

Enhancement of the Dewetability Characteristics of Fine Silica Particles

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Abstract

The dewatering of fine particles is the most difficult part of fine particle processing in preparation plants. The difficulty is due to the fact that fine particles have a higher specific surface area than coarse particles. For this reason, the currently used dewatering techniques (i.e., vacuum, pressure and centrifugal filters) cannot produce a desired moisture content of a filter cake that can be directly used in markets; therefore, most filter cakes are fed to thermal dryers. Thermal drying is costly, and creates environmental pollution where the operation is located.

In the present study, dewatering tests were conducted on fine size silica (SiO_2) powder in a vacuum filter using different chemicals. These include electrolytes, dodecylamine and a hydrophobizing agent. The test results showed that the electrolytes neutralized the particle surface charge in an aqueous medium and coagulated the suspension, which should assist moisture reduction of the particles. The dodecylamine made the particle surface slightly hydrophobic at pH 9.5 in order to adsorb the hydrophobizing agent on the fine silica surfaces. Afterwards, the particle surface became super hydrophobic; for example, the contact angle of the silica powder was improved from 44° to 89° , which was determined using the newly developed thin layer wicking method. As a result, the moisture content of the filter cake was decreased from 26.3% to 7.4% at 1.5 cm cake thickness and 85 kPa vacuum pressure. It was, therefore, concluded that changing the surface properties of the silica particles helped lower the dewatering cost of the fine particles and environmental concerns in plants.

Key words: Silica, Lime, Coagulation, Surface hydrophobicity, Dewatering aid, Kinetics and moisture content.

Introduction

Quartz is an important silica mineral (SiO_2) used in many industrial areas, such as glass, ceramic, casting and abrasive applications. This mineral is mainly supplied from quartz, sand deposits, sandstone and beach sands, which may not be significantly suitable for direct use in those industries (Mining Chem., 1989). For example, when a quartz sample is used for silica brick production, it is necessary that the fire resistance should be over 1700°C and SiO_2 , Fe_2O_3 , Al_2O_3 , CaO , and $\text{Na}_2\text{O}/\text{K}_2\text{O}$ contents are required to be in the ranges 95-99%, 0.3-1.3%, 0.1-2.8%, 0.2-

2.4% and 0.2-1.5%, respectively. For the glass industry, the undesired impurities in a silica sample are required to be less than the above contents due to the discoloring effects in glass production. Therefore, mineral processing is a necessary operation for high quality silica production in which fine grinding may be needed (Mining Chem., 1989; Teodorescu *et al.*, 1998).

It is well known that fine particle processing (size reduction, concentration and dewatering) is a difficult process in preparation plants (Svarovsky, 1990). The more difficult side of this processing is the dewatering of fine size silica samples. It is reported that

the finer the particle size (or higher the specific surface area), the smaller the capillary radii of the filter cake, and the more difficult the dewatering becomes. Therefore, one can change the surface characteristics of the fine silica sample for better cake dewatering. These include coagulation, surface hydrophobization and lowering the surface tension of the process water (Asmatulu, 2002; Tiller, 1996).

For many years, coagulation has been applied to fine particle processing to destabilize fine particle suspensions. In this process, electrolytes with different ions (i.e., Al^{+3} , Ca^{+2} , Fe^{+2} , Na^{+1}) specifically adsorb on the dissimilar surface of fine particles and neutralize the surface electric charge of those particles (Yildirim, 2001; Leja, 1982). These electrolytes can be in the form of sulfates, salts and chlorides (Fuerstenau, 1976). As soon as the surface charges are neutralized in a suspension, electrical repulsive forces are diminished, and van der Waals' attractive forces become dominant for the coagulation process. The fine particles then bind together by attractive forces, and settle on a membrane (or filter media) as larger particles (Rushton *et al.*, 2000).

This paper presents the results of the coagulation and surface hydrophobization of fine size silica powder ($-74 \mu\text{m}$) for dewatering. In the coagulation studies, NaCl , $\text{Na}_2\text{S}_2\text{O}_4$ (sodium hydrosulfite), $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ and CaO were used to improve the dewatering characteristic of the silica sample. In the hydrophobization studies, dodecylamine and a newly developed dewatering aid were used together to decrease the moisture content of the particles. When these two procedures (coagulation and hydrophobization) were combined in an appropriate way, dewatering of the silica sample was drastically increased, which may help lower the dewatering cost and unfavorable environmental impacts of thermal dryers.

Theory

Thermodynamics: It is known that silica particles are naturally hydrophilic, and water molecules can easily wet the particle surfaces. According to this

explanation, dewatering of the fine silica particles is shown in Figure 1, in which the contact area of a water droplet (2) is reduced from the surface of a silica plate (1) and oriented through air (3). In the present model, Figures 1a, 1b and 1c show the initial surface of the silica sample (complete wetting), the surface treatment after the flotation and surface hydrophobizing by the dewatering aid, respectively. As seen, the contact area of the water droplet on the silica plate decreased depending on the surface hydrophobicity (or contact angle). The free energy change (dG/dA) of the process can be given in the following equation (Adamson and Gast, 1997):

$$\frac{dG}{dA} = \gamma_{13} + \gamma_{23} - \gamma_{12} \quad (1)$$

where γ_{13} is surface free energy at the solid/air interface, γ_{23} is surface free energy at the water/air interface, γ_{12} is surface free energy at the solid/water interface and A is the area of contact at the solid water interface. The equilibrium of three interfacial energies can be given by Young's equation (Adamson and Gast, 1997):

$$\gamma_{12} = \gamma_{23} \cos \theta + \gamma_{13} \quad (2)$$

where θ is the the contact angle at the solid/liquid/air interface.

Substituting Equation [2] into [1], one can obtain the following equation:

$$\frac{dG_{dis}}{dA} = \gamma_{23}(1 + \cos \theta) \quad (3)$$

which suggests that dewetting is spontaneous if the free energy change is lower than 0 or contact angle is greater than 180° . This cannot be achieved in actual dewatering conditions. However, the work done on the dewatering (W_d) of fine silica particles can be minimized by adding hydrophobizing chemicals as shown below (Adamson and Gast, 1997; Leja, 1982):

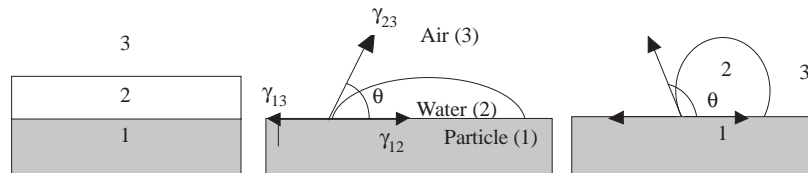


Figure 1. Schematic representation of water displacement from the surface of silica plates.

$$W_d = -\gamma_{23}(1 + \cos \theta) \quad (4)$$

which indicates that the work done on dewatering can be minimized by decreasing water/air surface tension and increasing the contact angle of the water droplet on the particle surface.

For the contact angle of powder samples, an extremely useful technique – the so-called thin layer wicking method was developed (Van Oss and Geise, 1995; Yildirim, 2001). In this technique, fine size powder samples were deposited on glass slides, and then immersed vertically in wetting liquids (i.e., hexane, heptane, octane and decane). Based on the liquid rise through the glass slides, one can determine the mean pore radius r^* and water contact angle θ values of the fine powders in water using the Washburn equation (Geise *et al.*, 1996):

$$l^2 = \frac{\gamma_{lv} r^* t \cos \theta}{2\eta} \quad (5)$$

in which l is the distance traveled by the liquid on the coated slides, t is the travel time, γ_{lv} is the liquid surface tension and η is the liquid viscosity.

Kinetics: The dewatering of fine particles can be described as a process based on the capillary water flow through the filter cake. Darcy derived the rate equation of a dewatering process in 1856, which has been used by filtration authorities (Rushton *et al.*, 2000):

$$\frac{dV}{dt} = K \frac{A \Delta P}{\eta L} \quad (6)$$

where V is the volume of fluid, t is the filtration time, ΔP is the pressure drop across the filter cake, L is the cake thickness, A is the cross-sectional area of the cake and K is the rate constant known as cake permeability.

It is assumed that the filter cake consists of a bunch of capillary tubes with different diameters. In the filtration, the Laplace equation is usually preferred for fine particle dewatering. According to this approach, the applied pressure should be larger than the capillary pressure, p for cake dewatering (Rushton *et al.*, 2000; Asmatulu, 2002):

$$p = \frac{2\gamma_{23} \cos \theta}{r} \quad (7)$$

where r is the capillary radius. The Laplace equation shows that p decreases with decreasing γ_{23} , increasing θ , and increasing r , which are all beneficial for a cake dewatering process. In the present tests, these parameters were changed to obtain a better dewatering for the silica samples.

Experimental

Sample

Silica samples used in the present work were high quality quartz mineral (99.2% SiO₂) received from a source located in the eastern part of the USA. The sample was crushed and ball mill ground to $-74 \mu\text{m}$. One half of the sample was treated using 200 g/ton of dodecylamine and 100 g/ton of methyl isobutyl carbinol (MIBC) at pH 9.5 to simulate the flotation conditions. This treatment process is a vitally important step in making the silica surfaces slightly hydrophobic by being able to better adsorb molecules of the dewatering aid. The solid content of the treated sample was 22.7%. The other half of the silica sample was used for coagulation and thin layer wicking tests without further preparation. The dewatering aid used for the hydrophobicity improvements of the silica particles was low Hydrophilic-Lipophile Balance (HLB) nonionic surfactant dissolved in an appropriate light oils (diesel, kerosene) or alcohols (butanol, ethanol). These dewatering aid and solvents were obtained from Cole-Parmer and Fisher chemical companies.

Procedures

Thin layer wicking technique: A silica suspension with 5% solid content was prepared in distilled water, and agitated by a magnetic stirrer in a 250 ml beaker. Approximately 3 ml of the suspension was withdrawn by means of a plastic syringe and sprayed over $1 \times 2.5 \times 7.5 \text{ mm}$ glass slides. After evaporation of the water at room temperature (one day later), the coated slides were dried in an oven at 105°C to remove the residual moisture in the silica pores. Afterwards, the coated slides were stored in a desiccator to protect the air moisture contamination until required (Van Oss *et al.*, 1992).

The wicking tests were conducted on the silica coated samples by immersing the slides vertically into 5 mm depth of nonpolar wicking liquids (alkenes) in 150 ml beaker. It was suggested that the coated slides were kept inside the container (beaker)

for an hour to introduce the vapor of the wicking liquids to the silica particles before the tests (Van Oss *et al.*, 1992). As soon as the slides were immersed into the nonpolar low energy liquids, the liquid traveled on the glass surface for 1 to 6 min. For high energy liquids or hydrophobic particles, this time can take more than half an hour. During the tests, the travel distance (l^2) was recorded as a function of time (t) and plotted to determine the mean pore radii r^* and contact angle θ values. For the value of r^* , the Washburn equation was chosen. For each silica sample, the plot of $2\eta l^2/t$ vs. γ_{lv} for the alkanes should be a straight line whose slope gives r^* . At this time, the contact angle θ was assumed to be zero (i.e., $\cos\theta = 1$) due to the low surface tension and apolarity of the wicking liquids, such as hexane, heptane, octane and decane. When the mean pore radius was determined, the contact angle values of high surface tension liquids, such as water, formamide, ethylene glycol, ethylene iodide and glycerol can be calculated on a solid substrate using the Washburn equation. Table 1 shows the surface tension components of selected liquids at 20 °C (Van Oss *et al.*, 1992; Asmatulu and Ipekoglu, 2001).

Dewatering tests: The silica sample was placed in a container and agitated for a period of time to keep the slurry in suspension form. A known volume of slurry was taken and transferred to an Erlenmeyer flask. A known amount of the reagents (electrolyte, amine and/or dewatering aid) was added to the flask, and shaken for 3 min before the dewatering tests. The electrolytes were mixed with distilled water to prepare 1% solution. The conditioned suspension was poured into a 6.5 cm diameter Buchner filter with a medium porosity glass frit, and vacuum was applied to the suspension for a desired period. After 2 min of cake dewatering time (started soon

after the cake formation time), the filter product was removed, weighed and dried in an oven at 105°C overnight, and then weighed again to determine the cake moisture content.

Results and Discussion

Contact angle measurements

In the thin layer wicking experiments, linear plots of l^2 vs. t on the silica powder were obtained using hexane, heptane, octane and decane (Figure 2). These were all apolar low energy liquids, and completely wetted the silica particles deposited on the glass slides, which means that $\cos\theta = 1$ (or contact angle is zero). Using these straight lines of each liquid, the value of the mean pore radii r^* was determined to be 7.12×10^{-5} cm (Figure 3) from the slope ($2\eta l^2/t$ vs. γ_{lv}). After the mean pore radii determination, the same wetting tests were performed with water on the silica sample in the presence and absence of Reagent U. In these tests, again linear plots (l^2 vs. t) of water were determined, and then the water contact angles were calculated from the slopes (Figure 4). The water contact angles obtained using the Washburn equation are given in Table 2.

As can be seen, the contact angle of the untreated silica sample was 44.1° due to the higher slope of the line. In this test, it was observed that water traveled faster on the silica coated slide. However, when different dosages of Reagent U were added to the treated silica suspension at pH 9.5, the slope of the lines was gradually decreased, and at 5 kg/ton of Reagent U the line became almost parallel to the x axis. Therefore, the water contact angle increased from 44.1° to 89.9°. This indicated that when the reagent dosage was increased, the silica particles be-

Table 1. Surface tension components (in mN/m) and viscosities (in poise) of the selected wicking liquids at 20°C.

Liquids	γ_l	γ_l^{LW}	γ_l^{AB}	γ_l^+	γ_l^-	η
Hexane	18.40	18.40	0	0	0	0.00326
Heptane	20.3	20.3	0	0	0	0.00409
Octane	21.6	21.6	0	0	0	0.00542
Decane	23.8	23.8	0	0	0	0.00907
Methylene Iodide	50.8	50.8	0	0	0	0.02800
Ethylene Glycol	48.0	29.0	19.0	1.92	47.0	0.19900
Glycerol	64.0	34.0	30.0	3.92	57.4	14.9000
Formamide	58.0	39.0	19.0	2.28	39.6	0.04550
Water	72.8	21.8	51.0	25.5	25.5	0.01000

came more hydrophobic, which should help lower the moisture content of the filter cake. For instance, when the contact angle of fine silica particles is increased from 44 to 89°, it will reduce the energy requirement of the cake dewatering 41-fold due to the $\cos\theta$ value in Equation [7]. In addition, hydrophobic coagulation also takes place at the higher contact angles, and improves the dewatering kinetics.

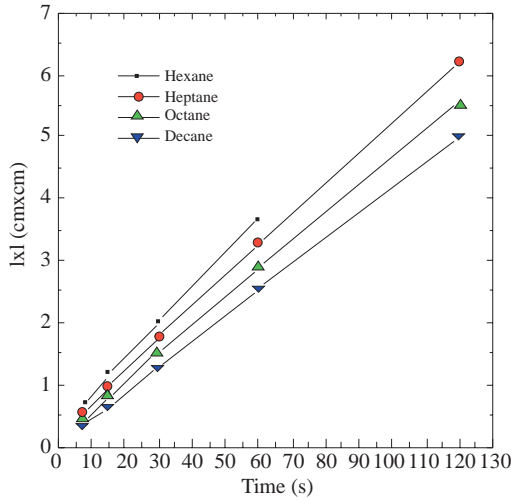


Figure 2. Wetting of a silica powder ($-74 \mu\text{m}$) with low energy liquids (alkenes) in the thin layer wicking experiments conducted on glass slides at 20°C .

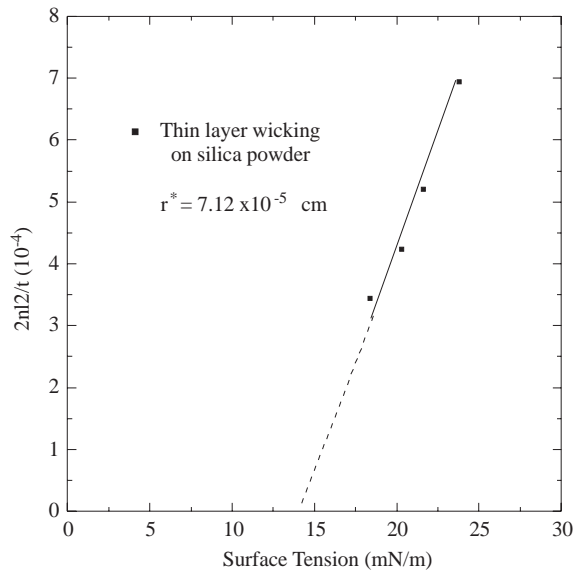


Figure 3. The plot of $2nl^2/t$ vs. surface tension of liquids obtained from thin layer wicking on a silica powder ($-74 \mu\text{m}$) with low energy liquids (hexane, heptane, octane and decane).

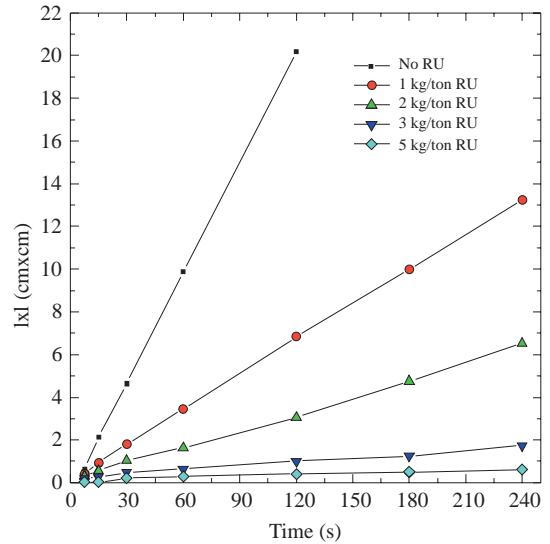


Figure 4. Wetting of a silica powder ($-74 \mu\text{m}$) with water in the presence of absence of Reagent U in the thin layer wicking experiments conducted on glass slides at 20°C .

Table 2. Contact angle values as a function of reagent dosage on the silica powder using thin layer wicking method.

Reagent U dosages (kg/ton)	Water Contact Angle ($^\circ$)
0	44.1
1	77.6
2	84.3
3	88.1
5	89.9

Dewatering tests

Coagulation tests: Four different reagents, namely NaCl, $\text{Na}_2\text{S}_2\text{O}_4$, $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ and lime (CaO), were used in the present studies. The dewatering tests were conducted on the ground silica suspension ($-74 \mu\text{m}$) at 85 kPa vacuum, 22.7% solid content, 2 min cake dewatering time and 1.5 cm cake thickness using these electrolytes. A 3 minute conditioning time was given for the reagent adsorption on the silica surfaces. The test results obtained using a 6.5 cm diameter Buchner funnel are given in Table 3.

Table 3. Effects of coagulation on dewatering of silica sample at 85 kPa vacuum pressure.

Reagent Dosage (g/ton)	Moisture Content (% wt)			
	NaCl	Na ₂ S ₂ O ₄	ZnSO ₄ ·7H ₂ O	CaO
0	26.3	26.3	26.3	26.3
100	25.9	26.0	24.3	19.6
200	25.3	25.8	23.4	17.4
300	25.0	25.4	23.0	16.8
500	25.2	25.5	22.8	17.5

A surprising result was obtained when CaO was added to the suspension. For example, a 200 g/ton of CaO dosage decreased the moisture content of the filter cake from 26.3% to 17.4%, which represents an approximately 34% moisture reduction. The further increase in CaO addition did not significantly change the overall moisture content. The moisture reduction may be due to the fact that calcium and/or calcium hydroxy species reacted with the negatively charged silica surfaces and neutralized them, which should help coagulate the suspension. Another important observation made in the present work was that the dewatering kinetics were four times higher with CaO addition. The author observed that at the higher CaO concentration, coagulation of the silica particles in a beaker was visually seen in 2 min.

Hydrophobization tests: A series of dewatering tests was conducted on the fine silica sample with and without Reagent U addition. Use of the surfactant further enhances the hydrophobicity of the particles, which is crucial for spontaneous removal of surface free water. The same Buchner funnel was also used for two sets of vacuum filtration tests at 85 kPa vacuum, 9.5 pH, 2 min cake dewatering time and 1.5 cm cake thickness. The sample was conditioned for 3 min before the dewatering experiments. The test results are given in Table 4.

The first set of tests was conducted using various

amount of Reagent U dissolved in diesel oil with and without coagulation and amine treatment. Without treatment and in the absence of Reagent U, the cake moisture was 26.3% and the cake formation time was 163 s. At 2 kg/ton Reagent U addition by itself, the moisture was reduced to 20.5% and cake formation time increased to 168 s. This moisture reduction was possibly due to the surface tension lowering of the process water (see the Laplace equation). This confirmed that the surface properties of the silica particles should be changed for higher moisture reduction from the filter cake.

The next series of dewatering tests were conducted on the treated silica sample with 200 g/ton lime, 200 g/ton dodecylamine, 100 g/ton MIBC at pH 9.5, which is also called first hydrophobization step. As seen, the lime and amine together reduced the cake moisture from 26.3% to 16.2%, and the cake formation time reduced from 163 s to 29 s. When the novel dewatering aid was added to the treated product as a second hydrophobization agent, the moisture was further reduced to 7.4% at 5 kg/ton Reagent U dosage. The cake formation time was also lowered to 16 s. The improved dewatering brought about by the lime, dodecylamine and dewatering aid together is most likely due to the coagulation and hydrophobicity enhancement of the fine silica particles. Thus,

Table 4. Effects of coagulation and sample treatment conducted on silica sample (-74 μm) dewatering using Reagent U dissolved 33.3% in diesel at 85 kPa vacuum pressure.

Reagent Dosage (kg/ton)	w/o Coagulation and Amine Treatment		w/ Coagulation and Amine Treatment	
	Moisture Content (% wt)	Cake Form. Time (s)	Moisture Content (% wt)	Cake Form. Time (s)
0	26.3	163	16.2	29
1	21.0	159	9.8	18
2	20.5	168	8.3	17
3	20.9	170	7.6	17
5	22.5	175	7.4	16

this single digit moisture content of the filter cake may not need further drying in thermal units because a zero moisture content product can cause a dust problem in preparation plants.

Conclusions

Contact angle, coagulation and hydrophobization tests were conducted on fine size silica samples (-74 μm). The contact angle data obtained using the thin layer wicking method showed that, in the presence of 5 kg/ton dewatering aid, the contact angle of the particles increased from 44.1° to 89.9°. This should help increase the particle hydrophobicity and hydrophobic coagulation and, hence, decrease the moisture content and cake formation time of the silica samples.

A series of coagulation tests was performed on the silica sample using different electrolytes. When only 200 g/ton of CaO was added to the suspension,

the moisture content was decreased from 26.3% to 17.4%, which may be due to the coagulation of the fine silica particles achieved by the calcium or its hydroxy species.

The hydrophobization tests were conducted on the untreated and treated silica samples. Without amine and CaO treatment, the moisture content difference between 0 and 2 kg/ton of Reagent U was only 5.8% at natural pH, which may be attributed to the surface tension lowering of the filtrate caused by the dewatering aid. In contrast, when the silica sample was treated using 200 g/ton of lime, 200 g/ton dodecyl amine and 100 g/ton MIBC at pH 9.5, the moisture content was reduced from 26.3% to 7.4% at 5 kg/ton of Reagent U. In addition the dewatering kinetics were improved approximately 10 -fold with surface treatment and dewatering aid; for example, the cake formation time decreased from 163 s to 16 s, which would greatly increase the throughput of dewatering devices in plants.

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