

SETTLING OF SUPERNATANT FROM SEMICONTINUOUS ELECTROKINETIC  
PROCESSING OF PHOSPHATIC CLAY SUSPENSIONS

By

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To my parents, sister, and friends

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## LIST OF SYMBOLS

### ROMAN

$a$	magnitude of initial turbidity
$A$	sectional area normal to the direction of current density, $m^2$
$b$	length of time required to reach low level of turbidity
$D_p$	particle diameter, $\mu m$
$E$	applied electric field, $V/cm$
$H$	height of the optical window, $h_2-h_1$ , $cm$
$h_1$	height from the top of turbidimeter holder to the top of the aperture, $cm$
$h_2$	height from the top of turbidimeter holder to the bottom of the aperture, $cm$
$I_o$	intensity of incident light
$I_t$	intensity of transmitted light
$j$	current density, $A/m^2$
$k_e$	electrokinetic permeability
$k_h$	hydraulic permeability
$K(D_p)$	extinction coefficient of a sphere of diameter $D_p$
$L$	optical path length, $cm$
$M_a$	anode metals
$M_i^{n+}$	any kind of cationic species $i$ that can be reduced
$N_p$	number concentration of particles, $mmol/mL$
$q$	charge, $C/cm^2$
$q_{eo}$	the flow rate of water, $m^3/s$
$t$	settling time, minute or hour
$v$	water velocity, $cm/s$

$V_s$	settling velocity, cm/s
$y$	turbidity of supernatant water, NTU
<b>Greek</b>	
$\gamma$	absorption coefficient
$\epsilon$	permittivity, F/cm
$\zeta$	zeta potential, mV
$\lambda$	Debye length, nm
$\mu$	water viscosity, g/cm · s
$\sigma$	electrical conductivity of clay suspensions, S/m
$\tau$	turbidity coefficient

Abstract of Thesis Presented to the Graduate School  
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SETTLING OF SUPERNATANT FROM SEMICONTINUOUS ELECTROKINETIC  
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Dilute suspensions of phosphatic clay, a waste product of the phosphate ore beneficiation, have been deposited in clay settling areas (CSA) in Central Florida for decades. The fine particle size and high surface charge density causes slow sedimentation of the suspensions, which may take decades to reach solids contents greater than 25 wt%. In this study, semicontinuous benchtop electrokinetic dewatering of phosphatic clay suspensions was performed to accelerate the dewatering process. Turbidity measurements were used to monitor the effectiveness of the electrokinetic separation. While electrokinetic dewatering reduced the turbidity of the supernatant liquid, subsequent settling greatly reduced the turbidity of the supernatant before. The settling process of the supernatant was monitored for different applied electric fields or flow rates. A relationship was established that related the decrease in turbidity to settling time. The supernatant pH was found to have little effect on free settling. Thus, the decrease in turbidity was attributed to the electrokinetic process. The settling model developed with different operating conditions can be used to guide design of electrokinetic dewatering.

## CHAPTER 1 INTRODUCTION

A dilute suspension of phosphatic clay (containing clay, silica, and residual phosphate ore) is a waste product of phosphate mining. Clay suspensions, which contain 3-5 wt% initial solids content (Carrier 2001), are pumped to clay settling areas (CSAs) for storage and gravitational sedimentation. The process of solid-liquid separation is first sedimentation followed by thickening. Hindered settling and self-consolidation requires 25 years to reach 40% solids content. The inefficiency of this process results in large numbers of clay settling impoundments that occupy about 100 square miles in Central Florida, or 37% of the land mined (Energy and the Environment 2006). Accelerating the dewatering of clay suspension would reduce clay settling areas and lead to more available lands for development.

Previously, Patrick McKinney (2010) used electrokinetic dewatering to enhance the dewatering process of the phosphatic clay suspension in a bench top experiment. This benchtop electrokinetic cell significantly improved dewatering of clay suspensions, with a cell potential of 4 V/cm in 9 hours achieving 35% solids content from approximately initial solids content of 10 wt%. Moreover, McKinney established a constitutive relationship between solids content variations, time, and electrical potential gradients, in different time-period frames. Rui Kong (2011) also documented that in a deep tank semi-continuous flow system, the average solids content approached 15 wt%, and the turbidity value of supernatant water decreased with elapsed time with the effect of the electrokinetic dewatering process. In this study, the settling supernatant water collected during the semi-continuous electrokinetic process was monitored. A simple analytic model was used to interpret the correlation of the supernatant turbidity with time.

A chemical property of the supernatant water, the pH value of supernatant, was examined for its effect on supernatant settling. The electrokinetic dewatering process was found to have an influence on free settling of supernatant liquid. The supernatant settling behavior can be a signal of the effectiveness of the electrokinetic process.

## CHAPTER 2 LITERATURE REVIEW

### **The Origin of Phosphatic Clay Suspensions**

Florida has been the mother lode of phosphate mining. There are more than 270 square miles of phosphate-mined lands in Florida. Figure 2-1 illustrates the location and layout of the phosphate mines in Central Florida (Bloomquist 1982). The phosphate mining industry was the third largest industry behind tourism and agriculture in the 20<sup>th</sup> century (Barnett 2008). The industry produces 75% of the phosphate that is supplied to the United States and 25% of the worldwide needs (IMC Phosphates 2002). A major percentage, as much as 90%, of the mined phosphate is used for fertilizer production (McKinney 2010).

Phosphate ore deposits lie under the top layer of sand, called overburden. In Figure 2-1, the inset presents the stratum of the Central Florida deposits (Bloomquist 1982). Under the vegetation layer, the overburden extends to a depth of approximately 25 feet, and the 25-50 feet phosphate matrix lies directly beneath it. Overburden is made of primarily sand and clay. Approximately one-third silica, one-third clay and one-third phosphate ores form the matrix, also known as phosphate ore deposits (Bloomquist 1982).

In phosphate mining, a large dragline excavation system is used to remove the overburden that lies above the phosphate matrix. The exposed phosphate matrix is continuously excavated by the dragline to a more shallow area, termed as a pit. High pressure water is shot onto the pit and turns the matrix into a slurry, which is pumped through a pipeline from the mine to the phosphate beneficiation plant. The phosphate, sand and clay of slurry are separated from each other in the beneficiation plant. The

leftover clays are sent to large impoundment areas, termed clay settling areas (CSAs) (Barnett 2008). The dilute clay slurry contains initially 3-5 wt% solids (Carrier 2001) with particles finer than 150 microns in diameter (Bloomquist 1982).

Disposal of the phosphatic clay suspensions poses a major environment impact on land utilization. In Central Florida, undeveloped clay settling areas occupy approximately 100 square miles, which comprise 37% of the mined lands (Energy and the Environment 2006, McKinney 2010). Furthermore, the poor settling characteristics of the clay cause that hindered settling and self-consolidation takes 25 years or longer to reach the solids content of 40 wt% (McKinney 2010). The increasing numbers of clay settling areas leads to an intense environmental awareness. The requirement to reduce the amount of land dedicated to clay settling areas imposes increasing demands upon conventional sludge dewatering technology for acceleration of clay dewatering process. Therefore, the goal of this study is to reduce clay settling areas for more mined lands reclamation.

### **Characteristics of Clay Suspensions**

In general, clay is a class of coarse dispersions, known as a suspension. A coarse dispersion is a heterogeneous mixture, in which solid particles suspend in liquid. The size of solid particles, that are larger than 1 micrometer in diameter, is sufficiently large to settle down eventually in the liquid. Another type of dispersions called a colloid, that contains particles with 1-1000 nanometer diameters, is distinguished from a suspension. The fine particles disperse in liquid and barely settle.

Dispersion stability, which means the capability of the system to resist change in its properties over time, is defined as the interaction forces between suspended particles at equilibrium (McClements 2005). Excluded volume repulsion, electrostatic

interaction, van der Waals forces, entropic forces, and steric forces are involved in the particle interactions. The unbalanced forces of the interaction cause destabilization. Destabilizations are classified into two major processes: migration phenomena (sedimentation) and particle size increase phenomena (flocculation, aggregation) (Figure 2-2). Sedimentation causes local changes in concentration, and flocculation or aggregation causes global changes in size.

A dispersion is a system that consists of two separate phases: a dispersed phase (or internal phase) and a continuous phase (or dispersion medium). Gravitational phase separation, which causes migration phenomena, is a result of dispersion destabilization when the dispersed phase is denser than the continuous phase. Dewatering processes accelerated by artificial forces are similar, in concept, to natural destabilization that disturbs dispersion stability and leads to solid-liquid separation. Multiple light scattering, coupled with vertical scanning, is widely used to monitor the dispersion state of a product, hence identifying and quantifying destabilization phenomena (Roland et al. 2003, Lemarchand et al. 2003).

Monitoring sedimentation (a destabilization phenomenon) of suspensions is of practical significance to evaluate the efficiency of a wide-variety of techniques in diverse areas such as marine geology, coastal and ocean science, hydraulic engineering, and solid-liquid separation technology (INTERCOH-2000 2002, Buah-Bassuah et al. 1998, Gibbs 1985, Hill et al. 1994). Sedimentation has been studied by using very simple vessels and either measuring the extinction of radiation or visible light by scanning the length of a glass cell containing the settling suspension to give the particle size or by determining the turbidity at fixed sedimentation depth.

Phosphatic clays are composed of approximately one-third phosphate ores, one-third silica, and one-third clay. The size of clay particles is less than 100 microns in diameter, and this characteristic of clay results in poor settling suspensions. However, the fine particle size is conversely a key element for electrokinetic dewatering process. Another factor of poor settling is that the large internal surface areas and a very small density of particles can cause some clay minerals to scatter at the surface of the suspensions. The average specific gravity of the dry particles of the phosphatic clays is 2.7 with a range between 2.6 to 2.9. The general shape of most clay particles is a plate- or flat-like shape leading to a large ratio of surface area to mass (Craig 1997). This high surface area causes hindered settling of clays. Other than the effect of particle size, the surface properties of the clays also dominate to enhanced sedimentation when an electric field is applied.

Typically, clay particles immersed in water have a negative surface charge. The magnitude of charge is usually expressed instead in terms of the zeta potential. The charge  $q$  is directly proportional to the zeta potential  $\zeta$  as

$$q = -\frac{\epsilon\zeta}{\lambda} \quad (2-1)$$

where  $\epsilon$  is the permittivity and  $\lambda$  is the Debye length, which represents the thickness of the diffuse part of the double layer. There are short-range attractions between particles due to van der Waals forces which decrease with increasing distance between particles (Craig 1997). When no electric field is applied, the repulsion due to the like charges between the particles as well as their large specific surface areas dominate in keeping the clays suspended in water and hindering settling. The charges on the clay particles

aid sedimentation when an electric field is applied, in which there is a counter force as the interaction of like charges between clay particles enhancing settling processes.

Phosphatic clays consist of clay minerals and non-clays. The composition of clay minerals are smectite (or montmorillonite), palygorskite and kaolinite, while carbonate-fluorapatite, quartz, wavelite and dolomite represent non-clay ingredients. For clay minerals, kaolinite particles have a plate-like shape with a negative surface charge on their faces and a positive surface charge on their edges (Ma 1999). On the other hand, the charges on palygorskite are much smaller than those on other clays and it has a higher surface area to mass ratio. Its minimal charge causes it not to respond favorably to an electric field and, in addition, its high surface area to mass ratio does not allow it to settle well naturally.

### **Electrokinetic Dewatering Theory**

Electrokinetic dewatering processes provide an attractive method to increase the final dry solids content and to accelerate the dewatering process of phosphatic clay suspensions with low energy consumption. The electrokinetic process is applied via an external electric field that induces the relative movement of solid particles and liquid in a suspension. The induced movement of solid particles and liquid accelerates the dewatering process and increases the solids content of suspensions. Electric field-assisted dewatering process is a technology that may be used in conjunction with a conventional dewatering mechanism, such as filter presses to improve solid-liquid separation (Hwang, Min 2003).

The mechanism is based on the interaction between the applied electric field and the diffuse double layer formed at the solid-liquid interface. The water flow induced by an electrical potential difference leads to the electrokinetic phenomena, which include

electromigration, electrophoresis and electro-osmosis (Newman, Thomas-Alyea 2004). Electrophoresis is the movement of charged particles under an applied electric field towards the electrode, which enhances sedimentation; the fluid driven towards the electrode, known as electro-osmosis, enhances consolidation. The electrokinetic process is applied an electric field to phosphatic clay suspensions with electrodes, which is the equivalent of an electrochemical cell. Therefore, electrochemical reactions are associated with an electrokinetic process.

An electrical double layer exists at the phase boundary when a solution is in contact with a solid. Fine particles in suspensions usually have negative surface charges, which attract cations to the surrounding solution. In this condition, suspended solid particles naturally settle under the combined gravitational and viscous forces. Moreover, as the repulsion force between same charged particles is larger than the attractive force of opposite charged particles, the clay suspensions will take a long period of time to settle completely.

The principle electrokinetic phenomena induced by an applied electric field are presented in Figure 2-3 (Mahmoud et al. 2010). When an electric field is applied, the negative charged particles move relative to a stationary liquid towards the positively charged electrode. This phenomenon is described as *electrophoresis* (Mahmoud et al. 2010). A condensed cake, which consists of a porous solid skeleton filled with mobile water, is formed due to the electrokinetic force. The liquid with cations migrates through the porous media towards the negatively charged electrode. This process is called *electro-osmosis* (Mahmoud et al. 2010, Shang, Lo 1997). The former phenomenon enhances the movement of negative-charged particles towards the positively charged

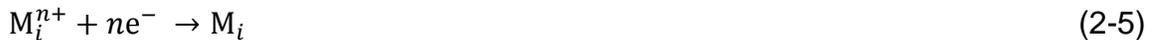
electrode, while the latter enhances the movement of liquid with cations towards the negatively charged electrode. These electrokinetic phenomena result in the acceleration of the dewatering process. Meanwhile, an electrochemical reaction, electrolysis, occurs at the site of electrodes which causes an effect on the performance of the electro-dewatering process.

The environment that the electrokinetic process creates is essentially an electrochemical cell. One electrode functions as the positively charged anode where oxidation reactions occur and the other functions as the negatively charged cathode where reduction reactions occur. At the anode, oxygen and hydrogen ions ( $H^+$ ) are produced, and then the surroundings become acidic. Another possible reaction that is involved is the corrosion of the electrode.



where  $M_a$  represents the anode metals.

At the cathode, the reaction involves hydrogen gas released and hydroxide ions ( $OH^-$ ) generated. The local basic environment is developed.



where  $M_i^{n+}$  represents any kind of cationic species that can be reduced (Mahmoud et al. 2010, Shang 1997).

The need for electrochemical reactions represents a disadvantage of the electrokinetic process. Hydrogen ions produced at anode and hydroxide ions created at cathode generate a pH gradient across the clay suspensions (McKinney 2010). The pH

gradient changes the zeta potential and affects the dewatering process. For kaolinite suspensions, the zeta potential increases from -90 to -20 mV when the suspension pH decreases from 10 to 3 during the electrokinetic process. The dispersed suspensions coagulate due to the pH decrease (Mahmoud et al. 2010).

Furthermore, oxygen generated at anode and hydrogen produced at cathode leads to voids in the solids and increases the electrical resistance of the system. The increasing resistance of the system results in a requirement of a higher energy consumption to maintain an electrokinetic process. Additionally, the corrosion of anode reduces the effectiveness of the electrokinetic process and increases the energy cost. This may also cause the clay contamination (Mahmoud et al. 2010).

There are two another important electrokinetic phenomena occur during the electrokinetic process. One is related to the motion of ions, called *electromigration* (Figure 2-3). *Electromigration* refers to the transport of ionic species in the pore fluid, and this is the main mechanism by which the electrical current flows through the sediment. This phenomenon is considered to be a special case of electrophoresis when the particle size is close to zero (Mahmoud et al. 2010, Reddy, Urbanek & Khodadoust 2006).

The other is related to the movement of charged particles under a non-uniform applied electric field, termed as *dielectrophoresis*. This phenomenon happens when non-uniform electric fields impose on charged particle suspensions during electrokinetic dewatering processes. Particles with surrounding diffuse double layers may be considered as equivalent dipoles controlled by charges in the double layer. In a non-uniform external electric field, the charges in the double layer located in the half of the

particle closest to the more intensive field will be acted upon by a stronger force, which generates a net force, *dielectrophoretic* force. This force is also a driving force that leads to the motion of particles with respect to the fluid; however, the magnitude and the influenced range of the force is smaller and shorter than that of electrophoresis. The total electrokinetic force on a particle in an external electric field is the vectorial summation of electrophoresis and dielectrophoresis (Shang, Lo 1997, Shang 1997, Pohl 1978, Shang, Inculet & Lo 1994).

During an electrokinetic process, the velocity of water  $v$  outside the diffuse double layer can be expressed as a function of the applied electric field  $E$ ,

$$v = -\frac{\epsilon\zeta E}{\mu} \quad (2-6)$$

where  $\epsilon$  is the permittivity,  $\zeta$  is the zeta potential, and  $\mu$  is the viscosity of water.

The water velocity  $v$  can also be defined in terms of the charges in the diffuse layer or the charges on the particles  $q$ ,

$$v = \frac{q\lambda E}{\mu} \quad (2-7)$$

where  $\lambda$  is the Debye length which represents the thickness of the diffuse part of the double layer and  $\mu$  is the viscosity of water (McKinney 2010, Newman, Thomas-Alyea 2004).

The effectiveness of electrophoretic dewatering can be evaluated by the relative magnitude of gravitational and electrokinetic sedimentation (Shang 1997). The effectiveness of electro-osmosis dewatering is governed by the electrokinetic permeability  $k_e$ , which can be calculated from an empirical relation (Mitchell 1993)

$$q_{eo} = k_e A \frac{j}{\sigma} \quad (2-8)$$

where  $q_{eo}$  is the flow rate of water in  $m^3/s$ ,  $A$  is the sectional area normal to the direction of current density in  $m^2$ ,  $j$  is the current density in  $A/m^2$ , and  $\sigma$  is the electrical conductivity of clay suspensions in  $S/m$ .

The technique of electrokinetic dewatering has been studied in clays and other sludges, including oily sludges (Yang, Nakhla & Bassi 2005), harbor dredges (Reddy, Urbanek & Khodadoust 2006), contaminated river sediment (Buckland, Shang & Mohammedelhassan 2000), waste sludge (Raats et al. 2002), and activated sludge (Saveyn et al. 2005), on laboratory, pilot, and full scale. However, technical problems have hampered its widespread application to date. These problems include the requirement for corrosion resistant electrode materials and high electrical energy consumption (Raats et al. 2002). Therefore, several research studies are aimed to optimize equipment designs, to evaluate the effect of various parameters on electrokinetic dewatering processes, and to establish theoretical equations to fit the process (Mahmoud et al. 2010).

McKinney and Orazem (2010) set up a cylindrical Plexiglas cell with a horizontal electrode configuration (Figure 2-4) to perform the electrokinetic dewatering process on phosphatic clay suspensions from Central Florida. The electrokinetic process with an applied electric field of 4 V/cm in the bench-top cell for 9 hours achieved a solids content of 35 wt% from about initial solids content of 10 wt%. Additionally, a constitutive relationship was established that relates the increase in solids content to operating time and to the applied electric field. While the electric field applied for less than 30 hours, the time required to achieve a given solids content is inversely related to the applied

electric field, whereas for longer periods the value of the maximum solids content achievable was found to be a function of the applied electric field.

Kong and Orazem (2011) conducted the electrokinetic dewatering process to phosphatic clay suspensions on a larger scale; a plastic storage box was used to operate a semi-continuous dewatering process with a closer horizontal electrode configuration. The solids content of suspensions reached 15 wt% under the semi-continuous operation, and the energy consumption was lower than that of the bench-top experiments due to the closer electrode arrangement. The turbidity of supernatant water was found to be low under the operation. The supernatant liquid collected during the operation settled to a low turbidity level after several days. The supernatant turbidity decreased with increasing time with the effect of the semi-continuous operation.

### **Electrokinetic Parameters**

The effectiveness of the electrokinetic dewatering process is determined by the performance of electrokinetic phenomena induced by an applied electric field. The factors that influence the performance of electrokinetic dewatering are discussed in this section.

### **Electrode Fabrication and Design**

One major issue for the electro-dewatering system is related to the electrode materials and relative positioning. In order to maintain the performance of the process, use of corrosion resistant electrode materials for the anode is essential to design considerations (Mahmoud et al. 2010, Shang, Lo 1997, Raats et al. 2002). According to the previous study, steel electrodes have the advantage of low cost whereas brass electrodes are more efficient on current conduction (Shang, Lo 1997). Mesh or porous

electrodes are preferred in the process for removing water through the electrodes and releasing gas generated in the reaction during the process (McKinney 2010).

Electrodes are configured in two layouts: vertical and horizontal. Conventional electro-dewatering techniques operated with a vertical electric field are usually performed in existing tailing ponds (Shang, Lo 1997). In recent literature, researches conducted with a horizontal electrode arrangement have been applied to the dewatering process. Horizontal electric field demonstrated in new disposal ponds is superior to enhance the dissipation of gases produced at the electrodes and to keep the anode immersed in liquid during the dewatering process. The advantages of a horizontal electrode arrangement compared to those of the vertical electrode arrangement are as follows: simple set-up, high effectiveness, and easy operation. Horizontal electrode configuration on a large scale is promising (Zhou et al. 2001).

### **Material Properties**

The physical and chemical properties of materials, including particle size, surface particle charge (zeta potential), pH value, salinity, conductivity and hydraulic permeability, determine the magnitude of the interaction with the applied electric field (Shang, Lo 1997, Fourie, Johns & Jones 2007). The surface properties of particles are dominant in fine-grained materials with large surface area. The critical surface property is surface particle charge, expressed in terms of zeta potential, which is a useful indicator for the effectiveness of electro-kinetic dewatering process. Chen, Mujumdar & Raghavan (1996) found that the percentage of water removed during dewatering of fine gold tailings was directly proportional to the zeta potential.

The electrical charges on particles vary with pH value and salinity of materials, which change the effectiveness of dewatering process and the power consumption.

Electrokinetics was not effective in a low pH environment ( $\text{pH} < \sim 6$ ) but was very effective in a high pH environment ( $\text{pH} > 9$ ) at even high salinity (Shang, Lo 1997). Electrochemical reactions associated with the dewatering process may result in a pH gradient across the filter cake, which may cause a deterioration of the product quality (Mahmoud et al. 2010). An environment with moderate salt concentrations results in a better dewatering effect, while the electrokinetic process is not effective in the environment with high salt concentrations which are associated with a lower zeta potential (Shang, Lo 1997).

The conductivity of an electrolyte solution is the ability to conduct electricity, which represents the ionic content of a solution. Over a material conductivity of 2.5 mS/cm, electrokinetic dewatering would not be feasible (Fourie, Johns & Jones 2007). The hydraulic permeability also plays a critical role in electro-osmotic consolidation. The flow in electrophoresis sedimentation and electro-osmosis consolidation depends on the relative magnitude of the hydraulic permeability  $k_h$  and electrokinetic permeability  $k_e$  of the material, respectively (Mitchell 1993).

### **Parameters Related to Operation Conditions**

There are two main types of factors involved in operating conditions of the electrokinetic dewatering system: process parameters and operation mode. Process parameters, such as total energy input and energy output distribution in time, influences the dewatering effect and overall energy efficiency. As an example of operation mode, one can hold voltage, current or electric field constant or change it with a certain pattern, such as a sine or block wave. The notable application is short to intermediate interruptions to the electric field, which apparently improves the process efficiency and reduces power consumption (Gopalakrishnan, Mujumdar & Weber 1996, Yoshida 2000).

Other crucial operating factors have been reported in the literature. The effective current density is determined by the applied voltage and spacing of electrodes. The increase in the volume of water collected accompanied high electric field intensity on electro-osmosis dewatering of kaolinite clay (Buckland, Shang & Mohammedel Hassan 2000). The voltage loss at electrodes during an electro-kinetic process is governed by the electrode materials (Buckland, Shang & Mohammedel Hassan 2000).

### **Effluent Analysis**

Concentration changes and the settling rate are two main indicators to understand the effectiveness of the electrokinetic process. Solid and liquid phase of suspensions are involved in these two investigations. A light scattering technique is most widely applied to detect the concentration of residues in liquid phase of suspensions by backscattering intensity. Optical turbidity is used as a surrogate for sampling the residue concentration of supernatant water at a fixed height during the electrokinetic dewatering process. Turbidity measurements do not disturb the equilibrium of the dewatering system, leave the sample intact for other studies, and allow for rapid analysis of samples (Caron et al. 1996).

According to the Lambert-Beer law, the well-established theory of photo-sedimentation, the attenuation ( $I_t/I_0$ ) in the intensity of light after transmission through a suspension of monodispersed, spherical particles is given by

$$\frac{I_t}{I_0} = \text{Exp} \left( -\frac{\pi}{4} L K(D_p) N_p D_p^2 \right) \quad (2-9)$$

where  $D_p$  is the diameter of the particle,  $K(D_p)$  is the extinction coefficient for particle size of  $D_p$ ,  $L$  is the optical path length, and  $N_p$  is the number of particles per unit volume.  $K(D_p)$  is a measure of the attenuation due to absorption and scattering. That is,

$K(D_p) = \tau + \gamma$ , where  $\tau$  is the scattering coefficient or turbidity coefficient and  $\gamma$  is the absorption coefficient. The extinction coefficient is a function of particle diameter, which is dominant for fine particles.

Fine particles have a large ratio of surface area to mass, which inclines the surface properties dominant in the optical technique. The scattering behavior of the particles is favorable in the phenomenon of attenuation. For non-absorbing particles that do not vary in size, the turbidity coefficient ( $\tau$ ) plays a primary role in the turbidity signal. The turbidity coefficient ( $\tau$ ) determines the fractional decrease in intensity of light and is proportional to the number concentration ( $N_p$ ).

$$\tau = \frac{1}{L} \ln\left(\frac{I_0}{I_t}\right) \propto N_p \quad (2-10)$$

This relationship indicates that a normalized turbidity signal can directly relate to the concentration changes of particles during the settling process.

For a uniform, dilute suspension of monodispersed spherical particles that settle with a single settling  $V_s$ , the turbidity signal remains constant when the settling path of the particles is above the optical aperture. The turbidity decreases linearly while particles pass the aperture to zero when particles have traversed the aperture (Figure 2-5). The normalized turbidity differences are divided by positions (Coutinho, Harrinauth & Gupta 2008),

$$\frac{N_p(t, V_s)}{N_p(0, V_s)} = \begin{cases} 1, & \text{for } t \leq \frac{h_1}{V_s} \\ 1 - \frac{V_s}{H} \left(t - \frac{h_1}{V_s}\right), & \text{for } \frac{h_1}{V_s} < t < \frac{h_2}{V_s} \\ 0, & \text{for } t \geq \frac{h_2}{V_s} \end{cases} \quad (2-11)$$

## Other Dewatering Methods

Dewatering techniques can be characterized as being either physical or chemical. Many examples of physical dewatering have been documented in the literature. Most of the physical dewatering methods are based on mechanical processes, which involve filtration, centrifugal applications, high temperature drying, magnetic mechanical dewatering, and acoustic mechanical dewatering (Mahmoud et al. 2010). For chemical dewatering, flocculant is a common and effective additive for the flocculation of clay suspensions. The Florida Institute of Phosphate Research (FIPR) reported numerous dewatering methods.

Flocculation is a behavior of colloidal particles that forms flocs or flakes suspended in the liquid by the addition of a clarifying agent (Figure 2-2). Inorganic salts and organic flocculants have been used to flocculate the clays. The former were inorganic electrolytes, including lime, calcium chloride, magnesium chloride, and alum, while the latter were either natural polymers or synthetic organic polymers. Starches, gum, tannins, and sodium algininate are natural polymers. Synthetic organic polymers are charged as anionic or cationic and the most applied synthetic organic flocculants are polyacrylamides (PAM) and polyethylene oxide.

Polyacrylamides were the most efficient flocculants (Bratby 1980, Rahman 2000). Both active and passive dosing of polyacrylamides reduced the turbidity of construction site water, which is a kaolinite suspension, by up to 88%, with turbidity levels <50 NTU in discharges (Bhardwaj 2008). Anionic polyacrylamides substantially reduced the turbidity of subsoils with little smectite or vermiculite from across North Carolina by > 90%. By contrast, the subsoils that had the higher content of smectite or vermiculite were in little response to polyacrylamide treatments (McLaughlin, Bartholomew 2007).

For phosphatic clay suspensions, flocculants accelerate the settling rate and release process water recycling to the phosphate beneficiation plant (Rahman 2000). The dilute suspension directly from the beneficiation plant is pretreated with flocculants that increases from 2 to 10 wt% solids content.

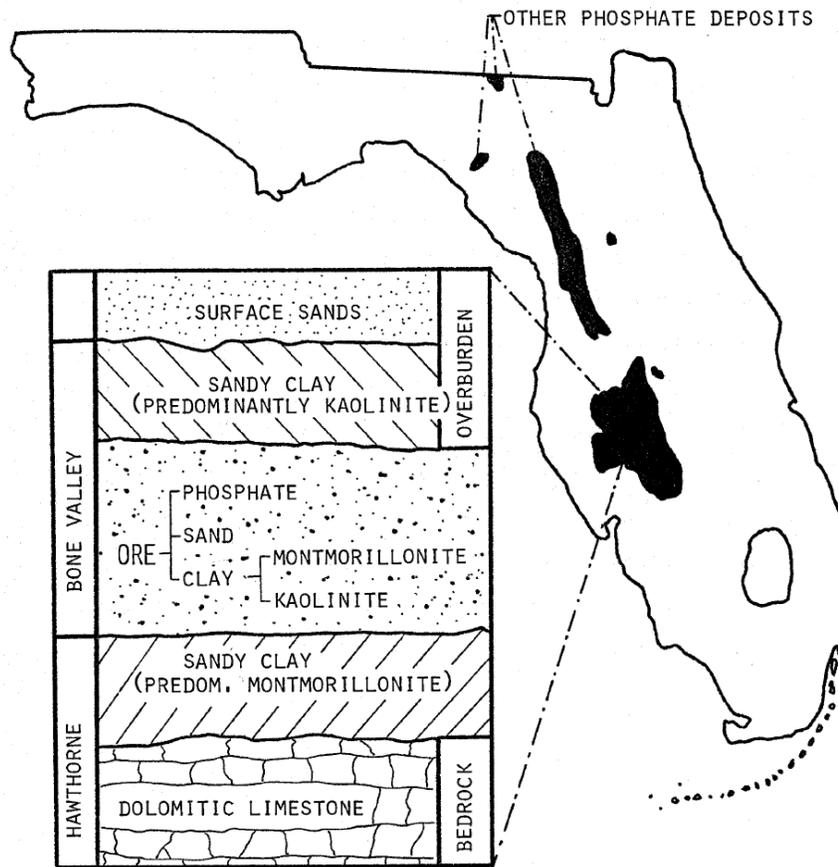


Figure 2-1. Regions of phosphate ore deposits in Florida (Bloomquist 1982). The inset is illustrated the general make-up of phosphate ore deposits in depth.

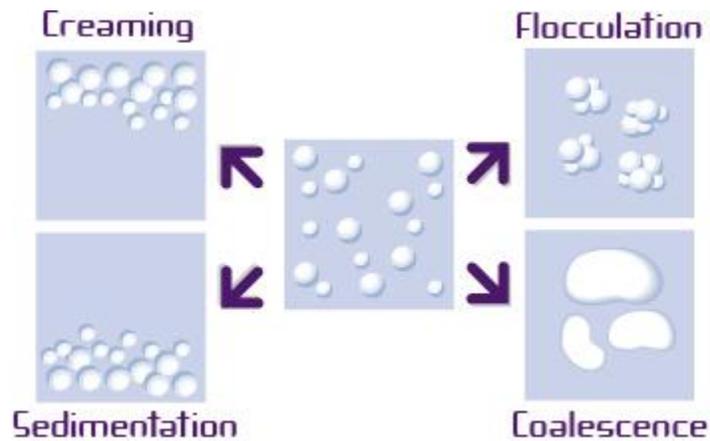


Figure 2-2. Schematic of major destabilization mechanisms of liquid dispersions.

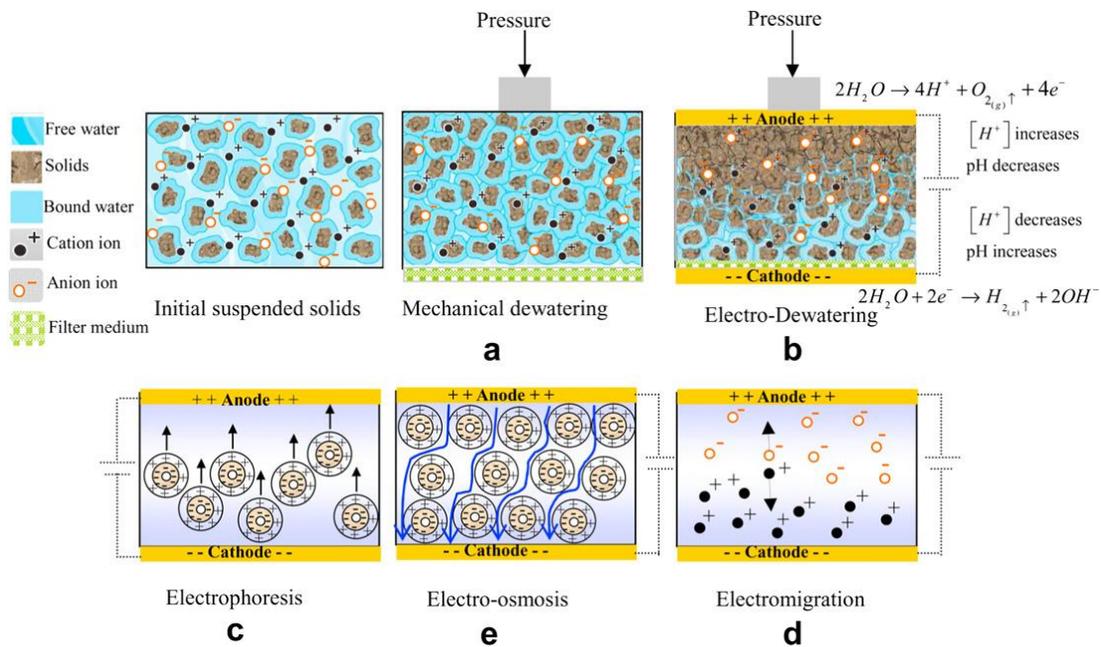


Figure 2-3. Schematic representation of mechanical dewatering and electro-dewatering phenomena for negative charged particles with an applied electric field (Mahmoud et al. 2010).

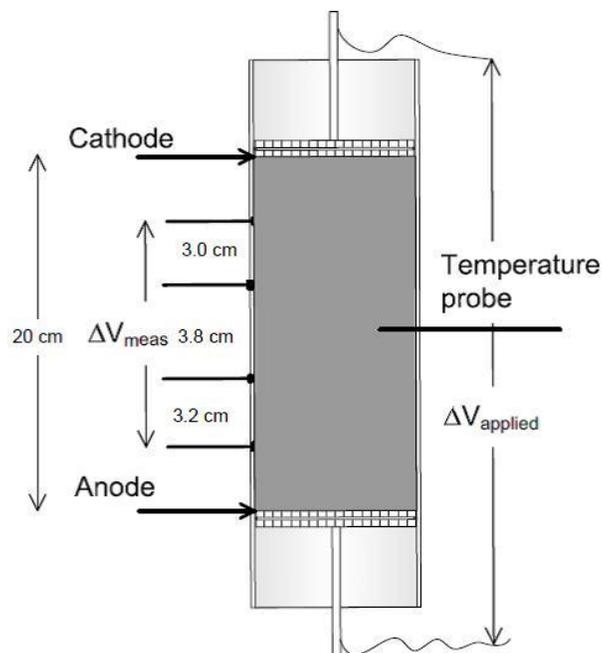


Figure 2-4. Schematic representation of a bench-top cell. The darker shaded area within the cell represents where the clay slurry is loaded for experiments (McKinney 2010).

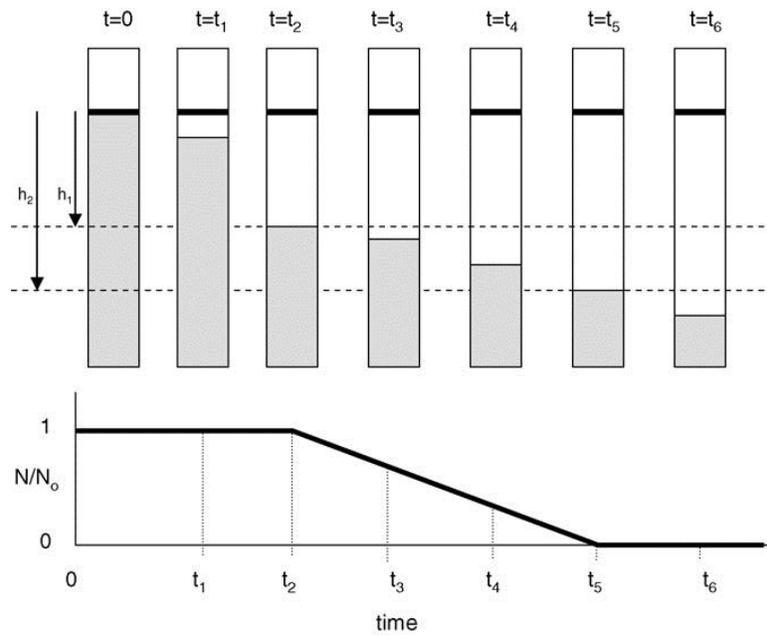


Figure 2-5. Schematic of the idealized settling of a uniform, monodispersed suspension and the normalized turbidity signal that will be expected as a function of time (Coutinho, Harrinauth & Gupta 2008).

## CHAPTER 3 EXPERIMENTAL

### **Source of Sludge**

Phosphatic clay suspensions were provided by Mosaic Fertilizer, LLC. The suspensions that are pretreated with flocculant have approximately 10 wt% of initial solids content.

### **Equipment and Instruments**

A Mastech Power Supply HY10010EX provided specific voltages for different operating conditions, and a Masterflex Model 77202-60 digital pump (Cole-Parmer Inc.) controlled the influent flow rate of phosphatic clay suspensions. A HACH 2100Q Portable Turbidimeter was used to measure the turbidity value of supernatant water, and an Orion 4-Star Plus pH/ISE Benchtop Multiparameter Meter (Thermo Scientific Inc.) was used to measure the pH value of supernatant water.

### **Apparatus**

The cell design for semi-continuous operation is shown in Figure 3-1. The electrode arrangement was, as is shown in Figure 3-2, a plastic storage box (88.9 cm×42.5 cm×32.7 cm) with two horizontally suspended metallic mesh electrodes which are made of titanium coated with iridium oxide on the surface (Water Star Inc.) (Kong 2011). The distance within the horizontal electrode configuration is adjustable, and gaps of 5 cm and 10 cm were set up in different operating conditions. A DC power supply provided adjustable voltage. Each mesh plate electrode was connected to a power supply by a titanium wire. The wire was sealed in a silicon tube to prevent exposure to water. A digital pump sent initial clay suspension from the right bucket through a PVC tube into the box to maintain a semi-continuous dewatering environment; meanwhile,

real-time effluent flowed out at the left top through the PVC tube to the left bucket. The solids accumulated in the bottom of the electrochemical cell. Figure 3-3 presents the semi-continuous experimental setup (Kong 2011).

### **Methods and Testing Procedure**

A pair of experiments was conducted to prove the concept of the semi-continuous system design. One experiment was applied with an electric field of 1 V/cm and a flow rate of 20 mL/min of clay suspensions. This experiment was intended to examine the effect of electrokinetic dewatering between the electrodes and gravity sedimentation under the electrodes. A second experiment with the same flow rate but no applied electric field was intended to explore a case where the clay suspension was affected only by gravity sedimentation. Supernatant water was collected at 1 hour, 8 hours, and 16 hours during operation in Round Media Storage Bottles (PYREX Inc.), respectively. The settling of supernatant water was monitored.

Experiments with applied electrical potential gradients of 2 V/cm, 3 V/cm, and 3.33 V/cm with a fixed flow rate and flow rates of 30 mL/min, 40 mL/min, and 60 mL/min with a fixed electric field were performed for 8 hours during daytime and rest for 16 hours during night until the feed suspension filled the tank. During the dewatering process, effluent samples of supernatant were collected every 30 minutes in Fisherbrand Class B Clear Glass Threaded Vials (Fisher Scientific Inc.). To monitor the changes of supernatant turbidity, turbidity was measured immediately after collected and after settling for 24 hours. To monitor the settling of supernatant water, effluent samples were taken during the pseudo steady state of the experiments at the beginning of the second-day of operation after supernatant water became turbid. The supernatant turbidity was measured every 10 minutes in the first 8 hours and at a longer period of time when the

value held steady. The pH value of supernatant water was measured along with the turbidity measurements.

A pair of experiments was conducted to examine the influence of pH on clay sedimentation. One cylinder contained the clay with the pH value adjusted by addition of KOH to 11.7, which is the same pH value of the supernatant liquid achieved under semi-continuous operation, while the other had the clay that retained the initial pH value of 7.1. The sedimentation phenomenon was observed before and after 10-days of gravity settling.

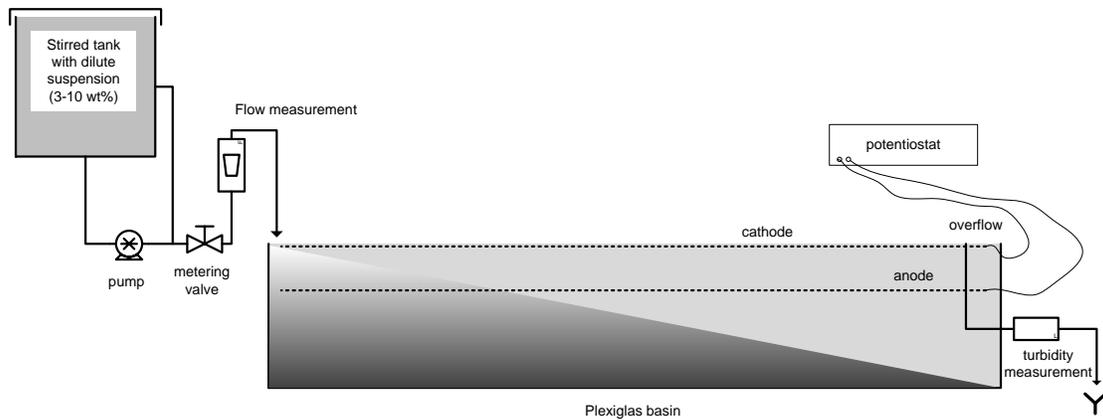


Figure 3-1. Schematic representation of the semi-continuous electrochemical cell.



Figure 3-2. Photograph of the empty experimental setup for semi-continuous electrokinetic dewatering (photograph by Rui Kong) (Kong 2011).



Figure 3-3. Photograph of the semi-continuous experimental setup (photograph by Rui Kong) (Kong 2011).

## CHAPTER 4 EXPERIMENTAL RESULTS AND DISCUSSION

### **Proof of Concept**

A pair of experiments was performed to prove the concept of the new semi-continuous electrokinetic dewatering system. One of the experiments was operated with an applied electric field of 1 V/cm and the other was under the same conditions except that no electric field was applied.

The tank loaded with the clay suspensions before the experiments started is presented in Figure 4-1A. The side view of the tank shows that after 15 hours of operation, a layer of clear water, approximately 1/7 height of the tank, formed at the top of the tank in the test with applied potential (Figure 4-1B). By contrast, there is only small amount of clear water appearing after 15 hours of operation in the control test (Figure 4-1C). The semi-continuous operation yielded a substantial solid-liquid separation for clay slurries.

### **Settling of Supernatant Water**

Rui Kong found that samples of supernatant water that collected during electrokinetic dewatering process after a few hours of operation were clearer than those collected at the beginning of the operation. Additionally, the turbidity of supernatant water from the operation decreased with increasing time, which was consistent with the observation of supernatant samples (Kong 2011). These phenomena were observed in a new semi-continuous electrokinetic experiment designed to verify the results.

Supernatant liquid was collected after 1-hour, 8-hour, and 16-hour of operation with an applied electric field of 1 V/cm and a flow rate of 20 mL/min, respectively. The clarity of supernatant water from the operation is evident in Figure 4-2 A.B.C. After

settling overnight, the supernatant water collected after 8 hours and 16 hours of the process became clear with deposits evident at the bottom of the bottles, whereas the sample collected after 1-hour of operation settled only slightly (see Figure 4-2 D.E.F).

The reproducible phenomena showed that the supernatant water collected during the electrokinetic process was clearer than that from the beginning of the operation. This suggested that the semi-continuous operation enhanced the solid-liquid separation and led to the clearer supernatant water. The supernatant liquid was collected and stored for 24 hours, and it was observed that the supernatant turbidity significantly decreased after overnight settling. The residues of clay suspensions under electrokinetic process presented a quick settling behavior.

### **Monitored Supernatant Turbidity**

Turbidity measurements were conducted in order to evaluate the settling behavior of the supernatant liquid. The approach is characterized by an experiment with an applied electric field of 3 V/cm and an input flow rate of 40 mL/min. Effluent samples of supernatant were collected every 30 minutes in cells during the process of electrokinetic dewatering. Turbidity was measured before and after free settling of supernatant water: one was measured immediately after the effluent was collected (marked as black circles), and the other was measured after 24 hours settling in the sample cells (marked as red circles) (Figure 4-3).

The initial turbidity of sample supernatant was 68,000 NTU. The turbidity decreased sharply at the beginning of experiment, and reached the steady state condition after about 4 hours. After achieving the steady state condition, the value of turbidity was stable at the low level until the flow-in clay suspensions filled with the tank,

which means the accumulating rate of the clay particles is larger than the effluent rate of the particles, resulted in the increasing turbidity of effluent.

The supernatant turbidity before and after settling was in a similar bathtub pattern. The turbidity of supernatant water after free settling decreased in the first 4 hours, and dropped to a value under 30 NTU during the steady state condition, and then increased in the last few hours (Figure 4-4). The supernatant water collected during the pseudo-steady-state operation was lower than 30 NTU after 24 hours settling, which satisfies the requirement for process water.

Supernatant turbidity before and after free settling revealed the influence of applied electric field on clay suspensions. An applied electrical potential promotes the movement of charged particles towards the bottom electrode. The concentration of charged particles in effluent samples of supernatant decreased under semi-continuous operation. Supernatant turbidity at the steady state of the operation was stable at the low level, which indicated that the electric field effectively separated charged and uncharged particles, and the supernatant turbidity showed the concentration of particle residues at the low level.

The supernatant water from the steady state of the operation had low turbidity after 24 hours settling. This indicated that the residues of supernatant demonstrated a quick settling behavior, and uncharged particles were the main particles in supernatant water due to free settling. These results suggested that the electrokinetic dewatering process performed effective solid-liquid separation, and enhances the free settling of supernatant water.

### **Effect of pH on Supernatant Settling**

The pH of the supernatant was measured and plotted before and after free settling of supernatant liquid in a similar mode (Figure 4-5). The pH of the initial clay suspensions was neutral, i.e., was equal to 7. As shown in Figure 4-5, the pH of the supernatant increased rapidly to 11.7 and was stable around this value until the solids content of the supernatant effluent increased due to a saturation of the solids-holding capacity of the tank. There was no significant change of pH before and after the free settling of supernatant water. The increasing pH of the supernatant is a result of the electrochemical reaction at the cathode which is occurring hydrolysis to generate hydrogen gas and hydroxide ions, OH<sup>-</sup>.

To examine whether the alkaline character of supernatant water could be a factor of the settling process (Figure 4-7, 4-9), experiments were performed in which sedimentation of clay suspensions with different pH values were observed in two cylinders as shown in Figure 4-6A. The alkalinity of one sample was adjusted by addition of KOH to a pH value of 11.7, which is the same as the pH of the supernatant water under semi-continuous operation, and the other had a pH unchanged at the original value of 7.1. After 10 days, a layer of water was observed to form at the top of both clay cylinders, but the smaller and more turbid layer was observed in the cylinder with higher pH (Figure 4-6B).

In contrast, the supernatant water from the electrokinetic cell showed a high degree of clarity after free settling (Figure 4-4). Supernatant water with a pH value of 11.7 demonstrated a free settling behavior, whereas clay suspensions with a pH value of 11.7 had a poorer sedimentation than those with pH value of 7.1. These two results show that the basic pH value of supernatant water does not improve the dewatering

process of clay suspensions. The small value of supernatant turbidity after settling is attributed to the electrokinetic process.

This deduction suggests that semi-continuous operation effectively separated charged and uncharged particles. The residues of clay suspensions under electrokinetic process are a majority of uncharged particles in supernatant water. Thus, alkaline character of supernatant had a little effect on uncharged particles in supernatant liquid. Uncharged particles are dominant in free settling of supernatant water.

Hindered settling, which is caused by the repulsion of charged particles, interferes the settling of clay suspensions. The surface charges of particles are affected by increasing pH value during the operation, which enhances the repulsion effect of negative-charged particles and hindered settling. Before the electrokinetic process, both charged and uncharged particles are in suspensions. Clay suspensions with the pH value of 11.7 showed less sedimentation than those with the pH value of 7.1. This result indicated that the pH value of 11.7 resulted in a stronger repulsion of negative-charged particles in clay suspensions and the particle dispersion.

### **Effect of Flow Rate on Supernatant Settling**

Table 1 lists the operating conditions of the fixed electric field experiments. Experiments were operated for 8 hours during daytime and rested for 16 hours during night until suspensions filled the basin at an applied cell potential of 2 V/cm and flow rates of 30, 40, and 60 mL/min. Supernatant samples, taken during the steady state of electrokinetic process, indicate that an applied electric field can provide steady enhancement to the solid-liquid separation. At steady state, the turbidity of the samples was at average 350 NTU under effective semi-continuous operation. Supernatant water gradually settled over time. The turbidity data measured for free settling of supernatant

and presented as the change of turbidity as a function of settling time, are given in Figure 4-7.

As shown in Figure 4-7, the initial turbidity of supernatant water collected during the steady state of the operation was 230-420 NTU. The turbidity dropped quickly in the first 24 hours to a value less than 10 NTU for experiments conducted at flow rates of 30 and 40 mL/min and applied electric fields of 2 V/cm. A turbidity of 30 NTU could be achieved within the first 12 hours of free settling. For a higher flow rate of 60 mL/min, the turbidity of the initial sample had a higher turbidity of 1500 NTU and had a supernatant turbidity value greater than 50 NTU after settling over the first 24 hours.

Supernatant turbidity was at average 350 NTU from the steady state of the experiments with flow rates of 30 and 40 mL/min and applied electric fields of 2 V/cm, which reduced from the initial turbidity of 68,000 NTU. This indicated that experiments at flow rates of 30 and 40 mL/min and applied electric fields of 2 V/cm performed effectively electrokinetic dewatering process of clay suspensions in benchtop semi-continuous model. The electrokinetic process separated the charged particles from uncharged clay particles and led to a low turbidity level of residues.

Contrarily, the higher turbidity of 1500 NTU from the experiment of a flow rate of 60 mL/min showed that, some charged particles were in the residues with uncharged particles. The flow rate of input suspensions was greater than the rate of motion of the charged particle that was generated by electrokinetic process. Some charged particles flushed out with uncharged particles in effluents of supernatant water.

An average supernatant turbidity of 350 NTU at the steady state of experiments with flow rates of 30 and 40 mL/min and applied electric fields of 2 V/cm, dropped to a

value less than 10 NTU in the first 24 hours, which indicated that the residues in supernatant water settled in a quick process, and supernatant water contained mostly uncharged particles. However, the supernatant sample collected from the experiment with the flow rate of 60 mL/min had a turbidity value more than 50 NTU after free settling. The high settled turbidity suggests that some charged particles were in the supernatant water and dispersed in it due to the repulsion of charged particles.

The relationship is evident in Figure 4-7. The decrease in turbidity was dependent on the settling time. The turbidity of supernatant liquid was found to be a function of the elapsed time, as shown in Figure 4-7. A relationship between the turbidity and the settling time was found to be

$$y/10^a = t^{-b} \quad (4-1)$$

where  $t$  is the elapsed time in hours and  $y$  is the supernatant turbidity in NTU. To interpret the physical meaning of parameters for the relationship, a log-log plot was developed as shown in Figure 4-8. The experimental data agrees well with the linear decline in the physical picture shown in Figure 2-5. The parameter  $a$  in the equation is the  $y$  intercept, which indicates the magnitude of initial turbidity, and for the parameter  $b$  of the equation, represents the slope of the linear correlation, which indicates the length of time required to reach low level of turbidity.

The results suggest that the semi-continuous operation with an applied electric field of 2 V/cm and flow rates of 30, 40, and 60 mL/min, effectively separated charged particles from uncharged particles during the steady state, which had supernatant water contain most of uncharged particles. Uncharged particles demonstrated a similar settling behavior to the ideal settling model of a uniform, monodispersed suspension.

The free settling of supernatant water shows qualitative agreement with a settling model of a uniform dilute suspension of monodispersed spherical particles. The established relationship is valid only when the electrokinetic dewatering process performs effectively on phosphatic clay suspensions, which includes the operating conditions of an applied electric field of 2 V/cm and flow rates of 30, 40, and 60 mL/min.

The agreement of the settling model of supernatant with experimental data showed in the experiments of an applied electric field of 2 V/cm and flow rates of 30, 40, and 60 mL/min. This suggests that the supernatant turbidity during the free settling can be predicted for a given flow rate as a function of settling time. Equation (4-1) is presented in Figure 4-7 with  $a$  and  $b$  as parameters. Furthermore, the relationship matches the changing turbidity of supernatant liquid with time during the electrokinetic process. It supports the experimental method and the analysis of the data as a valid approach to study the influence of electrokinetic process on supernatant water.

#### **Effect of Electrical Potential Gradient on Supernatant Settling**

The operating conditions of the fixed flow rate experiments show in Table 2. Similar experiments were performed with different applied potentials. Supernatant water was collected during the steady state of experiments with a flow rate of 40 mL/min and applied electric fields of 2, 3, and 3.33 V/cm. Turbidity measurements of supernatant liquid were conducted continuously over settling time (Figure 4-9).

In the experiments at a flow rate of 40 mL/min and applied electric fields of 2 and 3 V/cm, the turbidity of supernatant water was also related to settling time. Figure 4-9 shows that the supernatant turbidity was found as a function of time as well. A similar relationship of supernatant turbidity and settling time was established

$$y/10^a = t^{-b} \tag{4-1}$$

where  $t$  is the settling time in hours and  $y$  is the supernatant turbidity in NTU. Parameter  $a$  proves to be the magnitude of initial turbidity, and parameter  $b$  indicates the length of time required to achieve the low level of turbidity.

This relationship suggests that the settling behavior of supernatant liquid with different applied potentials (experiments with a flow rate of 40 mL/min and applied electric fields of 2 and 3 V/cm) was similar to that with different flow rates (experiments with an applied electric field of 2 V/cm and flow rates of 30, 40, and 60 mL/min). Semi-continuous operation led to a similar effect on phosphatic clay dewatering process. Experiments at the flow rate of 40 mL/min and applied electric fields of 2 and 3 V/cm performed effectively solid-liquid separation on phosphatic clay suspensions under the electrokinetic process.

The results have a good agreement with the developed relationship (Figure 4-9), which means the turbidity value of supernatant during the free settling can also be calculated for a given time point in the semi-continuous operations of a flow rate of 40 mL/min and applied electric fields of 2 and 3 V/cm. The relationship with parameters  $a$  and  $b$  (Equation 4-1) can be used to predict the supernatant turbidity during free settling. This model, that monitors the free settling of supernatant water, fits the settling process of supernatant accelerating by the semi-continuous electrokinetic dewatering process.

One of the great improvements in an electrokinetic dewatering technique is to reduce energy consumption. A common method for cutting energy costs is to reduce the distance of electrodes.

Figure 4-10 demonstrated the settling process of supernatant water from the steady state of the experiments with the flow rate of 40 mL/min and applied electric

fields of 2, 3, and 3.33 V/cm. The turbidity of supernatant water from the experiment at an applied electrical potential of 3.33 V/cm dropped rapidly in the first 8 hours and reached a plateau at a value of around 0.4 NTU. The experiment with higher applied electrical potential of 3.33 V/cm, which was generated by the shorter distance of electrodes, resulted in a faster settling process of supernatant liquid.

This settling phenomenon suggested that a rise of electric field of only 0.33 V/cm could cause this dramatic change to settling behavior due to the reduction of electrode distances. The semi-continuous operation with a higher applied electric field of 3.33 V/cm performed a better particle separation in the shorter electrode distance. The concentration of charged particles was lower in supernatant water from the operation with an applied electric field of 3.33 V/cm than that from the operation with lower electric fields. Higher concentration of uncharged particles could lead to a faster settling process.

The settling of charged particles that was driven by an applied electric field might not be disturbed by the bubbles of gases generated at the electrodes, especially with closer electrode spacing. The closer electrode spacing reduced the energy consumption but did not lessen the performance of semi-continuous operation, and even could enhance the dewatering effect.

To interpret the decay of supernatant water, a log-log plot illustrated the settling process of supernatant in a large time scale. Figure 4-11 indicated the settling process of supernatant liquid from different experiments with the flow rate of 40 mL/min and applied electric fields of 2, 3, and 3.33 V/cm in a long-time frame. The settling of supernatant water tended to a settling process of three phases with the experiment at

an applied electric field of 3.33 V/cm. This result also showed a faster settling process of supernatant water from the experiment with an applied electric field of 3.33 V/cm.

In the log-log plot, the settling process of the supernatant water showed a normal decay of three phases under the experiment with the flow rate of 40 mL/min and the applied electric field of 3.33 V/cm. This result suggested that an electrokinetic dewatering process with a higher applied electric field that was operated in a shorter distance of electrodes performed an effective particle separation. The primary residues of semi-continuous operation in supernatant water were uncharged particles. They could settle in a short period of time and demonstrate a whole settling decay.

The relationship that supernatant turbidity as a function of time, which is established from the experimental data of the flow rate of 40 mL/min and applied electric fields of 2 and 3 V/cm, could be one of these phases of the settling process (Figure 4-11). This indicated that the separation of charged and uncharged particles was less effective in experiments with applied electric fields of 2 and 3 V/cm than that in the experiment with an applied electric field of 3.33 V/cm. The residues of the operation contained a little concentration of charged particles with uncharged particles, which might require a longer time to settle completely in supernatant water. A settling process of supernatant water could reach other phases when supernatant water settled over a longer time.

An entire settling process of supernatant water could be reproducible under experiments with a higher applied electric field in closer electrode distance in semi-continuous or a larger scale.

Table 4-1. The operating conditions of electrokinetic dewatering experiments with a fixed applied electric field.

Test Number	Electrical potential gradient (V/cm)	Flow rate (mL/min)
1	2	30
2	2	40
3	2	60

Table 4-2. The operating conditions of electrokinetic dewatering experiments with a fixed flow rate.

Test Number	Electrical potential gradient (V/cm)	Flow rate (mL/min)
1	2	40
2	3	40
3	3.33	40

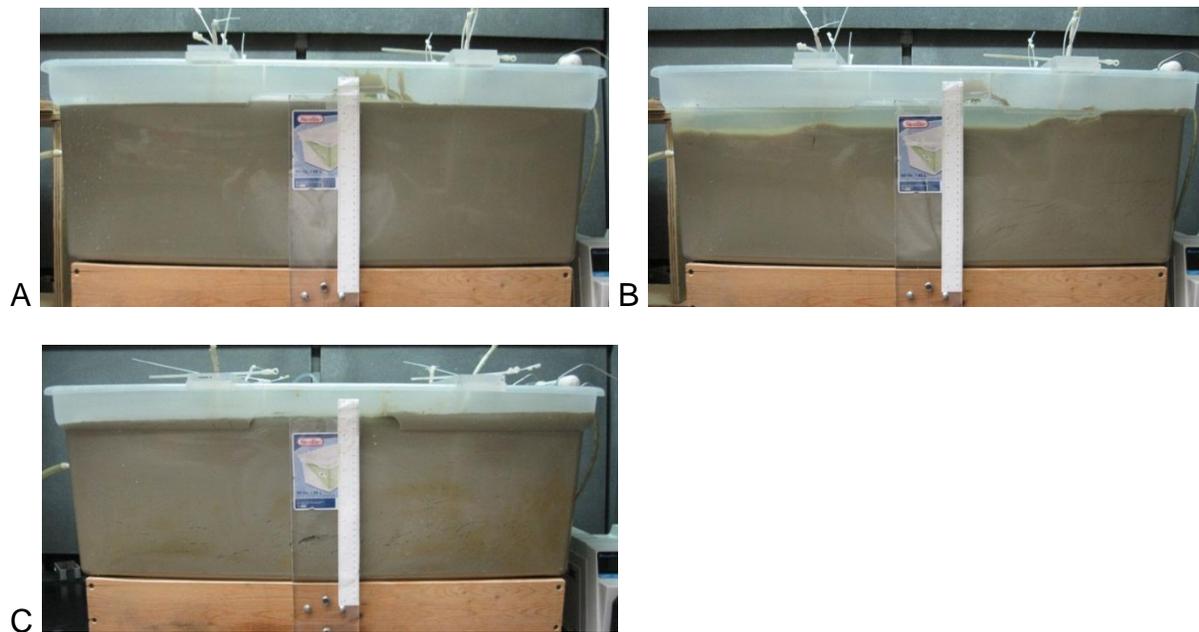


Figure 4-1. Photographs of the electrokinetic cell before and after the semi-continuous operation with a flow rate of 20 mL/min. A) side view before the operation, B) side view after 15 hours with an applied electric field of 1 V/cm, C) side view after 15 hours with no applied electric field (photographs by Rui Kong and Pei-Han Chiu).

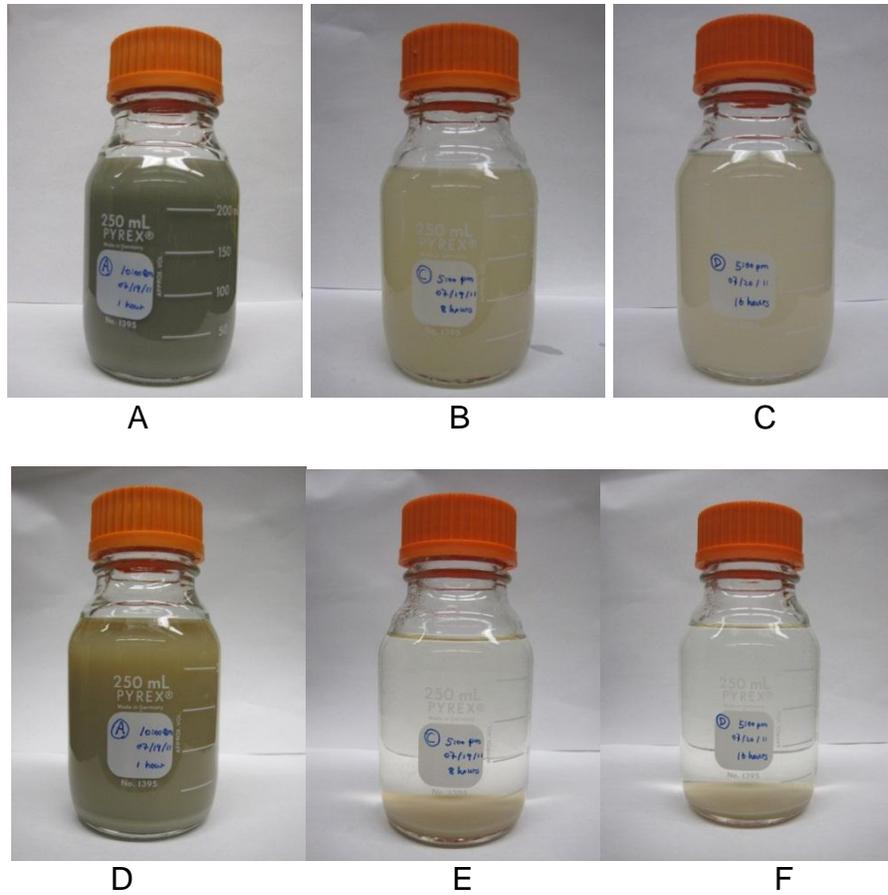


Figure 4-2. Photographs of the supernatant water collected during semi-continuous operation before and after settling. A) supernatant water collected after 1 hour of operation, B) supernatant water collected after 8 hours of operation, C) supernatant water collected after 16 hours of operation, D) supernatant water at 1 hour of operation after overnight settling, E) supernatant water at 8 hours of operation after overnight settling, and F) supernatant water at 16 hours of operation after overnight settling (photographs by Rui Kong and Pei-Han Chiu).

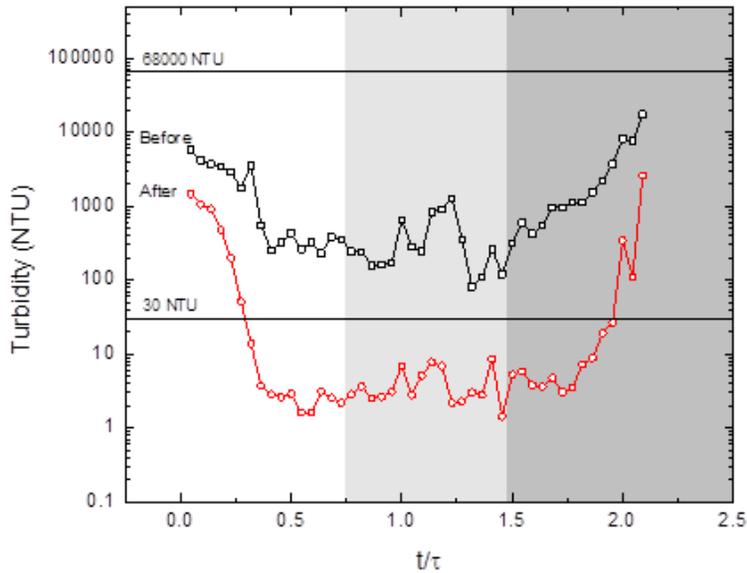


Figure 4-3. Turbidity of the supernatant liquid before and after settling with the applied electric field of 3 V/cm and flow rate of 40 mL/min. The black circles (upper line) represent the turbidity measured immediately after the sample is collected, and the red circles (lower line) represent the turbidity measured after 24 hours settling in the sample cell.

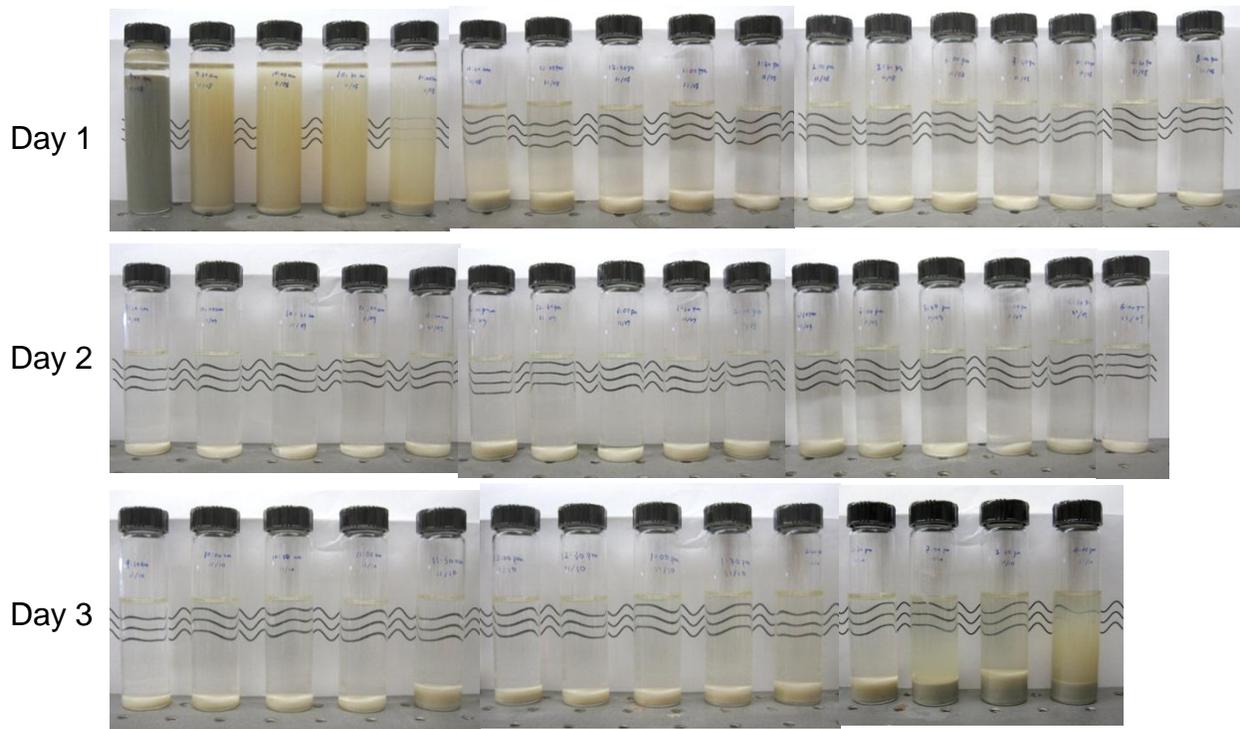


Figure 4-4. The samples of supernatant water from the electrokinetic cell after settling in the sample cell for three days.

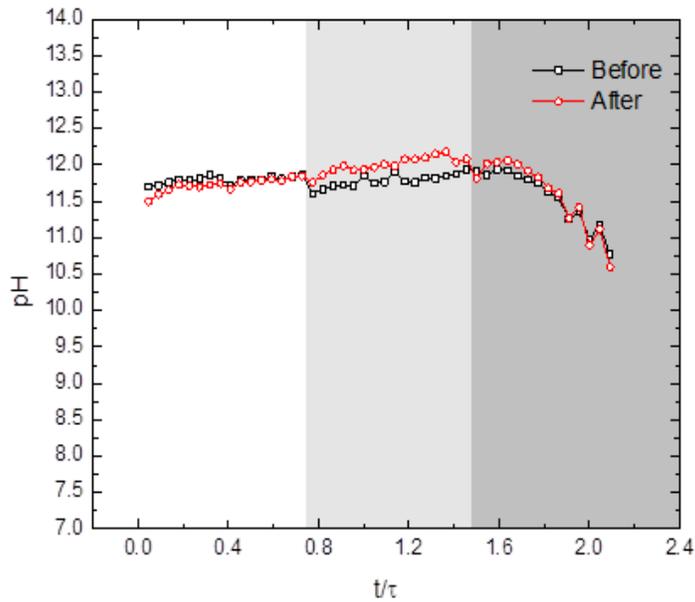


Figure 4-5. pH of the supernatant liquid before and after settling with the applied electric field of 3 V/cm and flow rate of 40 mL/min. The black circles represent the pH value measured immediately after the sample is collected, and the red circles represent the pH value measured after 24 hours settling in the sample cell.

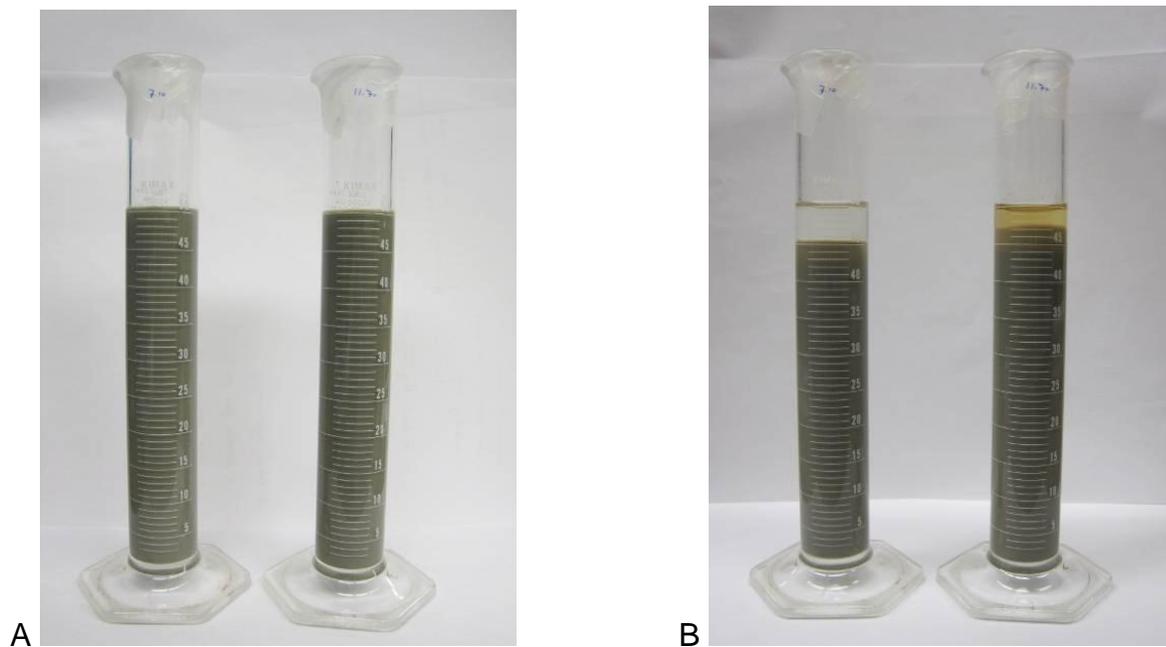


Figure 4-6. Test of the influence of pH on clay sedimentation. A) samples of clay suspensions before sedimentation with pH of 7.1 (left) and pH of 11.7 (right), and B) samples of clay suspensions after 10-days of gravity sedimentation.

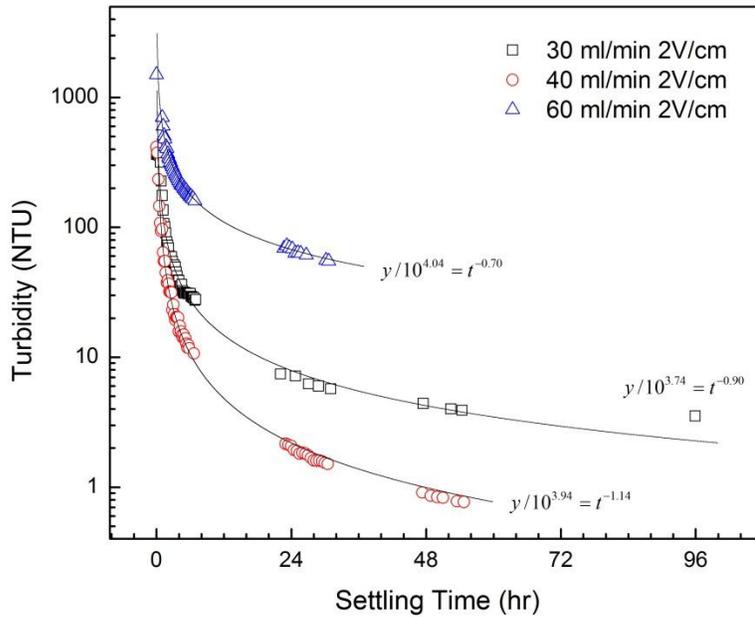


Figure 4-7. The turbidity of the supernatant water during free settling is as a function of settling time with different flow rates.

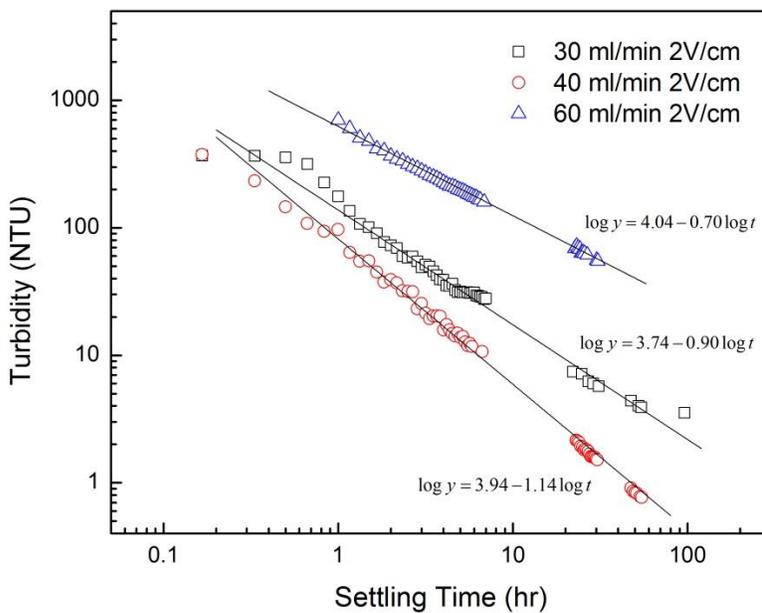


Figure 4-8. The turbidity of the supernatant water during free settling is as a function of settling time with different flow rates (log-log plot).

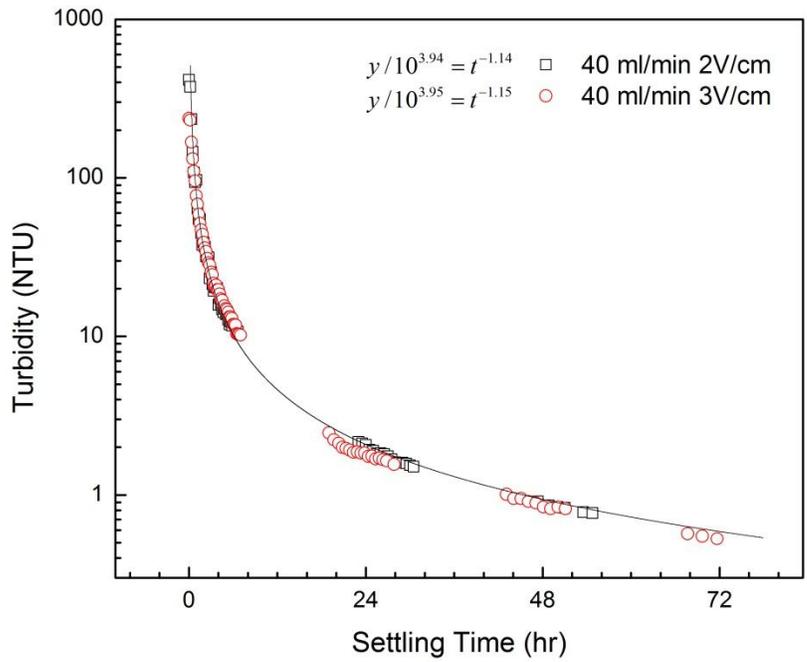


Figure 4-9. The turbidity of the supernatant water during free settling is as a function of settling time with different applied electric fields.

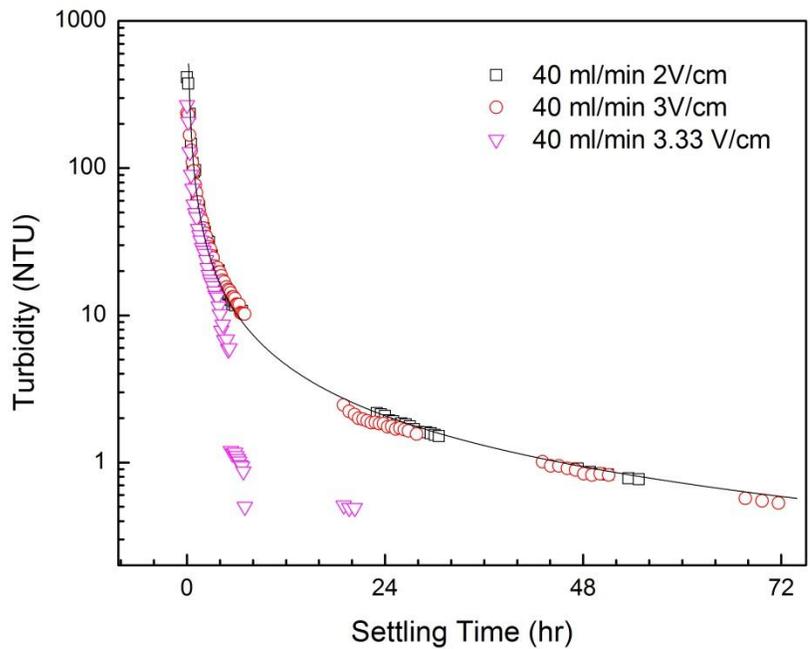


Figure 4-10. The turbidity of the supernatant water during free settling varied with time at different applied electric fields.

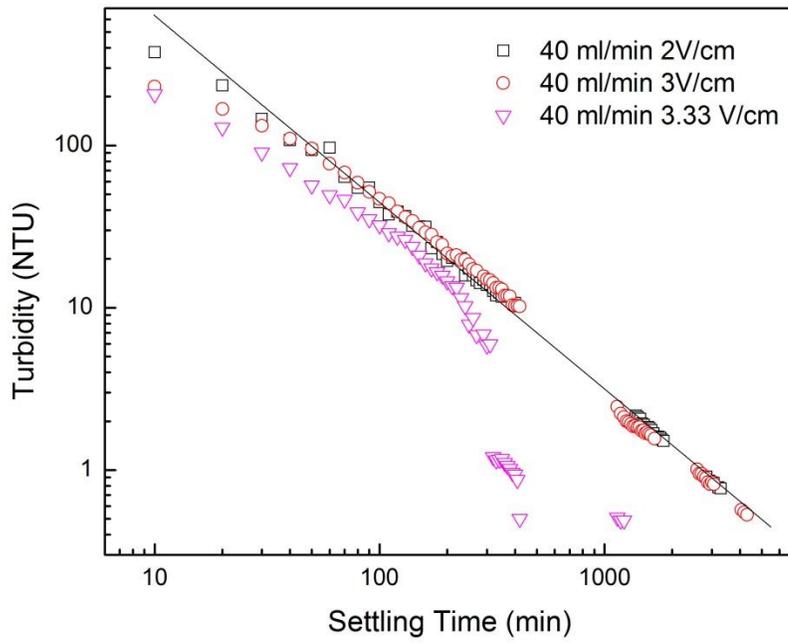


Figure 4-11. The turbidity of the supernatant water during free settling varied with time at different applied electric fields (log-log plot).

## CHAPTER 5 CONCLUSIONS AND FUTURE WORK

An electrokinetic dewatering process of phosphatic clay suspensions was investigated in semi-continuous model. The system of semi-continuous operation accelerated the dewatering process of phosphatic clay suspensions. The experiment with an applied electric field of 1 V/cm showed that a layer of clear water was approximately 1/7 height of the tank was produced after 15 hours of operation; whereas, there was no clear water layer observed in the experiment with no applied electric field. Electrokinetic parameters will be adjusted to optimize the operating conditions of semi-continuous operation and those in large scale.

The semi-continuous operation effectively performed a solid-liquid separation to phosphatic clay suspensions. The turbidity of supernatant water during the steady state of the electrokinetic process was stable at average 350 NTU, which decreased from the initial turbidity of 68,000 NTU. Moreover, the semi-continuous electrokinetic process enhanced the subsequent settling of supernatant water. In the experiment with an applied electric field of 2 V/cm and an input flow rate of 30 and 40 mL/min, the average 350 NTU of supernatant turbidity at the steady state of the operation dropped dramatically to a value less than 10 NTU in first 24 hours. A turbidity of 30 NTU could be achieved within first 12 hours of free settling.

Supernatant pH could not account for an improvement in the dewatering process of clay suspensions. There was no significant change of pH before and after the free settling of supernatant water. However, clay sedimentation experiments after 10 days, a layer of water was smaller and more turbid observed for the basic sample cylinder than that for the original neutral sample. An increase in the pH value of clay suspensions did

not enhance solid-liquid separation. Hence, the settling process of the supernatant water and the low supernatant turbidity achievable after settling were attributed to the electrokinetic dewatering process.

A settling model of supernatant water was developed for the supernatant collected during semi-continuous operation: the turbidity of supernatant water during free settling was found as a function of time. The experimental parameters included different flow rates (30, 40, and 60 mL/min) and the applied electric fields (2, 3, and 3.33 V/cm). This mathematical relationship showed a good agreement with the experimental results, even agreed with the settling process of clay suspensions enhanced by the semi-continuous operation. Thus, this model can predict a time period that the supernatant water reaches specific requirements for recycling process water.

The model did not work as well for the settling behavior of supernatant from semi-continuous operation with a higher applied electric field of 3.33 V/cm created by reducing the electrode spacing. Under these conditions, the supernatant settled faster than would have been predicted by the model. It is possible that higher concentrations of uncharged particles in the residues enhanced the free settling of supernatant water. Future work should be conducted to determine the explanation for this improved performance. Experiments should be performed with a higher electric field and shorter electrode spacing in both semi-continuous and continuous operations.

It is assumed that the semi-continuous operation accelerates the dewatering process of phosphatic clay suspensions due to the separation of charged and uncharged particles. An applied electric field induces the movement of charged particles, which congregates into solids at the electrode, while uncharged particles that remain in

the residues flush out with the supernatant water. An effective electrokinetic dewatering process leads to a well-performed solid-liquid separation and a settling process of the supernatant liquid. A settling process of the supernatant water could be an indicator to examine the effectiveness of the electrokinetic process on clay suspensions with different operating conditions. The settling process of supernatant water would be modified to fit electrokinetic dewatering processes with different operating conditions in large scale.

The composition of the solids precipitated from supernatant should be analyzed to verify the separation theory. The work presented in this thesis may be used to guide the design of large-scale dewatering equipment.

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## BIOGRAPHICAL SKETCH

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