan monooleate, 20g/ton  $AlCl_3$ , 3 lb/ton butanol spray and vibration at a 25-inch Hg vacuum pressure

and 2 min drying cycle time showed that moisture content would be less than 10% even with a thick cake. Also, high valence metal ions helped to decrease the reagent consumption by one-thirds. This is possible that metal ions enlarge the particle size at zero surface potential, and, thereby, further decrease the capillary pressure.

Vegetable oils and animal fats are naturally occurring hydrophobic substances, such as triacylglycerols, which are the triesters of glycerols with three long-chain carboxylic acids. These lipids are insoluble in water; therefore, they are used as solutions in appropriate solvents. The flotation product was conditioned for 2 minutes in Elenmeyer flasks with different amounts of soybean oil dissolved in diesel oil, kerosene, Fuel oil No. 4, gasoline, and butanol. The ratio between the soybean oil and the carrier solvents were 1:2 by volume. The filtration results showed that the mineral oils gave better results than butanol, and moisture reduction was closer to the pure reagents. Similar test results were also achieved on the fine coal samples by using fish oil, lard oil, sunflower oil, coconut oil, corn oil, etc.

Another set of pressure filtration tests was conducted on the Massey-West Virginia fine coal sample using a blend of sunflower oil and Span 80 as dewatering aid at a 150 kPa air pressure, 2 min drying cycle time and 0.5 inch cake thickness. As shown, sunflower oil gave considerably inferior results to those obtained with sorbitan monooleate. However, the results obtained with the blend were comparable to those obtained with sorbitan monooleate. Thus, blending a lipid with a low HLB surfactant provides a means of reducing reagent costs, as the former is substantially cheaper than the latter.

In addition to the low HLB surfactants, it was also found that dewatering with the lipids became very efficient when vibration, spray and metal ions were applied to the filter cake. Thus, proper combinations of: i) using the dewatering aids, ii) conditioning the slurry with trivalent (or divalent) cations, iii) spraying appropriate surface tension lowering agent(s) during drying cycle time, and iv) applying mechanical vibration, can help achieve deep levels of moisture reduction using small amounts of lipids as dewatering aids.

The dewatering tests were also applied on the coal sample after breaking the lipids molecules into individual molecules so that they could form a surface coating on the surface and, hence, render the surface more hydrophobic. Sunflower oil was transesterified by mixing with ethanol at an approximate molar ratio of 1:3, and agitated on a hot plate for one hour after adding acetic acid (2% by volume) to the mixture. The dewatering tests were carried out on the coal

sample using the modified reagents. The results show that the esterified sunflower oil gave considerably better results than the case of using the naturally occurring lipid without modification.

An animal fat (lard oil) was also modified and used as a dewatering aid with the same producers. The experimental tests applied on the Meadow River coal sample confirmed that the use of the modified lard oil reduced the cake moistures substantially below the values obtained using the lard oil without modification.

The dewatering aids outlined in the present studies should work with hydrophobic solids. To better understand these phenomena, several dewatering tests were conducted on the mineral samples including sphalerite, chalcopyrite, galena, talc, silica and clay. If a sample was naturally hydrophilic or superficial oxidized during shipment, it was ground and floated by using the original flotation reagents, and then subjected to the dewatering tests.

A series of filtration tests were conducted on a fine zinc sulfide concentrate from Sweden. The filtration tests were carried out using a 2.5-inch diameter pressure filter at a 100 kPa air pressure and 2 min drying cycle time. Various reagent dosages and cake thickness tested in the present experiments. At a 3 lb/ton fish oil, a 46% the moisture reduction was achieved from the cake. Higher reagent additions did not significantly decrease the moisture reductions.

The dewatering aids used in the present studies works well with hydrophobic particles. A set of filtration tests were conducted on clean talc mineral using sunflower oil as dewatering aid. The reagent was mixed with diesel oil as 1:2 ratio. The tests obtained using a 2.5-inch diameter pressure filter at a 200 kPa air pressure and 2 min drying cycle time gave 50% moisture reductions at a 0.4 inch cake thickness.

The dewatering tests were applied on fine silica powder (0.038 mm x 0). Without pretreatment (flotation) of the sample, the cake moisture reduction was only 16% and the cake formation time was 158 seconds. After the treatment, when the low HLB surfactants was added to the flotation product, the moisture reduction and cake formation time were 68% and 18 seconds at a 2 lb/ton Span 80 addition.

It is known that the kaolin clay is the most difficult mineral to dewater. Several dewatering tests were conducted on a Brazilian kaolin clay sample (-2 micron in size). To make the surface hydrophobic, the sample was floated and then subjected to vacuum filtration tests at a

25 in.Hg, 0.16 inch cake thickness and 3 min drying cycle time. It was seen that approximately 50% moisture reduction could be obtained using a 7 lb/ton Span 80.

Finally, it was clearly seen that the novel reagents had several advantages when they were used as dewatering aids. The experimental results have also shown that the kinetics of mechanical dewatering was substantially improved, which would greatly increase the throughput of dewatering devices in the plants. In addition, the dewatering aids of the present experiments have characteristics of anti-forming agents, which is very important for processing the particulate materials produced from flotation processes. Most of the reagents added as dewatering aids and blends thereof adsorb on the surface of the particles so that the water removed from the dewatering process can be recycled without creating problems at the upstream processes.

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