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ELECTROKINETIC SEPARATION OF ULTRAFINE MATERIALS : A REVIEW

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1 INTRODUCTION

1.1 Importance of Separation Technology

A report on Separation and Purification conducted by the National Research Council (NRC) emphasizes the necessity for more economically efficient technologies in the area of separation.[1] Separations (solid-liquid, liquid-gas, and liquid-liquid) are essential to most manufacturing operations in chemical processing industries in the United States. The efficiency of a given separation method is often a major factor in the cost of a manufactured product. This cost is in the form of equipment, energy, and time required to effect the separation. For example, in biotechnology, the separation of the final products from dilute aqueous solutions is a critical part of the process. In the area of strategic metal mining, the majority of domestic sources are dilute; they often contain low grade ores and produce process wastes that must be separated. In the area of waste treatment, as allowable pollutant release levels are reduced, the concept of removing pollutants from dilute solutions is increasingly important. Hence, environmental separations require the improved recovery and reuse (e.g., recycling) of waste materials. Environmental separations can also aid in the reduction of toxic and hazardous material released to the environment.

A recent study on future directions in separation technology, sponsored by the National Science Foundation[2], emphasizes the importance of field enhanced separations of dilute solutions. The transfer of combined field separation technology to commercial processes requires the development of innovative separations processes that utilize existing separation techniques in conjunction with external fields (e.g., electrical) and procedures for the subsequent design and scale-up. The primary issues in separations research are: (1) improvement of processing technology, (2) interfacial phenomena, (3) rate and capacity of separations, and (4) energy efficiency. The key element in this review is the improvement of electrokinetic processing technology. This includes the modification of current separation strategies in addition to the incorporation of various driving forces (e.g., gravitational, electrical) and combinations of these forces in separation procedures. This article begins with a review of the theory governing electrokinetic separations followed by an overview of early applications of electrokinetic separation processes. The remainder of the article focuses on the application of electrokinetic separations to uncharged systems through chemical modification and the present status of commercial electrokinetic techniques.

The rate and capacity of separations on both a large and small scale are influenced by a number of parameters. Interfacial phenomena can effect the rates of many separation processes by enhancement due to the presence of surface-active compounds. These compounds can alter the structure of the interface relative to the bulk phase or alter fluid mobility to improve the extent and rate of separation. The process complexity of a separation system is directly related to the equipment size and capacity. The capital costs associated with separation equipment often accounts for a large portion of plant capital costs. Therefore, any improvement in the efficiency of a process could have a substantial impact on the cost of the final product.

Energy costs in a separation process are most often associated with the input and removal of heat from the system. In solid-liquid separation, a clear need exists for the replacement or reduction of a high-energy consumption process (e.g., thermal drying) with a lower energy process (e.g., electro-osmotic dewatering).

The feasibility of a given dewatering technique is dependent on both the cost per unit slurry dewatered and the final desired moisture content. A factor critically limiting conventional dewatering methods is the size of the solid particles which governs the pore size in the resulting filtercake. The presence of ultrafines significantly reduces the hydraulic permeability, which is a measure of the dewaterability of a system under the influence of a pressure gradient.

For example, the effective dewatering and separation of ultrafine particle dispersions is a critical problem area in mineral processing.[3,4] As mineral ore grade decreases, finer subdivisions are necessary to isolate valuable material. This reduction in mineral grade results in the production of large quantities of mineral ultrafines. In industrial mineral processing, these ultrafines often constitute the premium product of the process. Fine particle dispersions, in the form of a tailing waste product, are also generated in the final steps of mineral processing. In order to adequately dispose of these materials, an efficient dewatering process must be developed.

1.2 Conventional Solid-Liquid Separation

Hydraulic dewatering is a term used to describe the removal of water under the influence of a pressure gradient. The two major divisions of hydraulic dewatering are gravity drainage and applied pressure differential. Pressure driven techniques utilized commercially are: vacuum drum filters, compression belt filters, rotary

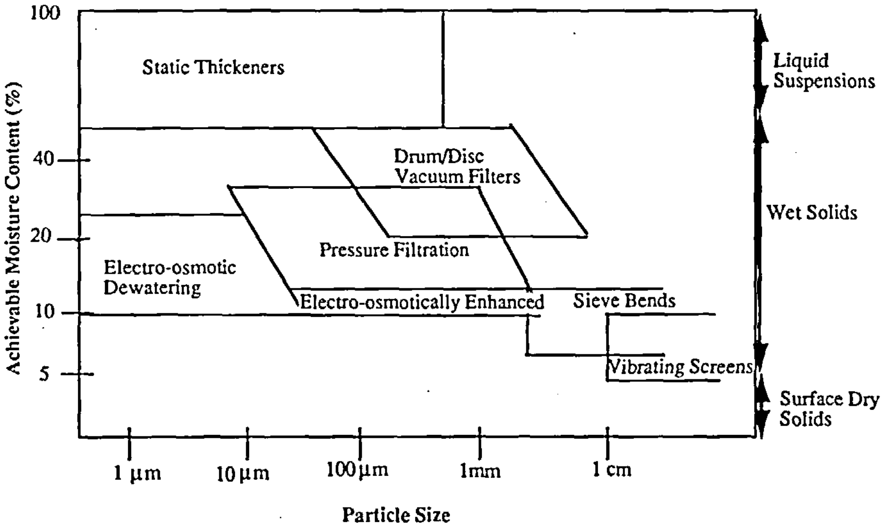


FIGURE 1. Range of application of various dewatering methods as a function of moisture content and particle size. [15,35,48]

vacuum filters, filter presses, and batch filtration. Examples of gravity drainage methods include lagooning and sedimentation basins. Gravity drainage is considered an easy, low maintenance operation with little capital outlay. However, gravity drainage has the disadvantages of being a time consuming, ineffective process, producing a relatively moist product and occupying large areas of land. When compared to gravity drainage, applied pressure techniques produce a considerably drier final product, but have high capital equipment and maintenance costs. This is especially true during batch filtration in which the process downtime for filling and emptying the vessel may result in a prohibitive cost. A factor severely limiting effective solid/liquid separation in both hydraulic dewatering processes is the presence of ultrafine particles.

The relationship between achievable moisture content as a function of particle size is illustrated in Figure 1. This figure shows the range of application of various solid-liquid separation techniques for coarse to colloidal particles. In the case of ultrafines dewatering, at the point where hydraulic separation becomes ineffective, thermal drying appears to be a viable alternative at this stage. Thermal drying is not limited by the presence of ultrafine particles, hence in a number of dewatering operations, thermal drying is implemented as the final drying step. Although thermal drying and steam dewatering processes have short process duration times, they require uneconomically large amounts of energy. Another disadvantage of thermal drying is that it is unsuitable for heat sensitive ultrafine materials (e.g., food additives, pharmaceuticals).[5] An attractive alternative process for producing ultrafine particles would be to dewater beyond the hydraulic dewatering limit, in order to reduce or eliminate the need for thermal drying. Electrokinetic dewatering in principle is independent of particle size and could be utilized as such an alternative.

1.3 Electrokinetic Separation

Previous research by Lockhart [5-8] and others indicates that electrokinetic dewatering techniques can be effectively applied to fine particle systems. However, the approach used by many researchers is largely empirical in that some fundamental parameters influencing electrokinetic separations (e.g., particle electric potential, state of aggregation and relative magnitude of surface charge) have remained unexplored.

Investigations into the application of electrokinetic dewatering to systems in the absence of a significant natural particle surface charge are also limited. The addition of surface active agents or potential determining ions to modify the particle surface by imparting the required electrical potential may facilitate electrokinetic separation in uncharged systems. The lack of dependence on original particle size and charge could make electrokinetic dewatering a more attractive technique to a wider variety of uncharged ultrafine systems.

Thus, the purpose of this review is to discuss the concept of electrokinetics in the solid-liquid separation of high and low value ultrafine slurries. The effect of conditioning agents in the form of ionic surfactants, electrolytes, and alkalies in the enhancement of electro-osmotic dewatering is also discussed.

2 ELECTRO-OSMOTIC THEORY

Electrokinetic theory is essentially concerned with the equations that govern the flow of liquid at a solid-liquid interface when an electrical potential is applied. Electrokinetic phenomena was discovered by Reuss in 1808 [9,10] when he demonstrated that under the influence of an applied direct current potential, water migrated through a porous clay diaphragm toward the negatively charged electrode, whereas free clay particles migrated toward the anode. [11]

The dominant factor affecting this flow is the interaction between the solid and the bulk liquid phase. Most substances acquire an electrical surface charge when placed in contact with a polar medium such as water.[10] The crystal lattice of a solid will contain a net positive or negative charge that results from interior structural defects, lattice defects or substitutions. The net charge in the solid is compensated by an equivalent ionic charge at the surface. When an insoluble ionic solid is dispersed in water, an equilibrium develops between the ions in the crystal surface and the same type of ions in solution. The charging mechanisms responsible for surface charge are ionization, ion adsorption, and ion dissolution. Ionization of surface groups is dependent on the pH at which the net charge due to ionization is zero. In ion adsorption, the net surface charge is obtained by the unequal adsorption of opposite charged ions. For an aqueous system, the solid surfaces are often negatively charged due to cations being more hydrated than anions. These cations have a greater tendency to exist in the bulk aqueous phase; corresponding anions are more likely to be specifically adsorbed because they are smaller and less hydrated. The unequal dissolution of opposite charged ions composing a substance can result in a surface charge by ion dissolution.

In an aqueous electrolytic solution, the solid has a charge density located in the surface plane (Figure 2). The bulk solution (liquid) consist of co-ions and counter-ions of the same and opposite charge, respectively, of the particle. The charge on the surface is balanced by excess counter-ions in the liquid thus neutrality is maintained. This produces a variation in the electrical potential between the solid surface and the bulk solution.

A sudden change in charge distribution should give rise to a sharp drop in potential across the double layer through the counter-ion layer. However, the ions in solution also experience diffusional forces resulting from thermal mixing of the liquid molecules. These forces produce a gradual decrease in potential as distance from the surface is increased. This variation in potential with the distance from the solid-liquid interface is illustrated in Figure 2. The revised model consists of an immobile surface-charge layer adjacent to a diffuse counter-ion layer in the bulk liquid. The potential of the solid surface with respect to the bulk liquid is represented by ψ_0 and is called the surface potential. The surface potential can become zero depending on the concentration of ions in solution; this particular value of surface potential is called the point of zero charge, often abbreviated as pzc.

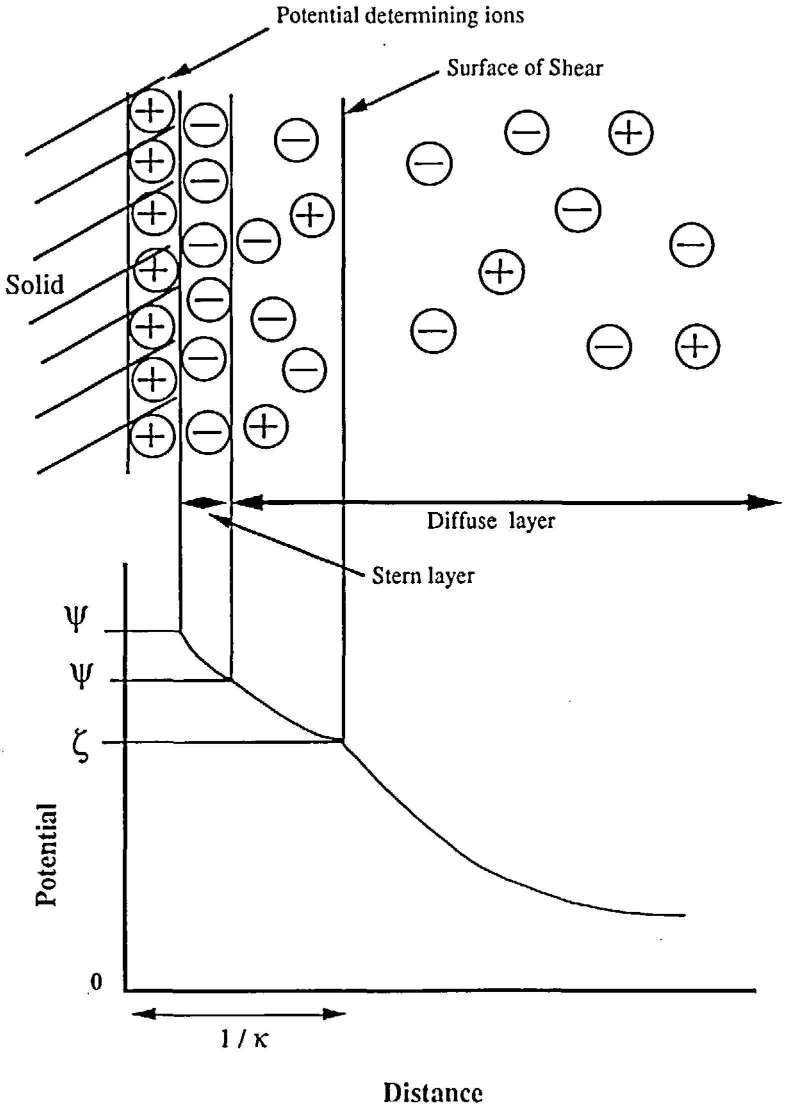


FIGURE 2. Model of the electrical double layer

Potential determining ions (pdi) are ionic species controlling the surface charge and the potential at the surface of the dispersed phase. The selective adsorption of ions determines the potential of the solid relative to the solutions. For example, the potential determining ions for most metallic oxides are OH^- and H^+. A change in potential at the solid surface, can be achieved by the addition of acids and bases to alter the concentration of hydroxide and hydrogen ions [12]. Oxide surfaces possess a large number of amphoteric hydroxyl groups that can react with either H^+ or OH^- as follows:

$$MOH_2^+ \xrightarrow{H^+} M\text{-}OH \xleftarrow{OH^-} M(OH)_2^- \qquad (1)$$

This reaction depends on the pH and can be termed as either an adsorption or a dissociation reaction.

Double layer theory also assumes that there is a shear plane within the diffuse double layer at a distance from the solid surface. In most instances, the precise location of the shear plane is unknown (usually from 3 to 5 Å). The average potential in this surface of shear is defined as the zeta potential, ζ. The zeta potential is the important experimentally determinable parameter in the evaluation of electrokinetic theory.

Electrokinetics includes four major classes of effects: (1) electrophoresis, (2) electro-osmosis, (3) streaming potential, and (4) sedimentation potential. Electro-osmosis and electrophoresis are the two classes of electrokinetics primarily utilized in solid-liquid separation. Electrophoresis is the movement of a charged species (particles or molecules) relative to a stationary liquid phase upon application of an external field (see Figure 3a). Electro-osmosis, the complement of electrophoresis, is the movement of a liquid relative to a stationary solid phase as a result of an externally applied electric field (see Figure 3b).

Electro-osmosis occurs when an external electric field is tangentially applied to a fixed surface, causing the mobile portion of the double layer to flow. The applied field induces the movement of excess counter-ions along the oppositely charged surface along with them, resulting in net liquid flow. A quantitative relationship may be established between the electro-osmotic velocity of flow, the zeta potential, and the externally applied electric field.

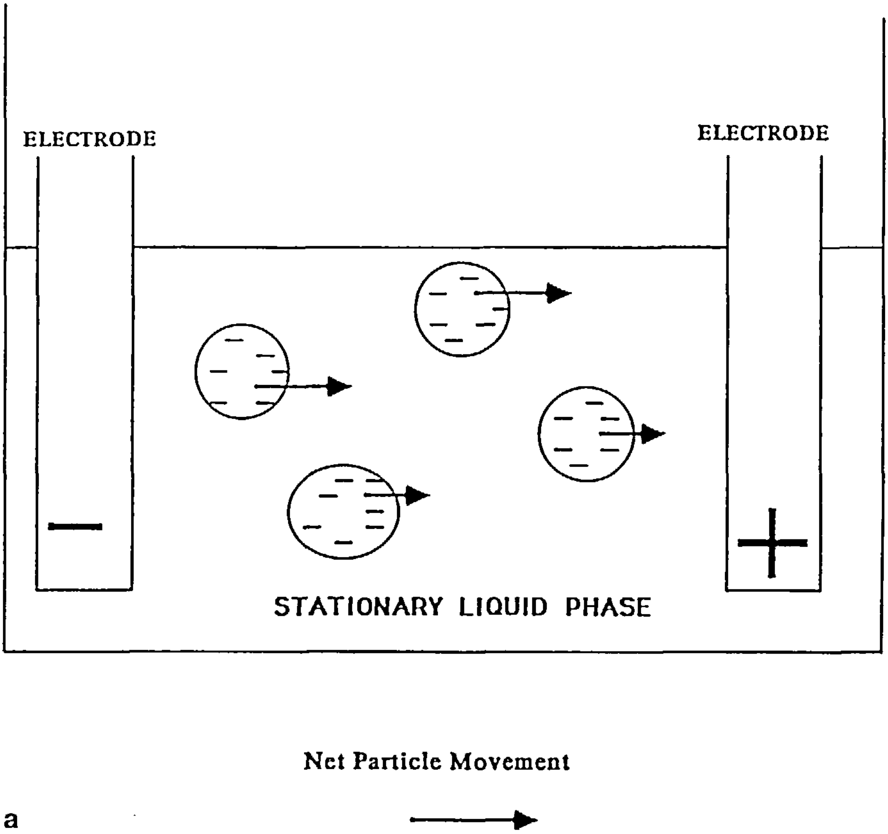


FIGURE 3a. Model of electrophoresis

2.1 Equations Governing Electro-osmotic Dewatering

Poisson's equation is the fundamental electrostatic equation in the description of the electrical double layer. In a dielectric medium such as water, electrical charge immersion will cause a reduction in the electric field strength (E). This field strength reduction is due to the tendency of the molecular dipoles to align themselves resulting in a cancellation of part of the field. The permittivity, ε, is defined as the capacity of a substance to affect an electric field. A correction factor must be implemented to correct for the effect of permittivity; the dielectric displacement , D, is defined by:

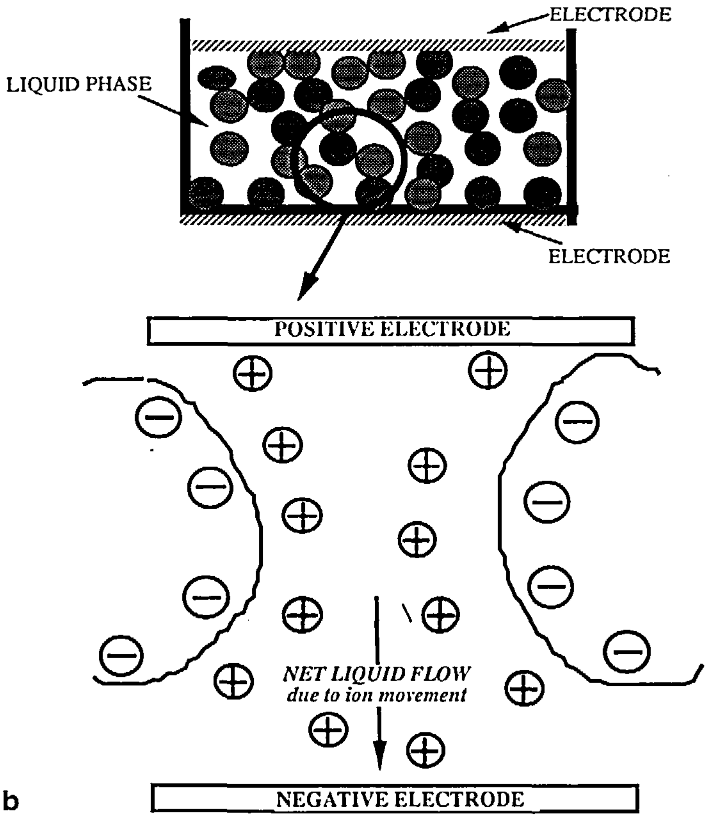


FIGURE 3b. Model of electro-osmosis

$$D = \varepsilon E \qquad (2)$$

Poisson's equation essentially states that the flux of the field into any element of volume is determined by the amount of charge in that volume:

$$\nabla^2\psi = \frac{\partial^2\psi}{\partial x^2} + \frac{\partial^2\psi}{\partial y^2} + \frac{\partial^2\psi}{\partial z^2} = -\frac{\rho}{\varepsilon} \qquad (3)$$

where ∇^2 is the Laplace operator, ψ is the double layer potential at distance x, y or z from the surface, ρ is the volume density of charge and ε is the corrected dielectric constant of the medium. In cartesian coordinates, Poisson's equation can be written as:

$$\nabla^2\psi = -\frac{1}{4\pi\varepsilon_o}\cdot\frac{4\pi\rho}{D} \tag{4}$$

where ε_o is the permittivity of a vacuum ($\varepsilon_o = 8.85 \times 10^{-12}$ farad m^{-1}). Applying the approximation of a large planar interface and a single flat condenser, Equation 3 reduces to:

$$\nabla^2\psi = \frac{d^2\psi}{dx^2} = -\frac{\rho}{\varepsilon} = \kappa^2\psi \tag{5}$$

where the fluid is assumed to be at rest in a plane coinciding with the charge on the wall. The Debye-Huckel parameter, κ, can be represented by: [12]

$$\kappa = \left(\frac{e^2\,\Sigma n_i^o z_i^2}{\varepsilon kT}\right)^{0.5} \tag{6}$$

where n_i^o is the electrolyte concentration, and z_i is the valency of the ion. Equation 6 can be rewritten to account for the effect of the electrolyte concentration on the system:

$$\kappa = \left(\frac{2000\ F^2}{\varepsilon_o DRT}\right)^{0.5} I^{\,0.5} \tag{7}$$

where F is the magnitude of the charge on a mole of electrons (a Faraday). The ionic strength, I, can be defined by:

$$I = \frac{1}{2}\Sigma\, c_i\, z_i^2 \tag{8}$$

where c_i is the concentration of a specific ion, i. An increase in the ionic strength of a solution results in an increase in the Debye-Huckel parameter causing the potential

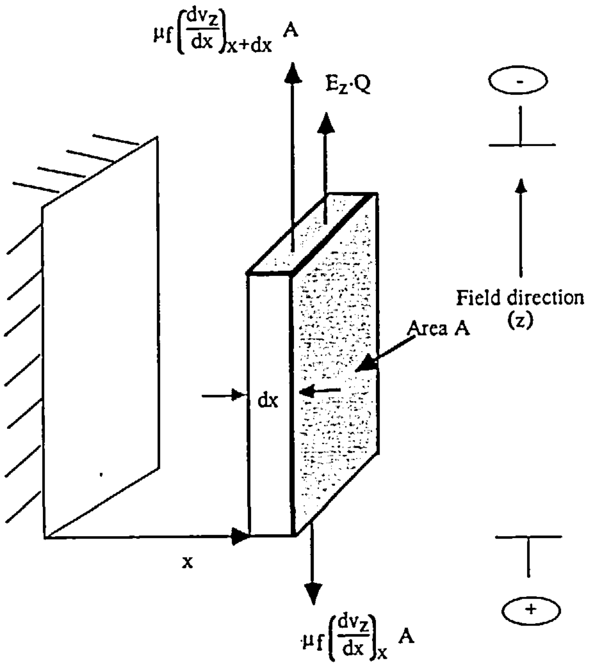


FIGURE 4. Force balance on column of liquid during electro-osmosis [after Hunter[12]].

to decrease more rapidly with distance away from the surface. This double layer compression is caused by the use of additives in the system.

When an external electric field of strength E_z is applied, there are resultant forces in each volume element of liquid thickness, dx, located at a distance x from the surface. Figure 4 shows the action of the various forces on a given volume element during electro-osmosis.[12] The force due to an external electric field is:

$$F_1 = E_z \cdot Q = E_z \rho A dx \tag{9}$$

where E_z is the magnitude of the field strength in the z direction. At steady state, a viscous drag on a liquid layer, occurs by adjacent layers moving at different velocities. The force of retardation on a surface located at a distance x from the surface is:

$$f_x = -\mu_f \left(\frac{dv_z}{dx}\right)_x A \tag{10}$$

and the force of acceleration on surface at x+dx is:

$$f_{x+dx} = -\mu_f \left(\frac{dv_z}{dx}\right)_{x+dx} A \tag{11}$$

where v_z is the liquid velocity in the z direction, parallel to the wall and μ_f is the liquid medium viscosity. After substitution of Poisson's equation with the planar estimation for ρ, the following boundary conditions are invoked: (1) the value of the liquid velocity, v_z , rises from a value of zero in the plane of shear to a maximum value of v_{eo} at some distance from the wall and (2) the value of the electric potential goes from a value of $\psi = \zeta$ at the shear plane to $\psi = 0$ at a point far from the solid. The final expression for the linear velocity of the liquid during electro-osmosis is:

$$v_{eo} = \frac{\varepsilon E_z \zeta}{\mu_f} \tag{12}$$

For a capillary with a constant cross-section of radius, r, the volume removed per unit time can be expressed as:

$$V_{eo} = \pi r^2 v_{eo} = \frac{\pi r^2 (4\pi\varepsilon_o) D E_z \zeta}{4\pi\mu_f} \tag{13}$$

where V_{eo} is the electro-osmotic volume flow rate, v_{eo} is the electro-osmotic velocity, r is the capillary diameter, and E_z is the magnitude of the field strength in the z direction. This equation is only valid when the double layer thickness $(1/\kappa)$ is much smaller than the capillary diameter (i.e., planar approximation is valid). Substitution using Ohm's law results in the final equation describing electro-osmotic dewatering in volumetric terms as:

$$V_{eo} = \frac{\varepsilon \zeta \; i}{\mu_f \lambda_o} \tag{14}$$

where λ_0 is the specific conductance of the liquid and i is the electric current passing through the capillary.

2.2 Electro-osmotic Dewatering Models

In a theoretical treatment of electro-osmotic dewatering, Yoshida et al. [13] describe constant electric current electro-osmotic dewatering as a two-stage process. The initial stage results in a decrease in the applied voltage as liquid is removed from the slurry. During the second stage, there is a sharp increase in the voltage due to the reduction of the liquid content in the layer next to the slurry (i.e., the partially dewatered slurry). This results in an increase in the electrical resistance of the slurry. The theoretical relationships developed by Yoshida et al. are applicable for the initial stage in the electro-osmotic dewatering process. The rate of dewatering and the electric power consumed are analyzed using a model in which the sludge bed is divided into two parts: the dewatered bed and the dewatering bed. Their theoretical design equations are applicable to the design of electro-osmotic dewatering equipment.

In contrast, Weber et al.[14] have developed a simplified model of electro-osmotic dewatering under constant voltage that describes the filter cake as a single partially dewatered area containing both solid and liquid. The pores in the cake are viewed as cylindrical capillaries. The primary difference in the models is that Yoshida's model requires information on the electrical conductivity throughout the bed.

3 LITERATURE REVIEW

The following terms are often used in the description of electrically driven separations:

> electroforced sedimentation, electrodeposition, electrofiltration, vacuum electrofiltration, electro-acoustic dewatering, electro endo-osmosis, electrochemical hardening, and electrokinetic densification.

In many instances, the above terms describe the combination of electrical and other driving forces to separate solids and liquids. They all include, however, a dependence on the concepts of electrokinetics as applied to separation processes. For example, electro-acoustic dewatering combines acoustic and electrical fields in the presence of pressure or a vacuum to dewater colloidal materials (e.g., coal slurry, municipal sludge and corn gluten slurry). [5,15-17] A complete review of early application of electrical dewatering in the ceramic industry was conducted by Carl

E. Curtis in 1938.[10] A more recent examination of electrokinetic dewatering and thickening applications was performed by Sunderland[18,19] in 1987; this work covers current industries with the most interest in use of this technology.

Count Botho von Schwerin of East Prussia is credited with the first conventional application of electrokinetic dewatering in the area of mineral processing.[11] In 1900, von Schwerin utilized electro-osmosis to partially dewater wet raw peat which had the consistency of mud. The electro-osmotic tray filter apparatus, the endless belt machine, the rotating anode electrophoresis machine and an electro-osmotic filter press were all developed by von Schwerin. Between 1910 and 1920, this electro-osmotic dewatering equipment was utilized on a large scale at plants in Germany and Czechoslovakia in the production of various clays. Later applications of electrokinetic dewatering (1920-1930) included various types of clay slurries, sewage sludges, and cement slurries.

In 1930, Casagrande proposed the use of electro-osmosis in the dewatering and stabilization of large blocks of semi-fluid soil *in situ*. During the electro-osmotic consolidation of soil, the driving force for the flow of water in pores exceeds the forces that tend to hold the water to the soil particles. [20,21] The resulting changes in the stress-strain and strength characteristics of the soils results in a deformation of the soil skeleton. [20,22] In this application, the main objective is to electro-osmotically remove just enough water to consolidate the soil in the desired area, while preventing the sloughing of the sides or upheaval of the bottom during an excavation operation. In a related application, electro-reclamation is utilized for the in-situ remediation of contaminated soils or sludges. [23] Electro-reclamation, however, often results in vitrification of the soil.

The application of electrokinetics to solid-liquid separation is quite varied and often complex in nature. Important parameters in the assessment of the various electrokinetic separation operations with examples are listed below:

1. Method: continuous, semi-continuous or batch
2. Material: fine particle, concentrated or dilute dispersion, charged particles, origin of material
3. Additional driving forces for separation: hydraulic, electrical, sedimentation, acoustic or a combination
4. Additives: chemical type, flocculants or dispersants
5. Economics: Relative to thermal or hydraulic techniques
6. Characterization of materials: Zeta potential, specific resistance, pH, particle size

7. Enhancement: Quantitative value of enhancement over other separation techniques
8. Limitation: Based on cost, size, power, efficiency of process
9. Configuration and scale of application: laboratory, pilot, large scale, construction materials, set-up.

There are two large categories of application of electrokinetic separation technologies; the batch separation of low-value materials[24-26] and continuous separation of high value products.[18,19] Batch consolidation of low value ultrafines on a large scale has been investigated by a number of researchers. One such example of batch consolidation is found in the mining industry. [7] In mining, a finely crushed waste from various ore concentration processes, called mill tailing, is often used as backfill in underground mine openings. Subsequent mining operations occur using this backfill as a structural support for mine workers and their equipment. The raw tailings from a mill often contains a large quantity of slimes consisting of very fine-grained material (e.g., less than 5 μm). These slimes are placed in large lagoons (e.g., above ground ponds, behind dams, abandoned mine openings): the slow gravitational settling of the slimes makes them unsuitable for backfill material.[27]

Sprute and Kelsh, a team of researchers at the U.S. Bureau of Mines, have conducted a number of studies in the area of electrokinetic densification or consolidation of large lagoons.[24] Electrokinetic consolidation and/or sedimentation combines the gravitational settling with electrophoretic and electro-osmotic solid-liquid separation. Their work on metal mine tailings, slimes, ultrafine coal and coal wastes, was initially performed on a laboratory scale; with subsequent scale up at actual mine sites. The field studies utilized existing sedimentation pits, with railroad tracks, iron fencing and floating metal used as electrodes. In tests on both thickened, settled slimes and old slimes, Sprute and Kelsh[24] demonstrated that electro-kinetics can be used to effectively consolidate and harden slimes. The primary differences between the old and thickened slimes are the particle size and composition (see Table I). In addition, the old slimes had been settling in a lagoon for almost a year.

The power consumption in the electrokinetic consolidation process is moderate (up to 30 kWh/yd^3 of consolidated fill). In both mineral slimes, however, electro consolidation was preferred over gravitational settling due to the relatively short

TABLE I

Electrokinetic consolidation of mineral slimes

Property	Thickened Slimes	Old Slimes
Composition of primary constituents (%)	Al = 7% Ca = 3% Si = 26% Fe = 4% Ti = 0.5% Pb = 2%	Al = 2% Ca = 0.13% Si = 30% Fe = 7.34% Ti = 0.15% Pb = 0.62%
Particle Size	90% < 6 mm	90% < 2 mm
Power requirement kWh/yd^3 consolidated fill	8.2	30
Volume change (initial/final)	150 yd^3 / 60 yd^3	NA
Resistivity: ohm-cm (@21°C)	830	950
Time of electro-kinetic consolidation	52 hours	53 hours

time it took to dewater. The resulting electrokinetically hardened material could be easily hydraulically transported. Further tests demonstrated that electrokinetic treatment of slime deposits hardens them sufficiently to permit removal and use as backfill for support in mine walls.[27] As with any mining process, safety precautions must be taken due to the production of potentially explosive trapped hydrogen gas at the cathodes, and physical contact of mining personnel with electrical apparatus.

Two Australian researchers, Lockhart and Stickland, have recently conducted studies on dewatering coal washery tailing ponds by electro-osmosis.[7] Their work consisted of small and large-scale laboratory tests using a horizontal electrode configuration. They concluded that large scale electro-osmotic dewatering of tailings ponds is unfeasible for coal tailings due to the high cost associated with construction and dismantling of the ponds, in addition to the removal of the dewatered material. However, when compared to the capital expense associated with a large scale dewatering apparatus that has a limited lifetime, large tailings pond would be cheaper. In addition, the tailings pond takes advantage of the natural drainage and sedimentation of the coarse fraction of the coal tailings reducing the need for continuous monitoring or maintenance.

Electrokinetic separation has also been implemented in the processing of sludge containing varying quantities and types of solid matter produced by sewage treatment plants. [24,25,28,29] As is the case in dewatering fine particles, the size distribution of these suspensions makes conventional hydraulic methods ineffective. Thermal drying or evaporation appears to be the appropriate (albeit expensive and energy intensive) method for sewage sludge treatment. Although the sludge accounts for only 1% of the total sewage volume, the expenses associated with it's disposal can account for up to 50% of the capital and operating cost of the sewage processing. Primary and secondary separation processes remove a portion of the water while producing a sludge which must be further treated for ultimate solids disposal. Most sludges are produced during the gravity sedimentation step; in some facilities, chemical flocculants are used to accelerate the settling process thereby thickening the sludge. The initial solids content of most raw sludges varies between 3 and 5%. Adequate disposal of the sludges requires an increase in solids content from 5% to 25%; this necessitates the removal of approximately 80% of the water from the sludge.

Early work on electrokinetically dewatering activated sludge in the form of filter cakes using a rotary vacuum filters was conducted by Robert E. Beaudoin.[26] By combining electrical and gravitational drainage in a batch mode lab scale set-up, Beaudoin observed the rate of water removal and studied the coagulation conditions of the initial slurry. He concluded that the electro-osmotic dewatering process for sludges was not economically feasible when compared to thermal drying. Subsequent studies by Cooling [30] on thickened digested sludge (9.5% moisture by weight), combined settling and electrokinetics in both laboratory and large scale sludge drying beds. The large scale beds were outside and were constructed similar to the aforementioned electro-osmotic tailings ponds. The energy consumption and cost of labor associated with initial installation and replacement of the electrodes deemed the process unsuitable for industrial scale implementation.

It should be noted that the economics affiliated with electrokinetic sewage treatment are largely governed by the fact that the final product is essentially valueless. In the two aforementioned sewage sludge studies[26,30] the electro-osmotic technique was utilized as a supplemental method causing it to appear uneconomic. However, the renewed interest in environmental issues such as waste minimization necessitates the development of separations technologies that effectively reduce the volume and quantity of solid and liquid waste. This supports an earlier assessment by Greyson[25] that electro-osmotic separation should be evaluated as an independent unit process in sewage treatment.

Studies have been conducted to evaluate the electro-osmotic flow patterns in sewage sludge suspensions to optimize equipment configurations. Sunderland conducted extensive studies on the effect of various electro-osmotic continuous cell configurations on overall dewatering efficiencies.[31] He discovered that on a laboratory scale electro-osmotic thickening of sewage sludge is possible on a continuous basis. Subsequent scale up, using a moving belt concept indicated that electrokinetic dewatering can be executed on the level of a large laboratory pilot plant. In both laboratory and large scale tests, the costs (e.g., energy requirements) are sharply dependent on the initial solids level. As is the case with earlier studies, the sewage disposal costs are pure expense in light of the valueless final product. Electrokinetic consolidation of these sludges can, however, reduce health risks, reclaim pond sites, and extend pond capacity.

The feasibility of electrokinetic separation of higher value ultrafine products has been examined by a number of researchers (see Table II). Shirato, et al.[32], conducted laboratory scale electrokinetic experiments on clays at constant temperature under conditions of varying: initial suspension heights, initial porosity's, and d.c. voltages. The heights of the sediments were continuously monitored as a function of time; the electrical potential distributions through the sediments were also measured.

In Shirato's work, emphasis was placed on the calculation or estimation of zeta potentials based on theoretical treatment of the experimental data. There was no attempt to measure particulate charge directly or to modify zeta potential to obtain further improvement of electroforced sedimentation. Shirato found that there was a significant increase in sediment settling rates with an increase in electric field intensity. This suggests that the industrial application of electrokinetic separation technology to higher valued products may be warranted.

Researchers in Yukawa's laboratory[37] studied the use of an Oliver rotary drum filter as a continuous electrokinetic filtration device. Earlier studies by Yukawa

TABLE II

Research on Electrokinetic Separation of High Value Ultrafines

Ultrafine Product	Application	Researcher (Year)
Kaolin	Paper Coating	Freeman (1982)[33]
Ball Clay	Pigments, Fillers, Cement	Sunderland (1987)[18] Bollinger (1984)[34,35]
Bentonite		Moulik et al. (1967)[36]
Gairome		Shirato (1979)[32]

indicated that when a d.c. electric field was applied to constant pressure batch filtration, the overall flow rate improved significantly due to the combined actions of electrophoresis and electro-osmosis. During dewatering, electrophoresis in the slurry decreases cake formation, while electro-osmosis in the filter cake results in an increased filtration flow rate. Yukawa applied this combined electrophoretic and electro-osmotic technique to the dewatering of bentonite and calcium carbonate slurries. These slurries are difficult to dewater hydraulically due to the formation of a gelatinous cake. The primary purpose of Yukawa's research was to adapt an already existing dewatering device to operate as an electrokinetic industrial device. By deriving a relationship for continuous electrokinetic filtration from batch electrokinetic dewatering, the authors are able to explain the experimental observations theoretically. Yukawa concluded that electrokinetic filtration increases the rate and extent of water removal from fine particle slurries that may form gelatinous cakes. Constant current and constant voltage studies were also performed on these gelatinous sludges.[37,38]

4 CHEMICALLY ENHANCED ELECTROKINETIC SEPARATION

Electrical methods of separation take advantage of the fact that most fine particles suspended in water tend to be negatively charged.[15] In the majority of the studies reviewed, electrical separation is rarely applied to positively charged particles. In principle, a simple reversal of electrode polarity would result in an effective electrical separation of these positive species. In research conducted on mine slurries, Kelsh and Sprute postulated that although they did not encounter solids with high positive charge, the methods of electrical treatment would be effective if the particle zeta potentials were higher than 16 mV.[8] Investigations into the application of electrokinetic dewatering to systems in the absence of a significant natural particle surface charge are limited. The lack of dependence on original particle size and charge makes electrokinetic separation a more attractive technique for a wider variety of uncharged ultrafine systems.

4.1 Action of Chemical Additives

A technique often used to change surface electrical properties is the addition of chemicals in the form of electrolytes, acid/bases or surfactants. The mode of chemical action is to alter the nature of the electrical double layer surrounding the particle. The double layer properties result from the charge on the particles and govern the type of electrostatic interactions between particles. The state of aggregation of particles is also determined by the surface electrical properties through the mechanisms of attraction and repulsion. The resulting particle size governs the associated hydraulic dewatering characteristics.

The attractive and repulsive interactions of colloidal particles is often characterized by zeta potential measurements. The potential energy of interaction, V_R, is changed through either: (1) increasing the ionic strength of the solution through the addition of an indifferent electrolyte or (2) changing the surface potential on the particles.[12] At constant pH, the variation in particle charge with ionic strength is a function of the valence of the added counterions. An increase in the electrolyte concentration decreases both the zeta potential at the surface and the barrier to coagulation. At the point of critical coagulation concentration (ccc), the potential energy barrier to coagulation disappears. The Schultze-Hardy rule defines the strong dependence of this concentration on the valency, z, as:

$$\text{ccc (mole/l)} = \frac{(4\pi\varepsilon_o)^3\, 0.107\, D^3\, (kT)^5\, \gamma^4}{N_A \cdot A^2\, (ze)^6} \tag{15}$$

where N_A is the Avogadro number, A is the Hamaker constant, γ is defined as:

$$\gamma = \frac{\exp\,(\psi_o/2)\, -1}{\exp\,(\psi_o/2)+1} \tag{16}$$

and ψ_0 is the electrostatic potential at the surface.

With plurovalent counterions this can lead to a charge reversal after the particle attains a net zero charge (this usually occurs at very low ionic strengths). The valence of the electrolyte will determine the electrolyte concentration at which the particle is at the point of zero charge.

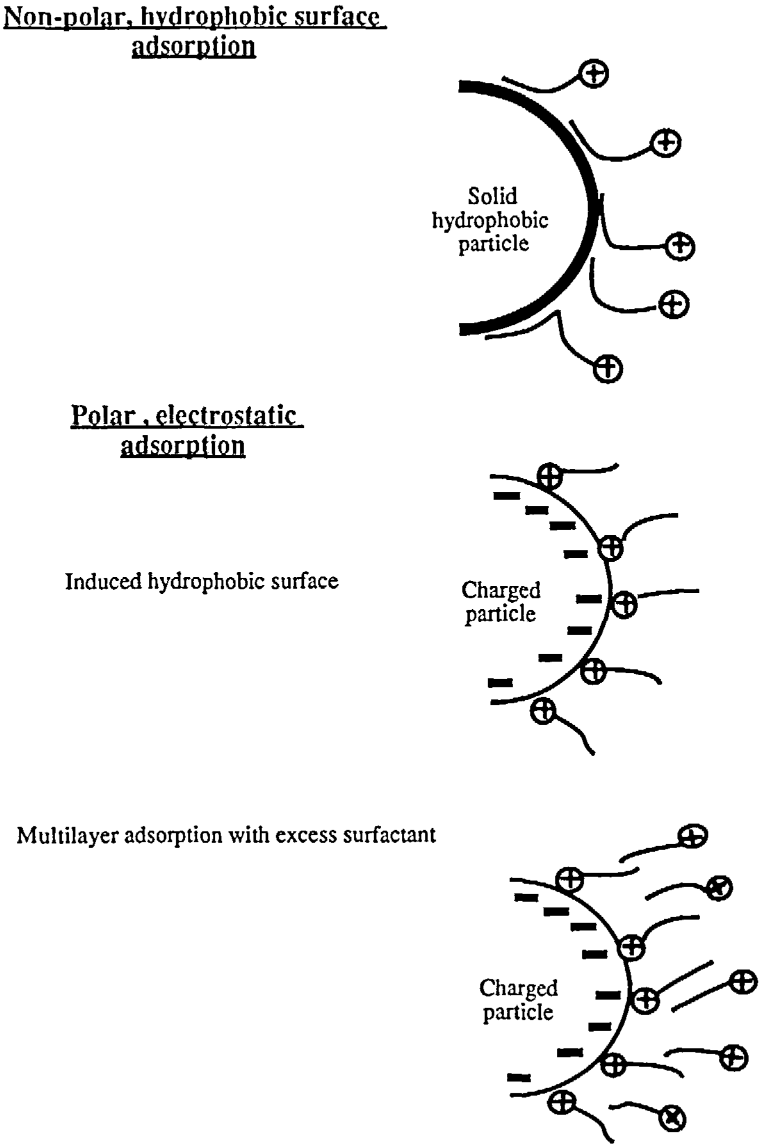
The presence of cationic (e.g., cetyl trimethyl ammonium bromide, CTAB) or anionic (e.g., sodium dodecyl sulfate, SDS) surface active agents changes the particle surface structure through adsorption of the surfactant. The adsorption characteristics of the surfactant are governed by the molecular structure of the surfactant (e.g., length of hydrocarbon chain) and characteristics of the original surface (e.g., charge, hydrophobicity). On hydrophobic surfaces (e.g., AgI) the surfactant molecule displaces water from the surface and adsorbs in a horizontal orientation (see Figure 5).

When the surface is charged, the surfactant (with an opposite charge) will adsorb vertically and the hydrophobic portions of the molecules will interact. In the case of a hydrophilic surface (e.g., oxides) the surfactant head group adsorbs to the oppositely charged surface groups through electrostatic interactions. Multilayer adsorption may occur on highly charged surfaces resulting in a zeta potential reversal. A number of researchers have investigated the adsorption of surfactants on oxides[39,40], AgI[41-43] and quartz.[44] Dewatering aids in the form of flocculants and dispersants are often used to control the state of aggregation of particles by modifying the surface electrical properties.[44]

A summary of chemically enhanced electrokinetic separations is presented in Table III. In early work by Curtis[10], ammonium hydroxide, sodium silicate and sodium hydroxide were used in the electrophoretic separation of kaolin clay. In that work, important factors in the selection of the final parameters for the kaolin dewatering were the cost of the chemicals, the odor associated with the process and the conditions that produced the best dewatering performance.

Curtis et. al.[10] observed that the concentration of electrolyte resulting in the maximum dispersion (i.e., highest zeta potential), as determined by settling tests, corresponds to the concentration producing the best electro-osmotic dewatering results. The dispersing agents (e.g., sodium hydroxide) increase the potential determining ion (pdi) concentration on the clay particles resulting in an increase in the driving force for electrokinetic separation.

In studies on washed and unwashed sodium kaolinite slimes, Lockhart[6] studied the effects of electrolytes, acid, salt and non-ionic flocculants on the electro-osmotic



Non-polar, hydrophobic surface adsorption

Polar, electrostatic adsorption

Induced hydrophobic surface

Multilayer adsorption with excess surfactant

FIGURE 5. Model of surfactant adsorption

TABLE III

Summary of Chemically Enhanced Separation Applications*

Solid	Chemical Additives	Electrokinetic Enhancement/Vacuum	Reference
Mica Kaolin**	Ammonium - hydroxide Sodium silicate Sodium hydroxide	yes/no	Curtis [10]
Sodium kaolinite Sandwashing slime	HCl Polyacrylamides	yes/no	Lockhart[6,45,46]
Ball Clay	Sodium hydroxide	yes/no	Sunderland[18]
Iron Oxide	Sodium hydroxide Cetyl trimethylammonium bromide (CTAB)	yes/ yes	Grant [4,45]
Metal hydroxide sludges Sewage sludge Pig manure	SDS CTAB	yes/no	Van Diemen et al.[46]
Sand Cement	SDS	yes/no	A.J. Kuin [49]
Kaolin (electrodialyzed)	Tetra sodium pyrophosphate	yes/no	Speil and Thompson[9]

* Liquid medium is water in all cases.

**Kaolin from deposit in Mica, Washington.

dewatering process. He reported that electrolytes increased the conductivity of the liquid in proportion to their concentration. The added anions and cations are current carriers that migrate in opposite directions and no additional electro-osmotic water transport should be derived from the extra current. The zeta potential of the kaolinite was decreased through a compression in the electrical double layer by the electrolytes. Lockhart also observed that the presence of soluble salts in the clay slimes form cations, which also influence electro-osmotic dewatering.

In the case of kaolinite slimes, the presence of acid changes the adsorption of the potential determining ion (H^+) onto the edges of particles thereby decreasing the zeta potential. The presence of the H^+ ions may also have an effect on the following possible electrolysis reactions at the electrodes:[47]

$$2\,H_3O^+ + 2e^- \longrightarrow 2\,H_2O + H_2 \quad (17a)$$

$$2\,H_2O + 2e^- \longrightarrow 2\,OH^- + H_2 \quad (17b)$$

Although, Lockhart found a large improvement in the rates of sedimentation and drainage upon the addition of flocculants, there was not a significant improvement in electro-osmotic dewatering. He concluded that sedimentation and drainage techniques should be used as far as possible before implementing electro-osmotic separation techniques.

Research by Sunderland[18] on the electrokinetic thickening of ball clay consisting of 52% kaolin and 48% mica, used sodium hydroxide to modify the surface electrical properties of the particles. They observed that the increased pH (from 7.2-9.2) increased the final percent solids from 31% to 44% in the electrokinetic dewatering process. As the pH rises the concentration of potential determining OH^- ions increases with a corresponding increase in the negative zeta potential.

4.2 Chemical Enhanced Sludge Dewatering

Recent studies [3,45,46,48] indicate that chemical modification of naturally uncharged particulate systems can improve the electro-osmotic dewatering efficiency of a variety of fine particle slurries. Van Diemen et al.[46] investigated the influence of sodium dodecyl sulphate, and cetyltrimethylammonium bromide in the electro-osmotic dewatering of metal hydroxide sludges, sewage sludge and pig manure. The aforementioned waste streams are difficult to process based on their high water content. In addition, the expense and time associated with the sedimentation and filtration prohibit their use on a large scale. The aqueous sludge dispersions were electro-osmotically dewatered at room temperature in a batch mode; the pH of the sludges was modified through the addition of sulfuric acid or potassium hydroxide solution. An improvement in the dewatering, F', was defined in terms of the quantity of water removed during a specific time period with and without an applied voltage:

$$F' = \frac{G_{eo5}\,(20V)}{G_{eo5}\,(0V)} \quad (18)$$

where G_{eo5} (20V) is the amount of water removed after 5 minutes at 20 volts, and G_{eo5} (0V) is the amount removed in the absence of an applied voltage.

For sewage sludge, the addition of 0.05 M SDS at a pH of 8.5 results in an F' value of 3.67 compared to an F' value of 1.43 without surfactants. Van Diemen et al.[46] reported that there is a significant improvement in the dewatering efficiency of metal hydroxide sludges, sewage sludges and pig manure when SDS and CTAB are added to the systems.

Van Diemen et al. also report that the electro-osmotic dewatering efficiency of the chemically treated sludges may be adversely affected by: (1) dissolution of the solids which increases the electrolyte content and reduces the zeta potential, (2) dispersion or reduced coagulation of particles causing a densification of the filter cake, (3) the sludges approaching the effective isoelectric point through a variation in the zeta potential and, (4) a blockage of the filter medium by small particles which break away from the filter cake. They conclude that electro-osmotic separation of sludges is feasible with respect to energy consumption in the presence of surfactants at the proper pH.

4.3 Surfactant Enhanced Electro-osmotic Separation of Mineral Ultrafines

The author [3,48,49] has studied the synergistic effect of sodium hydroxide and cetyl trimethyl ammonium bromide (CTAB) on the combined vacuum and electro-osmotic dewatering of naturally occurring iron oxide ($Fe_2O_3 . H_2O$) ultrafine (≈2 µm) slurries. The absence of a significant particle zeta potential (measured zeta potentials for the untreated slurry were zero) for electro-osmosis was overcome by increasing the concentration of potential determining ions, through the addition of sodium hydroxide. The resulting electrostatic dispersion of the particles significantly reduced the rate and extent of hydraulic separation. Subsequent addition of small amounts of CTAB reflocculated the particles through electrostatic adsorption of CTA^+ ions; while maintaining sufficient zeta potential to utilize electro-osmotic separation techniques.

At a NaOH concentration of 9×10^{-3} molar, the highest base concentration used in this series, the CTAB concentration is increased from 5.2×10^{-4} M to a value of 4.8×10^{-3} M. When compared with untreated ochre slurry under vacuum alone conditions in the vacuum portion of the curves, there is an increase in the rate and extent of dewatering as the concentration of CTAB is increased. Earlier tests indicate that NaOH concentrations of 9×10^{-3} cause a significant decrease in the dewaterability of the slurry in the absence of surfactant. A comparison of this base

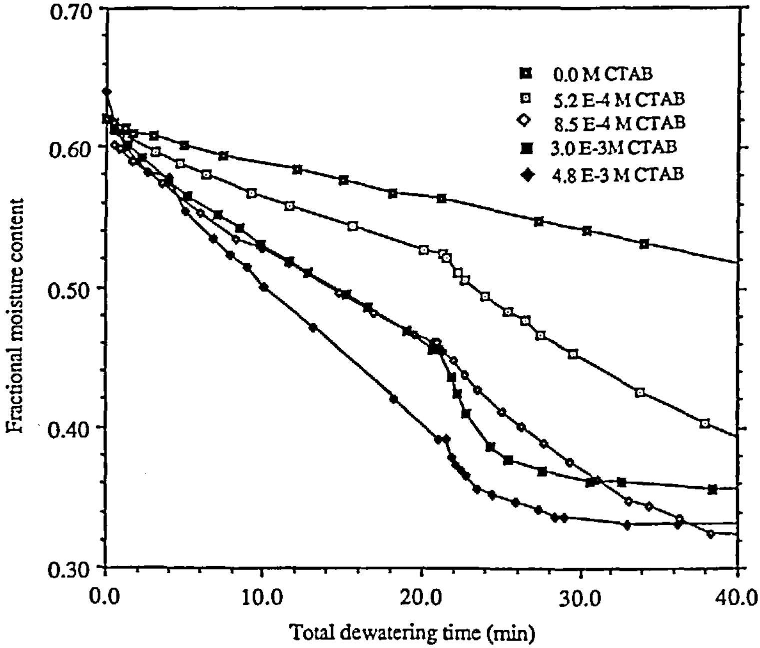


FIGURE 6. Electro-osmotic dewatering at sodium hydroxide concentration of 9.8 E-3 M with applied potential of -45 volts (for 0.0 CTAB sample no applied potential). Note increase in rate of hydraulic dewatering as surfactant concentration is increased.

alone test to one with a small amount of CTAB (5.4 x 10^{-4} M) supports the proposed adsorption mechanism of reflocculation of base dispersed particles through hydrophobic attraction of the adsorbed CTAB tails.

Figure 6 illustrates that at a total dewatering time of twenty minutes, an applied potential of -45 volts causes an electro-osmotic enhancement over the entire CTAB concentration range at a constant NaOH concentration of 9.3 x 10^{-3} M. However, the rate of electro-osmotic enhancement is not as pronounced at the lowest CTAB concentration (5.2 x 10^{-4} M). For the ochre slurry at 9.8 x 10^{-3} M NaOH, the lowest final fractional moisture content of 0.351 is achieved at a CTAB concentration of 3.0 x 10^{-3} M. In this system, the combined electro-osmotic improvement and high hydraulic permeability resulted in optimal extent of dewatering conditions.

Electrostatic adsorption of excess CTA^+ ions can diminish or eliminate the electro-osmotic effects of the hydroxide ions with an associated reduction in electro-osmotic dewatering. Subsequent increases in CTAB concentration resulted in charge reversal of the particles through the mechanism of multilayer adsorption (see Figure 5). The use of both NaOH and CTAB as surface conditioning agents promoted a synergistic reduction (over 40%) in the final cake moisture content during combined hydraulic and electro-osmotic dewatering.

5 ENERGY REQUIREMENTS AND ECONOMICS

Speil and Thompson[9] state that if electrical dewatering is to be economically feasible, the system must have: (1) a low energy consumption per unit of product, (1) a high rate of deposition and (3) a low moisture content of the final product. The continuous separation of fine particles from high value product streams for more efficient transport and/or processing is the focus of the majority of electrokinetic separation research efforts.

The energy requirements for the electrokinetic separation of fine slurries are reported as: (1) energy per volume of filtrate removed, (2) energy per mass of final dried or initial wet material or, (3) energy per volume of initial wet or final dried material. Table IV provides an overview of the energy requirements (converted to energy/volume of filtrate removed) for a variety of electrokinetic separations. Although not emphasized in this table, the particle size, solid composition and the solids content of the initial slurry have a major impact on the energy requirement. Yet another important factor in comparing energy costs is the configuration of the electrokinetic separation apparatus. A value of 1.29 kWh / liter of water removed will be used to compare the energy requirements associated with thermal drying.[15]

Lockhart and Strickland[7] report that the energy required to dewater a coal tailing consisting of 45 wt% solids can not be compared with data for other types of dewatering processes because electrokinetic machines dewater in a more difficult solids regime (55-67 wt%) as opposed to the 25-60 wt% range for other machines. These energy values are, however, relative to the material properties and the initial solids content.

In their work on a scale-up of electro-osmotic processes for sewage sludge, Ellis and Sunderland[31] observed that electrokinetic costs are strongly related to initial solids concentration. The electrokinetic techniques compare favorably with conventional techniques above an initial solids content of 8% (see Table V). For

TABLE IV

Energy Requirements for Electrokinetic Separation

Researcher	Material Composition	wt. % Solids initial/final	Energy Required (kWh/liter of filtrate)
Muralidhara[15]	Coal slurry Sewage Phosphate Slimes	50 / 78 2 / 35 5 / 40	0.176 0.044 0.02
Lockhart [6,50]	Sand washing slimes		2.7 x 10^{-6} - 2.57 x 10^{-4}
Curtis [10]	Mica Kaolin* (45% SiO_2, 39% Al_2O_3, 1.37% Fe_2O_3)	2-28 / 50-60	0.048
Sunderland[18,19]	Ball Clay (52% Kaolin, 48% mica)	20 / 60-70	0.0215 - 0.0365
Lockhart[47,50]	Sodium kaolinite	18 / 68.1 18 / 68.8	0.0855 (50V const.) 0.0174 (1,2,4,10,50 volt steps)
Van Diemen et al. [46]	Metal Hydroxide B (16.2% Fe, 11.6% Zn, 0.2% Cd, 0.1% Ca) • w/ 0.05 M SDS[a] Sewage Sludge • w/ 0.05 M SDS	34.8 / 47 5.2 / 12	≈ 0.598 @ pH 6.0 ≈ 0.070 @ pH 6.25 ≈ 0.152 @ pH 3.0
Ellis and Sunderland[31]	Sewage	2.6 / 26-30	0.09 - 0.13
Lockhart and Strickland[7]	Coal washery tailing ponds	45 / 75	0.074
Sunderland[18,19]	Peat Limestone Kaolin	17.5 / 67.4 30 / 65	0.013 0.0945

* Kaolin from a deposit in Mica, Washington

[a] sodium dodecyl sulfate

TABLE V:

Sewage dewatering cost* for different types of dewatering apparatus[31]

Dewatering Apparatus	**Final cake composition (% solids)**	**Cost** per tonne of dry solids**
Centrifuge	15-24	20 pounds
Rotary vacuum filter	25-30	16 pounds
Filter press	35-40	20 pounds
Electrokinetic process	Initial - 2.63 Final 26-30	44 pounds for 2.6% sewage 13 pounds for 10% sewage

*Operating costs only, does not include equipment costs.

** @ English pounds (1977)

sewage treatment plants the regime for separation is approximately 2% solids; in this instance electrokinetic dewatering would be at a disadvantage compared to other techniques due to the low initial solids content. Ellis and Sunderland concluded that for sewage sludge the economics of large scale electrokinetic separation was prohibitive compared to centrifugation, rotary vacuum filters and filter presses.

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5.1 Commercialization of Electrokinetic Separation Processes

Scientists and engineers at Dorr-Oliver Technology developed a technique employing electrodeposition and vacuum filtration in cooperation with the kaolin industry. The device known as an Electrofilter or an Electrically Augmented Vacuum Filter (EAVF) produced filter cakes up to 50% drier than those produced by conventional hydraulic devices.[34,35] The assumption in Dorr-Oliver's research is that the slurry to be dewatered has a sufficient zeta potential to make the process feasible. The authors do not discuss the alteration of surface electrical properties prior to the use of the EAVF device. Although no longer commercially available, the unit had limited use in the electrofiltration of clay dispersions, titanium dioxide, dyes, polymer latexes, and synthetic zeolites. Recent technological advances in electroacoustic dewatering by Muralidhara et al.[5,15-17] have resulted in the development of commercially available continuous electroacoustic dewatering (EAD) device currently marketed by Ashbrook, Simon and Hartley.

6 SUMMARY

The presence of ultrafine particles in slurries restricts the implementation of hydraulic dewatering techniques. Electrokinetic dewatering is a viable process that can be implemented in conjunction with or as a substitute for conventional methods of dewatering. Electrokinetic dewatering processes have not been used extensively in the mineral and chemical process industries. Yoshida and Yukawa[13] state that a primary reason for this is the absence of engineering data for design and operating purposes. While there are a number of experimental studies indicating the feasibility of electrokinetic dewatering, the development of fundamental electrokinetic dewatering mechanisms are scarce.[13] Although the aforementioned electrokinetic dewatering models can be used to predict electrokinetic separation, their extension to chemically modified systems must be investigated experimentally.

The primary goal of most electrokinetic research is the determination of the factors governing electrokinetic separation. Researchers have focused on the overall minimization of electrical energy, while maintaining a reasonable dewatering rate for the process.[4] The implementation of electro-osmosis on a industrial scale has been investigated by a number of researchers resulting in a wide variety of physical configurations. In an effort to optimize the electrokinetic dewatering process, researchers have studied the: (1) process flow configuration, (2) physical and electrical contacting associated with the dewatering apparatus, and (3) electrode material and configuration.[51]

In addition to the configuration of the electrokinetic device, future work on ultrafine slurries should focus on implementation of the chemically enhanced dewatering techniques to actual industrial operations. A key factor in the treatment of uncharged particles is the identification of a chemical species that balances the degree of particle aggregation (important for hydraulic dewatering) and the resulting particle charge (an important factor in electrokinetic separations).

The majority of electrokinetic dewatering processes have been applied to fine particle systems that are naturally charged. The concept of zeta potential enhancement through the addition of potential determining ions, surfactants or electrolytes can be extended to particles with a slight charge, thereby making them more amenable to electrokinetic dewatering. There are many questions to be answered with regard to the scale-up of a chemically enhanced dewatering process such as: Will the chemicals utilized corrode the electrode material typically used in a device? What is the potential for recovery and recycle of the chemicals utilized? How does the use of chemicals affect the integrity of the final product? Ultimately, these questions will have to be addressed through research on laboratory and industrial scale prototypes of electro-osmotic and electrophoretic separation devices.

Electrokinetic and flocculation information obtained from the literature can be used in the prediction of dewatering behavior of other fine particle systems. The use of information already tabulated for flotation studies may be expanded to predict flocculation behavior based on pH change and surfactant collector addition. Similarly, the characterization of electrokinetic properties has been performed by a number of researchers on high value ultrafines. Determination of the relationships between flocculation, electrical properties and chemical additives will provide useful information to control combined hydraulic and electrokinetic dewatering performance.

Chemically enhanced electrokinetic separations are a logical extension of chemically enhanced hydraulic separation studies. For example, the economic use of peat as an alternative energy source necessitates the effective dewatering of crude peat found in a drained bog. Ayub et al.[52] have studied the use of cationic and anionic surfactants in the effective hydraulic dewatering of highly decomposed peat. Although, the researchers do not perform an electrokinetic separation of the peat, they provide an extensive overview of the best conditions for mechanical dewatering. The degree of flocculation is important and the surface charge plays a major role in the dewatering of the peat. Ayub's group conclude that the surface characteristics of the peat must be taken into account prior to hydraulic dewatering. This type of study could be the starting point for the investigation of a combined chemically enhanced electrokinetic/hydraulic dewatering processes.

The predication of electrokinetic separation behavior should be applied with caution to impure fine particle systems or mixtures. The impurities may act like indifferent, potential determining or specifically adsorbed ions resulting in a modification of the electrokinetic and coagulation properties of the system.

In conclusion, the following criteria exist for implementing chemically enhanced electrokinetic dewatering within an existing industrial process: (1) an additive must be used that will impart sufficient zeta potential to the particles in small quantities, (2) the additive should be compatible with other chemical species in the slurry (i.e., no adverse reactions) (3) final product integrity should be maintained (4) identification of the best commercially available electrokinetic dewatering apparatus, and (5) use of an additive with maintains or increases the hydraulic dewaterablity of the slurries. The continuing search for more efficient environmental and biological separations processes necessitates the development of combined field techniques. Chemically enhanced electrokinetic methods have the potential to make a significant impact in this important area.

7 ACKNOWLEDGEMENTS

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8 NOMENCLATURE

$2d$	distance of separation between two plates
A	Hamaker constant
ccc	critical coagulation concentration (see Eqn. 15)
c_i	concentration of a specific ion, i
D	dielectric displacement
d_e	equivalent diameter of particle mixture
ΔP	pressure drop (Poiseiulles equation)
ΔP_c	capillary pressure drop
dx	liquid thickness of volume element (Eqn. 9)
E	electric field strength
E_z	magnitude of field strength in z-direction
F	magnitude of the charge on a mole of electrons (Faraday)
F'	improvement in the dewatering (see Eqn. 18)
G_{eo5}	amount of water removed in 5 minutes at specific voltage (see Eqn. 18)
I	ionic strength

i	current
k	Boltzmann constant
l	interstice length
l'	interelectrode distance
N_A	Avogadro number
n_i^o	electrolyte concentration
P	capillary suction pressure (CST)
P_T	total pressure difference across filter cake medium
Q	volumetric flow rate
r	capillary radius
r_i	interstice radius
T	absolute temperature
t	time
u_e	electrophoretic mobility
V_{eo}	electro-osmotic volume flow rate (theoretical)
ν_{eo}	electro-osmotic velocity
v_z	liquid velocity in z-direction
w	mass of dry solids in cake
x, y, z	distance from solid surface (double layer theory)
z_i	valency of the ion (see Eqn. 6)

GREEK SYMBOLS

ε	corrected dielectric constant of the medium
ε_0	permittivity of a vacuum ($\varepsilon_0 = 8.85 \times 10^{-12}$ farad m^{-1})
γ	defined by Eqn. 16
κ	Debye-Huckel parameter: see Eqn. 6 (inverse double layer thickness)
λ_0	specific conductance of liquid
μ_f	liquid medium viscosity
θ	liquid particle contact angle
ρ	volume density of charge
ρ_p	particle density
ψ	double layer potential at distance x from solid surface
ψ_d	potential midway between two planes in DVLO theory
ψ_o	surface potential
ζ	zeta potential

9 BIBLIOGRAPHY

1. C. J. King, "Separation and Purification: Critical Needs and Opportunities", (1987).

2. A. Ciric, G. Lipscomb and D. B. Greenberg, "Future Directions in Dilute Solution Separation Technology", (1991).

3. C. S. Grant, M. J. Matteson and E. J. Clayfield, *Sep. Sci. Tech.*, 26, 773 (1991).

4. C. S. Grant and E. J. Clayfield, "Surfactant Enhanced Electro-osmotic Dewatering in Mineral Processing", *International Symposium on Interfacial Phenomena in Biotechnology and Materials Processing*, Boston, MA., 413 (1987).

5. H. S. Muralidhara Beard and Senapati, N., *Filt. and Sep.*, **24**, 409 (1987).

6. N. C. Lockhart, *Int. J. Mineral. Process*, **10**, 131 (1983).

7. N. C. Lockhart and R. E. Stickland, *Powd.Tech.*, **40**, 215 (1984).

8. D. J. Kelsh and R. H. Sprute, *Drying Tec.*, **1**, 57 (1984).

9. S. Speil and M. R. Thompson, *Trans. Elec. Soc.*, **81**, 119 (1942).

10. C. E. Curtis, *J. Electrochem. Soc.*, **7**, 503 (1938).

11. C. Rampacek,in "Solid-Liquid Separation: A Review and A Bibliography", J. B. Poole. and D. Doyle, eds., Her Majesty's Stationary Office, London, 1966,

12. R. J. Hunter, "Zeta Potential in Colloid Science: Principles and Applications", Academic Press, London, 1981.

13. H. Yoshida and H. Yukawa, *Int. Chem. Eng.*, 28, 477 (1988).

14. M. E. Weber, S. M. Witwit and A. S. Mujumdar, *Drying Technology*, **5**, 467 (1987).

15. H. S. Muralidhara, N. Senapti, D. Ensminger and S. D. Chauhan, *Filt. and Sep.*, 351 (1986).

16. H. S. Muralidhara, H. Hampel and H. Kroening, *Drying Tech.*, 535 (1988).

17. H. S. Muralidhara, S. P. Chauhan, N. Senapati, R. Beard, B. Jirjis and B. C. Kim, *Sep. Sci. Tech.*, **23**, 2143 (1988).

18. J. G. Sunderland, *J. of App. Electrochem.*, **17**, 1048 (1987).

19. J. G. Sunderland, *J. of App. Electrochem.*, **17**, 889 (1987).

20. T. Kondo and T. Tsuchida, *Soils Found.*, **28**, 38 (1988).

21. D. H. Gray, *Geotechnique*, **20**, 81 (1970).

22. J. K. Mitchell and T. Y. Wan, *ICSMFE*, **1**, 219 (1977).

23. R. Lageman, W. Pool and G. Seffinga, *Chem. Ind.*, **18**, 585 (1989).

24. H. Yukawa, H. Yoshida, K. Kobayashi and M. Hakoda, *J. Chem. Eng. Japan*, **11**, 475 (1978).

25. J. Greyson, *Yale Sci. Mag.*, XLIV, 6 (1970).

26. R. E. Beaudoin, *Sewage Works Journal*, **15**, 1153 (1943).

27. R. H. Sprute and D. J. Kelsh, "Electorokinetic Consolidation of Slimes in an Underground Mine", Rep. Invest. 8190, 28 pp., (1976).

28. H. Yukawa, H. Yoshida, K. Kobayashi and M. Hakoda, *J. Chem. Eng. Japan*, **9**, 402 (1976).

29. H. Yukawa, H. Yoshida, K. Kobayashi and M. Hakoda, *J. Chem. Eng. Japan*, **13**, 390 (1976).

30. L. F. Cooling, E. E. Jones and A. E. J. Pettet, *Wat. Sanit. Eng.*, 246 (1952).

31. D. Ellis and J. G. Sunderland, "Dewatering Sewage Sludge by Electro-Osmosis. Part II. Scale-Up Data", Electricity Council Research Centre, Capenhurst (England) (1977).

32. M. Shirato, T. Aragki and A. Manube, *AIChE Journal*, **25**, 855 (1979).

33. M. P. Freeman, *Chem. Eng. Prog.*, **78**, 74 (1982).

34. J. M. Bollinger and R. A. Adams, *Chem. Eng. Prog.*, **80**, 54 (1984).

35. J. M. Bollinger, *Chem. Eng.*, 38 (1984).

36. S. P. Moulik, F. C. Copper and M. Bier, *J. Coll. Inter. Sci.*, **24**, 427 (1967).

37. H. Yoshida, T. Shinkawa and H. Yukawa, *J. Chem. Eng. Japan*, **13**, 414 (1980).

38. H. Yoshida, T. Shinkawa and H. Yukawa, *J. Chem. Eng. Japan*, **18**, 337 (1985).

39. S. G. Dick, D. W. Fuerstenau and T. W. Healy, *J. Colloid Interface Sci.*, **37**, 595 (1971).

40. T. Wakamatsu and D.W. Fuerstenau, "Advances in Chemistry Series", American Chemial Society, Washington, D.C., 1968.

41. R. H. Ottewill and M. C. Rastogi, *Trans. Farraday Soc.*, **56**, 880 (1960).

42. R. H. Ottewill and A. Watanabe, *Kolloid-Zeit.*, **170**, 132 (1960).

43. D. W. Fuerstenau, in "Chemistry of Biosurfaces", M. L. Hair, ed., Marcel Dekker, New York, 1971, p. 143.

44. P. Somasundaran, T. W. Healy, and D. W. Fuerstenau, *J. Phys. Chem.*, **68**, 3562 (1964).

45. C. S. Grant, M. J. Matteson and E. J. Clayfield, *Colloids and Surfaces*, (1992).

46. A. J. G. Van Dieman, M. J. H. De Vet and H. N. Stein, *Colloids Surfaces*, 35, 57 (1989).

47. N. C. Lockhart, *Colloids and Surfaces*, 6, 229 (1983).

48. C. S. Grant, "Surfactant Enhanced Electro-osmotic Dewatering of Mineral Ultrafines", Doctoral Dissertation, Georgia Institute of Technology (1989).

49. C. S. Grant, "Electro-osmotic Dewatering of Mineral Ultrafines", Masters Thesis, Georgia Institute of Technology, Atlanta, Georgia (1986).

50. N. C. Lockhart, *Colloids and Surfaces*, 6, 239 (1983).

51. N. C. Lockhart, *Colloids and Surfaces*, 6, 253 (1983).

52. A. L. Ayub and J. D. Sheppard, *Colloids Surfaces*, **18**, 43 (1986).